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ORIGIN OF GROUNDWATER IN THE ORDOVICIAN-CAMBRIAN AQUIFER SYSTEM IN ESTONIA

Master Thesis

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1. Introduction

The Baltic Artesian Basin is a multi-layered Phanerozoic sedimentary basin that contains groundwater of various residence times and recharge histories. The types of groundwater found in this geological structure range from saline formation waters at greater depths to dilute modern meteoric waters at shallower depths. Throughout geological time waters in these kinds of sedimentary basins have been subject to flushing and replenishment with freshwater in response to tectonic movement, sea-level changes and climatic fluctuations such as glacial-interglacial cycles in the Quaternary Period (Edmunds, 2001). All this has resulted in the co-existence of groundwaters with different chemical and isotope composition. The presence of different types of groundwater in sedimentary basins gives rise to mixing processes which modify the chemical and isotope composition of these waters.

The stable isotopes of hydrogen and oxygen have many applications in the hydrogeological studies (e.g. tracing the origin, the mode of recharge and the mixing processes in groundwater) (Geyh, 2000). The combined interpretation of the isotope composition of groundwater together with other data (e.g. chemical composition) can give insights into the history of aquifer evolution (Hiscock, 2005; Darling, 2011). Understanding the processes that influence recharge, mixing and geochemical evolution of groundwater is crucial for predicting the effects of groundwater abstraction on its chemistry and availability.

The isotope and chemical composition of groundwater has been successfully used in a number of studies in mid-latitude Europe and North America to trace the geochemical evolution of groundwater and distinguish between waters recharged by modern precipitation and waters recharged in different climatic conditions in the past (e.g. Rozanski, 1985; Deak et al., 1993; Elliot et al., 1999; Kortilainen and Karhu, 2004; Zuber et al., 2004; McIntosh and Walter, 2006; Mokrik et al., 2009; Stotler et al., 2012). Many studies have shown a direct influence of Quaternary glaciations on the formation of groundwaters mainly through the recharge of glacial meltwater into sedimentary basins (e.g. Boulton et al., 1995, 1996; Vaikmäe et al., 2001; McIntosh and Walter, 2006; Pietrowski, 2006; Raidla et al., 2009, 2012).

So far most studies in isotope hydrogeology in Estonia have dealt with the Cambrian-Vendian aquifer system (e.g. Vaikmäe et al., 2001, 2008; Karro et al., 2004; Marandi, 2007; Raidla et al., 2009, 2012). The main reason for this is the fact that the groundwater in the northern part of this aquifer system has the lightest isotope composition in Europe (Vaikmäe et al., 2001). Other aquifer systems, which are located in the upper parts of the Estonian bedrock have received less attention. Some data describing the chemical and isotope composition of groundwater in these aquifer systems has been published in the reports by the Estonian Geological Survey (Savitskaja et al., 1995, 1996a, 1996b, 1997, 1998). Additional isotope data has also been published in a paper by Vaikmäe et al. (2001). Overviews characterizing the chemical and isotope composition of groundwaters in the Baltic Artesian Basin have been published by Mokrik (1997) and Babre et al. (2012).

The current study concentrates on the origin of groundwater in the Ordovician-Cambrian (O-Cm) aquifer system in Estonia, which overlies the Cambrian-Vendian aquifer system. The groundwater in this aquifer system accounts for approximately 12% of total groundwater supply in Estonia (Vallner and Savitskaja, 1997). The study uses both stable isotope and hydrochemical data to trace the origin of groundwater in the aquifer system. The study has been conducted to achieve the following aims:

- to describe different types of groundwater found in the aquifer system in terms of their chemical and stable isotope composition;
- to trace the sources of water in the aquifer system by studying the isotope composition of groundwater and the isotope composition of precipitation in the research area;
- to trace the mixing processes between different types of groundwater in the aquifer system;
- to give first insight into the geochemical evolution of groundwater in the aquifer system.

This study is a contribution to the IUT19-22 project “Groundwater flow history, global palaeoclimate signals and anthropogenic influence in the Baltic Artesian Basin: a synthesis of numerical models and hydrogeochemical data” which aims to merge hydrogeochemical data and numerical modelling to gain better understanding of the link between glaciations and groundwater flow systems in the Baltic Artesian Basin.

2. Theoretical background

2.1. Environmental isotopes as tracers

The stable isotopes of hydrogen and oxygen are ideal tracers of water sources and storage. As a part of the water molecule, they are conservative in reactions with bedrock and soil materials, meaning that water from a distinct source can retain its unique isotope composition until mixing with other waters (Kendall and Caldwell, 1998; Kendall and Doctor, 2003). The isotope compositions of different waters can be viewed as a distinct "fingerprint" of their origin (Kendall and Doctor, 2003).

The abundance of stable environmental isotopes is measured as the ratio of the two most abundant isotopes of a given element. The isotope abundance ratio (R) is defined as the ratio between the abundance of a rare isotope (the heavy isotope) and the abundance of an abundant isotope (the light isotope). The average terrestrial abundance ratios of the heavy and light isotopes for oxygen ($^{18}O/^{16}O$) and hydrogen ($^{2}H/^{1}H$) are 1:500 and 1:6410, respectively (Kendall and Caldwell, 1998). For better understanding, it should be noted that both ^{2}H and D are used in this study as notations for deuterium, the heavy stable isotope of hydrogen.

The absolute abundance ratios of the isotopes of a given element are seldom measured due to several technical difficulties (Mook, 2000). Fortunately, the main interest concerning environmental isotopes has to do with comparing the variations in stable isotope ratios rather than their actual abundance. The apparent ratio can be measured by comparing the isotope ratios in a sample with those in a common reference standard.

This deviation is expressed using δ (delta) notation as:

$$\delta = (R_{sample} - R_{reference})/R_{reference} = (R_{sample}/R_{reference}) - 1 \qquad (1)$$

The δ-values in nature are small and usually expressed as parts per thousand or per mil (‰). Negative δ-values indicate a lower abundance of heavy isotopes in a sample relative to the reference and positive values point to higher rare isotope abundance in a sample.

The basis of environmental isotope geochemistry is the global comparison of data sets, which demands standardization of measurements in laboratories (Clark and Fritz, 1997). The first standard used as a reference point for isotope ratio measurements called SMOW (*Standard Mean Ocean Water*) was defined by Craig (1961b). Since then new reference materials have been established with an isotope ratio very close to the original SMOW. The most recent of these is called VSMOW2 (*Vienna Standard Mean Ocean Water 2*) and has been used since the year 2006 (Lin et al., 2010).

The variability of stable isotopes in nature has to do with slight differences in the chemical and physical properties of the isotopes of a given element. This phenomenon is called isotope fractionation. There are two main types of isotope fractionation: equilibrium and kinetic fractionation (Clark and Fritz, 1997; Kendall and Caldwell, 1998; Mook, 2000; Gat et al., 2001).

Equilibrium isotope fractionation means the redistribution of isotopes of an element among various species or compounds in isotope exchange reactions. The concept of equilibrium fractionation of isotopes is similar to the chemical equilibrium, where the reaction or the redistribution proceeds at essentially the same rate for forward and backward reactions and the reactions are reversible. Statistically, stronger bonds survive for a longer time and heavy isotopic species are usually partitioned into a more condensed phase.

The isotope fractionation can be described mathematically by comparing the isotope ratios of two compounds in a chemical equilibrium or by comparing compounds before and after the chemical or physical transition process. This ratio between two isotope ratios is called the isotope fractionation factor (α) and is expressed as:

$$\alpha = \alpha_{B/A} = R_B/R_A \qquad (2)$$

Kinetic fractionation occurs in systems out of thermodynamic equilibrium and accounts for chemical and physical processes which are irreversible. Thus, lighter isotopes react faster and become concentrated in the products while the residual products become enriched in heavy isotopes. In these conditions the forward reaction rate accelerates and the backward reaction rate diminishes. The kinetic fractionation factors are usually larger than the equilibrium fractionation factors for the same reaction in most low-temperature environments. It is important to note that natural processes are usually not purely kinetic or irreversible. One may refer to these processes as *non-equilibrium fractionations* instead of *kinetic fractionations*.

2.2. Isotope and chemical composition of groundwater

In this study the term groundwater is used for water stored in the zone of saturation (Fetter, 2001). The zone of saturation is the zone where water pressures are greater than atmospheric and the pores are saturated with water (Fitts, 2002).

The rock matrix containing groundwater may be divided into aquifers and aquitards on the bases of permeability. Aquifer is a body of rock that is sufficiently permeable to conduct groundwater and is capable of serving as a groundwater reservoir (Poehls and Smith, 2009). Aquitard or a confining bed is a confining unit that retards but does not prevent the flow of water to or from the adjacent aquifer (Poehls and Smith, 2009). An aquitard does not readily yield water to wells or springs but may serve as a storage unit and can transmit water slowly from one aquifer to another.

2.2.1. Isotope composition of precipitation

Most groundwaters are of meteoric (i.e. atmospheric) origin (Geyh, 2000). This accounts for groundwater formed by the infiltration of precipitation. The stable isotopes in precipitation are affected by meteorological processes that provide a fingerprint of their origin. This is an important characteristic for investigating the provenance of groundwater.

The global major water source is the ocean as about 86% of the water in the global hydrological cycle originates from there (Gimeno et al., 2012). Of all the water that is evaporated from the ocean only about 10% reaches the land surface (Clark and Fritz, 1997). The meteoric waters (i.e. the atmospheric moisture, precipitation together with ground- and surface water derived from them) are mostly depleted in heavy isotope species (i.e. ^{18}O and ^{2}H). This is due to the Rayleigh rain-out effect, operating on a limited water (vapour) reservoir in the atmosphere (Gat et al., 2001). The water in the ocean has the $\delta^{18}O$ value of 0‰ on the VSMOW scale (Muehlenbachs, 1998). Craig and Gordon (1965) estimated that the average $\delta^{18}O$ value of all the water in the water cycle is about −0.64‰, with the average $\delta^{18}O$ value in glacier ice, groundwater and precipitation being −30‰, −7‰ and −4‰, respectively.

The isotope composition of precipitation is changed by the successive cycles of condensation and re-evaporation that include both evaporation from open water bodies and evapotranspiration as the vapour mass moves away from its source area over the ocean. Craig (1961a) showed that the $\delta^{2}H$ and $\delta^{18}O$ values for global meteoric water samples show a close relationship, when plotted on a $\delta^{18}O$ - $\delta^{2}H$ diagram. This covariance has been given the name of Global Meteoric Water Line (GMWL) and is described by the relationship (Craig, 1961a):

$$\delta D = 8\delta^{18}O + 10 \qquad (3)$$

GMWL is the result of kinetic fractionation during evaporation from the ocean producing a vapour isotopically more depleted than the ocean, followed by subsequent equilibrium condensation of the vapour along a slope described by $\alpha^{2}H/\alpha^{18}O$ (Ingraham, 1998). Dansgaard (1964) proposed the value *d* or “deuterium excess” to characterize the extent of kinetic fractionation in precipitation for a line with a slope of 8. The *d*-excess value is a result of the kinetic fractionation being greater for both δ^2H and $\delta^{18}O$ with respect to equilibrium fractionation. The parameter can be used to describe the non-equilibrium conditions during the vapour formation (Dansgaard, 1964). The deuterium excess (*d*) can be calculated as (Dansgraad, 1964):

$$d = \delta D - 8\delta^{18}O \qquad (4)$$

In-cloud processes do not modify the deuterium excess value as long as the formation of rain is considered (relative humidity being 100%). Thus, the *d*-excess can be viewed as a good indicator of the moisture provenance (Darling, 2011).

The line that characterizes the local meteoric conditions is known as Local Meteoric Water Line (LMWL). Craig's GMWL is essentially an average of many LMWLs, each controlled by different climatic factors (e.g. enhanced partial evaporation of raindrops below the cloud base during summer months and/or seasonally varying conditions in the source areas for the vapour) (Rozanski et al., 1993; Darling, 2005). For regional and local investigations, it is important to compare surface water and groundwater data with a LMWL (Clark and Fritz, 1997). The freshwaters of meteoric origin which have not undergone additional fractionation after the formation of their parent precipitation usually plot on the GMWL (Gat et al., 2001).

2.2.2. Isotope composition of groundwater

The isotope composition of precipitation in a region strongly effects the isotope composition of local groundwater. Recharge rates in temperate climates are seasonal and not uniformly distributed throughout the year. Recharge rates are generally highest during the spring, when the soils are saturated with water due to snowmelt and the effects of evaporation are small due to low temperatures and inactive vegetation (Clark and Fritz, 1997). In summer recharge is minimal as most precipitation is transpired back to atmosphere by plants (Clark and Fritz, 1997).

In mid-latitude regions pronounced seasonal variations in the isotopic composition of precipitation occur. The seasonal variations of δ^2H and $\delta^{18}O$ in precipitation are manifested in isotopically depleted precipitation in the winter and enriched precipitation in the summer (Rozanski et al., 1993). As the summer precipitation contributes little to recharge and winter precipitation is recharged during spring run-off, the net isotope composition of groundwater tends to be biased between spring and autumn precipitation, which will be close to annual mean of precipitation. Thus, the isotope composition of shallow groundwaters in temperate climates is usually close to local-mean annual precipitation (Clark and Fritz, 1997; Darling, 2004).

In a region where there are two or more aquifer units overlying one another, each unit may have a distinct isotope composition due to differences in the mode of recharge, catchment altitude, residence times or other factors (Clark and Fritz, 1997). The original isotope composition of groundwater in an aquifer can be modified by mixing between groundwaters with different recharge histories and thus different isotope compositions. Groundwaters recharged under different climatic conditions in the past differ from groundwater recharged by modern precipitation in their isotope composition. These waters are often called paleogroundwaters. Paleogroundwaters or paleowaters are those groundwaters, formation waters, interstitial waters of sediments or water of mineral crystallization originating from water cycles under environmental conditions which are different from the present ones (Fontes, 1981, cit. Rozanski, 1985; Edmunds, 2001).

2.2.3. Chemical composition of groundwater

The origin of groundwater cannot be studied using only its isotope composition. This is due to a possibility that waters with different recharge histories are characterized by similar stable isotope compositions. Thus, data about chemical composition of groundwater is also needed for an unambiguous interpretation of isotope results as the different residence times are also manifested in water-rock interactions.

As most groundwaters recharging to the water table are of meteoric origin, the chemical composition of infiltrating waters is at first influenced by the chemical composition of precipitation. Various factors can affect the chemical composition of precipitation at a given site, including type and distribution of aerosols sources, local emissions, regional scale components, transport and scavenging processes and meteorological conditions (Jaunat et al., 2013).

Weathering and dissolution of carbonate, silicate and evaporate minerals releases elements to water and so the composition of soil water and groundwater will depend on the rock type through which it flows (Appelo and Postma, 1999). The principal dissolved components in groundwater in natural conditions are six major ions of sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^-), bicarbonate (HCO_3^-) and sulphate (SO_4^{2-}) together with minor ions such as potassium (K^+), iron ($Fe^{2+/3+}$), strontium (Sr^{2+}) and fluoride (F^-) (Hiscock, 2005). The various ions containing nitrogen such as NH_4^+, NO_3^-, NO_2^- are indicators for inputs from surface waters.

The most important chemical interactions between groundwater and the surrounding rock matrix in both unsaturated and saturated zone include mineral precipitation/dissolution reactions (e.g. carbonate and silicate dissolution) and absorption/desorption reactions (e.g. ion exchange, surface complexation processes) (Deutsch, 1997).

Geochemical evolution of groundwater follows a distinct pattern. Chebotarev (1955) recognized this pattern in the distribution of groundwaters with different chemical composition with groundwaters evolving from bicarbonate waters at the outcrop area to chloride waters at depth in the Earth's crust. The geochemical evolution of groundwater along a flowpath can be illustrated by the classic sequence of hydrochemical change of groundwater (Hiscock, 2005):

- Rainwater of a NaCl water type containing CO_2 enters the soil zone, where the dissolved CO_2 produces a weakly acidic solution of carbonic acid, H_2CO_3;
- The carbonic acid promotes the dissolution of calcium and magnesium thus forming a $CaMgHCO_3$ water type. The agricultural chemicals of anthropogenic origin can also add ions such as Na^+, K^+, Cl^-, NO_3^- and PO_4^{3-} to the solution;
- Moving along the flowpath to greater depths the water becomes progressively anoxic with the progressive reduction of oxygen, nitrate and sulphate in bacterial respiration processes and mineralization of organic matter which can lead to mobilisation of Fe and Mn and the precipitation of metal sulphides;
- In the presence of disseminated clay materials within the aquifer cation exchange processes cause the Ca^{2+} to be replaced by Na^+ in the solution and the water evolves to a $NaHCO_3$ water type;
- In deeper section of the aquifer mixing with brine waters with high salinity occurs to produce NaCl-type water before a region of static water and aquifer diagenesis is reached.

3. Precipitation and hydrogeological setting of the research area

3.1. Isotope and chemical composition of precipitation in the research area

The RCWIP (*Regionalized Cluster-based Water Isotope Prediction*) model by IAEA places the Estonian precipitation to the zone of −70‰ to −102‰ for mean annual δ^2H values (Figure 1) and to the zone of −10‰ to −12‰ for mean annual δ^{18}O values (Figure 2) (Terzer et al., 2013; IAEA, 2013).

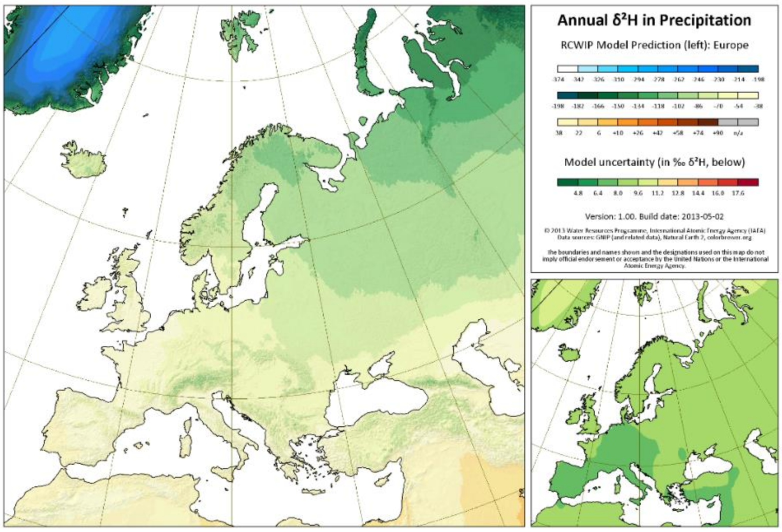

Figure 1. Mean annual δ^2H values in European precipitation calculated using the RCWIP model prediction. (IAEA, 2013; Terzer et al., 2013). (from: IAEA, 2013)

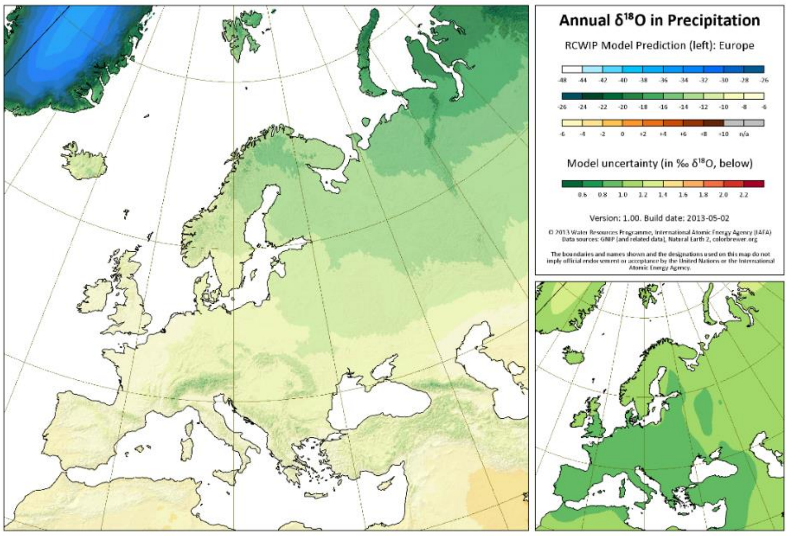

Figure 2. Mean annual δ^{18}O values in European precipitation calculated using the RCWIP model prediction. (IAEA, 2013; Terzer et al., 2013). (from: IAEA, 2013)

The measured long-term weighted mean δ^{18}O value of modern precipitation in GNIP stations near the research area ranges from −9.74‰ in Riga, Latvia (56°58'12"N; 24°04'12"E) to

−11.54‰ in Espoo, Southern Finland (60°10'48"N; 24°49'58"E) (IAEA/WMO, 2013). The long-term δ^2H values for the same stations are −73.3‰ and −82.0‰, respectively. The average values for these two stations were calculated for the periods of 1981-1984 and 2000-2005, respectively.

For the period of 2000-2002 a LMWL for Espoo was described by the equation $\delta^2H = 7.84\delta^{18}O + 9.35$ with a correlation coefficient (r^2) of 0.99 (Kortilainen and Karhu, 2004). The line is very close to the GMWL, which is a characteristic feature of the northern hemisphere continental stations (Dansgaard, 1964). The *d*-excess values calculated using long-term mean $\delta^{18}O$ and δ^2H values are 11.0 and 10.3 for Riga and Espoo, respectively.

The oxygen isotope composition of Estonian precipitation has previously been studied by Punning et al. (1987). The study used the data collected in the period of 1982-1985 from Tiirikoja station, Eastern Estonia (58°51'55"N; 26°57'08"E). The monthly weighted mean value of $\delta^{18}O$ in precipitation was −10.4‰. The difference between the summer and winter $\delta^{18}O$ values was 9.1‰ on average. The weighted mean $\delta^{18}O$ values of winter and summer months during the observation period were −13.8‰ and −8.4‰, respectively.

In July 2013 two new GNIP stations were established in the Estonian territory. The stations are located in Vilsandi Island near Saaremaa (58°22'58"N; 21°48'51"E) and in Tartu/Tõravere meteorological station in Southern Estonia (58°15'50"N; 26°27'41"E). The composite monthly samples of precipitation have been collected according to IAEA/WMO guidelines (IAEA/WMO, 2012). Due to the short collection period the results from these stations are not used in this study.

The chemical composition of bulk precipitation in 10 stations across Estonia was studied by Treier et al., (2004) in the period of 1994-2001. The concentrations of anions (SO_4^{2-}, NO_3^- and Cl^-) and cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) were measured. The chemical composition of precipitation in Estonia is influenced by both natural and anthropogenic sources. Despite the fact that both Cl^- and SO_4^{2-} in precipitation are of marine origin in natural conditions, the concentrations of both anions in Estonian precipitation are influenced by the Estonian oil shale industry and are thus of anthropogenic origin (Treier et al., 2004). Cations originate from natural sources such as sea salt (Mg^{2+} and Na^+) and soil dust (Ca^{2+}, Mg^{2+}, K^+ and Na^+), as well as from oil-shale fly ash (Ca^{2+}, Mg^{2+}, K^+ and Na^+) (Treier et al., 2004).

3.2. Geology and hydrogeological setting

Geologically, Estonia is situated in the north-western part of the East European platform on the southern slope of the Fennoscandian Shield with its extreme south-western and southern parts forming the wings of the Baltic Syneclise and the Mõniste-Lokno Uplift, respectively (Raukas, 1997). The bedrock consists mainly of Ediacaran and Palaeozoic sedimentary rocks which overlie the Paleo-Proterozoic crystalline basement. The crystalline basement gradually slopes towards the south by 2-4 m/km.

Hydrogeologically the Estonian territory is situated in the northern part of the Baltic Artesian Basin (BAB) (Figure 3). BAB is a complex multi-layered hydrogeological system in the south-eastern Baltic covering about 480000 km^2 (Virbulis et al., 2013). The BAB covers the territories of Estonia, Latvia, Lithuania and parts of Russia, Poland and Belarus. Approximately half of the BAB is covered by the Baltic Sea. The thickness of the sedimentary cover reaches 5000 m in the south-western part, while the crystalline basement reaches the surface at the northern and south-eastern parts of the BAB (Virbulis et al., 2013). General flow of the groundwater in the BAB is directed from southeast to northwest, but the local topography shows a strong influence on the shallower aquifers.

Although Estonian groundwater has been mainly considered a part of BAB, Perens and Vallner (1997) argue that from the applicational point of view, the Estonian water-bearing formation can be considered an independent artesian basin. This assumption can be made because the exchange of groundwater with the neighbouring areas is less than 0.1% of the total annual groundwater recharge.

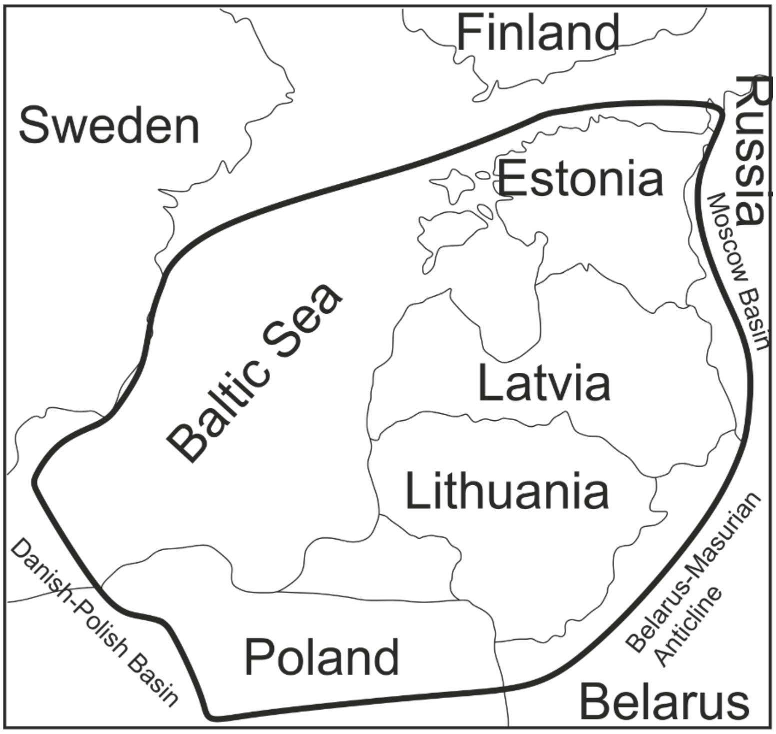

Figure 3. The location and boundaries of the Baltic Artesian Basin. (after: Virbulis et al., 2013)

Perens and Vallner (1997) divide the groundwater system in Estonia into three principal hydrostratigraphical units on the basis of groundwater formation and circulation:

- The Quaternary deposits, which are directly influenced by meteorological conditions and where a lot of water circulates by the agency of capillary force or evaporates, in addition to the filtration flow;
- The bedrock, which consists of terrigeneous and carbonate Palaeozoic and Proterozoic (Ediacaran) rocks that form porous, fissured and karstified mostly confined aquifers, which are isolated from each other with aquitards of different isolation capacity. In the deeper strata the pre-Quaternary groundwater is high in total dissolved solids (TDS) and moves very slowly under natural conditions;
- Predominantly pre-Quaternary groundwater in the fissures of igneous and metamorphic rocks (crystalline basement), that contains a high rate of TDS and under natural conditions is sporadically almost stagnant. The lower portion of the crystalline basement serves as an aqifuge for the whole overlying water-bearing formation in Estonia.

The distribution of main aquifer systems together with regional aquitards in the hydrogeological cross-section of the Estonian territory is shown in Figure 4.

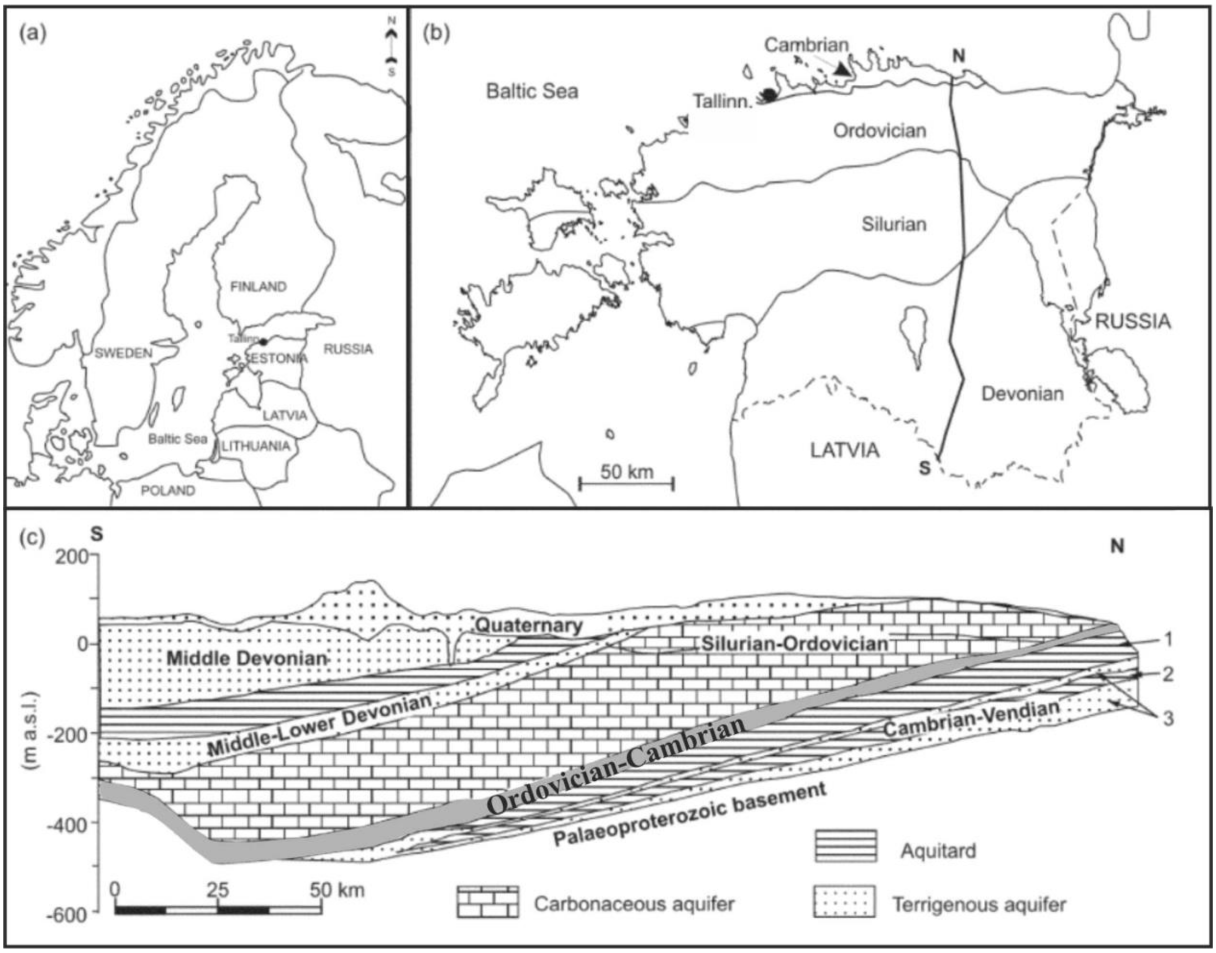

Figure 4. (a) Schematic map showing the location of Estonia. (b) Geological map of Estonia showing the outcrop areas of geological systems together with the position of the line of the cross section. (c) North-south cross section of major aquifer systems in Estonia. 1 - Lontova regional aquitard; 2 - Kotlin aquitard; 3 - Voronka and Gdov aquifer. The investigated Ordovician-Cambrian aquifer system is shown with grey colour in the north-south cross section. (modified from: Karro et al., 2009)

3.3. Hydrogeological characterization of the Ordovician-Cambrian aquifer system

The O-Cm aquifer system is a confined water body in the northern part of the Baltic Artesian Basin. The aquifer system is distributed in most of the Estonian territory, except the North-Estonian coastal region and Mõniste-Lokno uplift area (Figure 5). The aquifer system consists of fine-grained sandstones and siltstones of the Lower Ordovician Kallavere Formation and the Lower Cambrian Tiskre Formation (Perens and Vallner, 1997). The mean thickness of the aquifer system is 20-60 meters increasing from north to south to 105 meters (Savitskaja et al., 1995; Perens and Vallner, 1997). The depth from the ground increases from 10-20 m at Northern-Estonia up to 500 m on Estonia's southern border. The lateral conductivity of the aquifer system ranges from 1 to 3 m/d (Perens and Vallner, 1997). Transmissivity ranges from

25 to 50 m^2/d in northern Estonia increasing to 80-130 m^2/d in Southern Estonia due to the increased thickness of the water-bearing formation (Perens and Vallner, 1997). The water in the aquifer system is confined. The head of the aquifer system is generated in the Pandivere Uplands (Figure 5). The recharge to the aquifer systems occurs via the Silurian-Ordovician aquifer systems and through the ancient buried valleys in Northern Estonia (Savitskaja et al., 1995).

The previous studies show that the chemical composition of the groundwater in the aquifer system is diverse. In northern Estonia the water is predominantly of $MgCaHCO_3$-, $NaMgHCO_3$- or $NaMgCaHCO_3Cl$-type with the TDS concentrations of 200-500 mg/l (Perens et al., 2001). In Southern Estonia and in Western Estonian Archipelago the chemical type of groundwater changes to $NaMgClHCO_3$-, $NaCaClHCO_3$- and NaCl-type with TDS values up to 2000 mg/l together with the increasing depth from the surface (Perens et al., 2001).

The O-Cm aquifer system is underlain by the Lükati-Lontova regional aquitard (C_1lk-C_1ln) which is represented by siltstones and clays of the Lower Cambrian Lükati and Lontova Formations and has the transversal conductivity of 10^{-7} - 10^{-5} m/d (Perens and Vallner, 1997). In Western Estonia and in the West-Estonian Archipelago the Lükati and Lontova Formations are laterally replaced by siltstones and sandstones of the Voosi Formation (Figure 5). The aquitard becomes sandier and thinner with its transversal permeability increasing to $>10^{-5}$ m/d (Perens and Vallner, 1997). In the West-Estonian Archipelago and South-western Estonia, the Ediacaran deposits underlying the Lükati-Lontova regional aquitard pinch out (Figure 5). South and south-west from this line the water-bearing terrigeneous rocks consist only of Cambrian sand- and siltstones with interlayers of clay (Perens and Vallner 1997).

The aquifer system is confined by the overlying the Silurian-Ordovician regional aquitard. Silurian-Ordovician regional aquitard consist of limestones, marls, siltstones, clays and argillites of the Toila, Leetse, Varangu and Türisalu Formations of Lower Ordovician Series, extending at a length of 30 km southward from the North-Estonian Klint (Perens and Vallner, 1997). The whole of Silurian-Ordovician aquifer system and the rock matrix can be viewed as a regional aquitard at increasing depths (Perens and Vallner, 1997). Further in the south in most of the Estonian territory the aquitard includes all Silurian and Ordovician rocks with its thickness increasing from a couple of metres in northern coastal area up to 200-350 m near the southern border of Estonia. The transversal conductivity of the regional aquitard ranges from 10^{-7} to 10^{-5} m/d (Vallner, 1997).

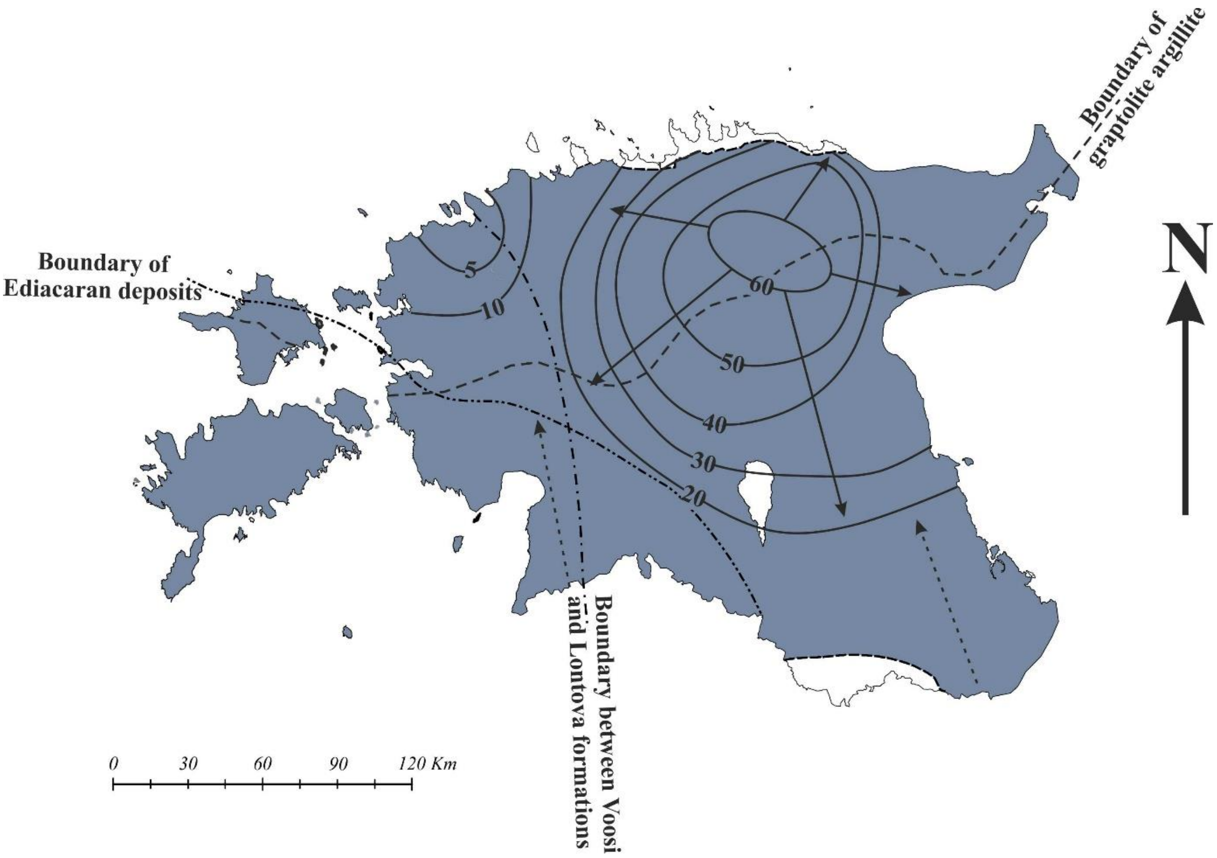

Figure 5. The distribution of the Ordovician-Cambrian aquifer system in Estonia. The closed lines indicate the height of potentiometric surfaces above sea-level in meters (Marandi, 2010). The 60-m-isoline represents the approximate location of the recharge area in the Pandivere Uplands. The boundaries between Lontova and Voosi Formations together with the boundaries of Ediacaran deposits and the graptolite argillite are shown for reference (Perens and Vallner, 1997; Hade and Soesoo, 2014). Dashed arrows indicate the flow of groundwater from the southerly direction.

3.4. Whole-rock mineral composition in the Ordovician-Cambrian aquifer system

O-Cm aquifer system consists mainly of the sandstones of Lower Ordovician and Cambrian age. The unlitified and silty clays of Lükati and Lontova/Voosi Formations which underlie the aquifer system consist mainly of illite and illite-smectite followed by kaolinite and chlorite (Kirsimäe and Jørgensen, 2000). Clay minerals make up 45-70% of the rock, with lower contents of 35-50% found in Voosi Formation in Western Estonia (Raidla et al., 2006). Quartz is the most abundant of the non-clay minerals (Kirsimäe and Jørgensen, 2000). The amount of organic matter in the Cambrian clays ranges from 0.79 to 2.56% (Raidla et al., 2006).

The Lükati and Lontova/Voosi Formations are overlain by sandstones of the Sõru, Lükati and Tiskre Formations of the Dominopol Stage which are distributed mainly in Western Estonia. These formations are overlain by Paala Formation in Eastern Estonia and Ruhnu and Irben

Formations in the Western Estonia. The Furongian aged Petseri, Ülgase, Tsitre and the lower portion of the Kallavere Formation are distributed only occasionally in the northern and south-eastern parts of the country (Raidla et al., 2006). The uppermost part of the aquifer system consists of the upper portion of the Kallavere Formation in Lower Ordovician Series.

The sandstones in Cambrian and lowermost Ordovician are mainly quartz arenites or subarkoses, with quartz content up to 90% in Tiskre and Paala Formations (Raidla et al., 2006). The feldspars are exclusively K-feldspars (Raidla et al., 2006). The sandstones are weakly cemented with authigenic carbonate minerals (Fe-rich dolomite, calcite, siderite) (Raidla et al., 2006). The authigenic apatite (shell detritus of phosphatic brachiopods) is found in Kallavere Formation.

The graptolite argillite of the Lower Ordovician Türisalu Formation overlies the aquifer system in northern part of the country and acts as a aquitard between the O-Cm and Silurian-Ordovician aquifer systems. The graptolite argillite is an argillaceous rock which is characterized by high content of organic matter (15-20%) and pyrite (2.4-6%) (Voolma et al., 2013). The mineral assemblage of the graptolite argillite is dominated by K-feldspar, quartz and clay minerals (illite, illite-smectite, chloride) (Voolma et al., 2013).

4. Material and methods

The study is based on a hydrogeochemistry database which consists of 31 groundwater samples collected from wells screened in the O-Cm aquifer system in Estonia and in the Cambrian aquifer system in Latvia. The samples have been collected by the Estonian Geological Survey (EGS) and the Department of Isotope-palaeoclimatology at Institute of Geology, Tallinn University of Technology from operational private, municipal water supply and observation wells. The location information, depths and stratigraphic position of the sampled wells is provided in Table 1. The study uses data from fieldworks carried out in 2013 to supplement the existing database of groundwaters in the aquifer system for new locations and δ^2H data, previously not measured for groundwaters in the aquifer system. Of the 31 measured samples 17 have been collected during the year 2013 and 5 samples represent the unpublished data from the period of 2001-2012. The dataset includes 9 results from earlier studies published in the reports of Estonian Geological Survey (Kivit et al., 1993; Savitskaja et al., 1995). The earlier publications have been used for wells which are no longer in use or were not accessible for sampling in 2013. The well locations were chosen to achieve a diverse spatial sampling both in depth and laterally across the Estonian territory. The locations of the sampled wells together with the locations of the GNIP stations mentioned in the text are given in Figure 6.

The dataset includes hydrochemical data of the major elemental composition of the studied groundwaters. This data is accompanied by stable isotope data of $\delta^{18}O$ for all samples and by both $\delta^{18}O$ and δ^2H data for samples collected during the period of 2010-2013.

Samples for the chemical analyses were filtered in the field prior to the analysis of main and minor ionic components and analysed in the Geochemistry Laboratory of Estonian Geological Survey using the flame photometry (K^+, Na^+) method and volumetric (HCO_3^-, Cl^-, Ca^{2+}, Mg^{2+}) and gravimetric (SO_4^{2-}) analysis. The precision of the analysis for the given elements was ±16%, ±19%, ±2%, ±3%, ±6%, ±10% and ±9%, respectively. Eleven samples were analysed in the Laboratory of Hydrogeochemistry in the Department of Hydrogeology and Engineering Geology of Vilnius University using DIONEX ICS-5000 ion-chromatograph. The precision for major ionic components was ±1%. The original measured concentrations expressed in mg/l were converted to the molarity units expressed in mmol/l. The quality of all the water chemistry analyses was screened and those where the charge balance error exceeded ±5% were not included in the study.

Stable isotope ratios of hydrogen and oxygen in water were analysed in the Laboratory of mass spectrometry at Institute of Geology, Tallinn University of Technology. Isotope ratios are expressed in standard δ-notation relative to Vienna Standard Mean Ocean Water (VSMOW). Prior to July 2006 the stable isotope ratios of oxygen were measured with Finnigan MAT Delta-E mass spectrometer using the conventional CO_2 equilibration technique (Epstein and Mayeda, 1953). For samples collected since the year 2010 both isotope ratios of hydrogen and oxygen were measured with Picarro L2120-i Isotopic Water Analyzer using the cavity ring-down laser spectroscopy (CRDS) method (Brand et al., 2009). Reproducibility of the stable isotope measurements was ±0.1‰ for $\delta^{18}O$ and ±1‰ for $\delta^{2}H$. The *d*-excess value for samples measured for both hydrogen and oxygen was calculated using the equation no. 4.

To establish the isotopic input signal for the modern water that recharges to the groundwater table, the information about the isotopic composition of precipitation from Estonian territory (Punning et al., 1987) and the nearby stations of the GNIP database (IAEA/WMO, 2013) is used. The study uses data describing the chemical composition of modern precipitation in Estonia published by Treier et al., (2004). The data has been generalized to Estonian territory by the author by calculating the mean values from data published for different stations. The original concentrations of the major elements expressed in mg/l have been converted to molarity units.

Table 1. Well locations and hydrogeological characteristics of the studied wells (EELIS, 2014). * - A. Babre (pers. comm., 13 September 2012). O-Cm – Ordovician-Cambrian aquifer system; Cm – Cambrian aquifer system; O_3vr – Kõrgessaare and Tudulinna Formations in Upper Ordovician Series; O_2on – Hirmuse Formation in Upper Ordovician Series; O_1pk - Kallavere Formation in the Lower Ordovician and Furongian Series; C_1ts – Tiskre Formation in the Lower Cambrian Series; C_1lk – Lükati Formation in the Lower Cambrian Series; C_1ln – Lontova Formation in the Lower Cambrian Series; C_1ir – Irben Formation in the Lower Cambrian Series; C_1vs – Voosi Formation in the Lower Cambrian Series.

No.	Well ID	Location	Aquifer system	Complex	Depth	Start of open interval
					m	m
1	13872	Hiiumaa island, Nõmme	O-Cm	O_1pk-C_1ln	138.0	99.7
2	8104	Nõva commune, Nõva	O-Cm	O_1pk-C_1ts	85	69.5
3	16413	Padise commune, Vihterpalu	O-Cm	O_1pk-C_1ts	81	66.8
4	1333	Padise commune, Harju-Risti	O-Cm	O_1pk-C_1ts	100	75.45
5	1183	Vasalemma commune, Rummu	O-Cm	O_1pk-C_1ln	115	82
6	14109	Vasalemma commune, Rummu	O-Cm	O_1pk-C_1lk	110	73.5
7	15346	Keila commune, Karjaküla	O-Cm	O_1pk-C_1ts	68	52
8	574	Keila	O-Cm	O_1pk-C_1ts	88	56.65
9	766	Harku commune, Vääna	O-Cm	O_1pk-C_1ts	50	26
10	213	Saku commune, Saku	O-Cm	O_1pk-C_1ts	90	63
11	218	Tallinn	O-Cm	O_1pk-C_1ln	81.5	59
12	204	Saku commune, Saku	O-Cm	O_2kk-O_1pk	92	41
13	1630	Kiili commune, Kiili	O-Cm	O_1pk-C_1ln	94	60.2
14	1037	Kuusalu commune, Kolgaküla	O-Cm	O_1pk-C_1ln	34	9.9
15	3688	Haljala commune, Aaviku	O-Cm	O_1pk-C_1ts	17.2	7.2
16	4207	Haapsalu	O-Cm	O_1pk-C_1ln	220	174
17	9483	Lääne-Nigula commune, Risti	O-Cm	O_1pk-C_1lk	209	162
18	1576	Nissi commune, Turba	O-Cm	O_1pk-C_1ts	175	142
19	2063	Nissi commune, Riisipere	O-Cm	O_1pk-C_1ts	160	131
20	8365	Rapla	O-Cm	O_2on-C_1lk	250	195.4
21	4107	Tapa	O-Cm	O_1pk-C_1ln	160	128.8
22	2739	Rakvere	O-Cm	O_1pk-C_1lk	100	69.8
23	2268	Jõhvi	O-Cm	O_1pk-C_1ln	82	61
24	10057	Jõgeva commune, Tooma	O-Cm	O_1lt-O_1pk	255.3	240
25	4486	Pärnu	O-Cm	O_3vr-C_1ln	455	382
26	7298	Viljandi	O-Cm	O_1pk-C_1ln	480	417
27	1222	Tartu	O-Cm	O_1pk-C_1ln	410	359.05
28	3950	Värska commune, Värska	O-Cm	C_1ts-C_1ln	500	470
29	8021	Häädemeeste	Cm	C_1ir-C_1vs	610	560
30	50202 LV	Kemeri, Latvia*	Cm		999	
31	50194 LV	Riga, Latvia*	Cm		1027	

5. Results and discussion

5.1. Major ion chemistry and isotope composition of the studied groundwaters

The data for isotope and major elemental composition of the sampled groundwaters together with that of the precipitation in the research area is presented in Table 2.

The sampled groundwaters are characterized by great variety in chemical and isotope composition. The $\delta^{18}O$ values vary from −11.3‰ to −22.4‰ with more negative values found in North-western Estonia. TDS concentrations increase in southerly direction from 100 mg/l in Northern Estonia to 1950 mg/l in Southern Estonia. Distinct differences are also evident in major elemental composition of the sampled groundwaters. In Northern Estonia HCO_3^- is the dominant anion with concentrations of 1.2-6.7 mmol/l. In southern Estonia Cl^- becomes the dominant anion with concentrations of 9-32 mmol/l. The cation portion of groundwater is dominated by Ca^{2+} and Mg^{2+} in Northern and North-eastern part of Estonia with Na^+ being the dominant cation in North-western and Southern Estonia. The concentrations of SO_4^{2-} range from 0.01 to 0.7 mmol/l and do not show any distinct pattern in geographical distribution.

The waters in the O-Cm aquifer system in Estonia can be divided into three major groundwater types on the basis of their major elemental and isotope composition:

1. The I-type of waters are primarily located in coastal region in Northern Estonia and in North-Eastern Estonia (Figure 6b) at depths from 7 meters up to 250 meters (Table 1). The TDS concentrations in these waters range from 118 to 625 mg/l. The dominant cations and anions in this water type are Ca^{2+}, Mg^{2+} and HCO_3^- with concentrations of 0.5-2.5 mmol/l, 0.1-1.5 mmol/l and 1.2-6.7 mmol/l, respectively. The Cl^- concentrations of the waters are low having values of 0.2-0.5 mmol/l. Waters of the I-type are characterized by $\delta^{18}O$ and δ^2H values that range from −11.3‰ to −13.8‰ and from −81‰ to −88‰, respectively. The mean δ^2H and *d*-excess values of −84‰ and 10.3 in this water type are very close to the values found in modern precipitation in the research area (Table 2). The mean $\delta^{18}O$ value of −11.9‰ is slightly lower than the weighted mean value for the research area (Table 2). The lowest measured $\delta^{18}O$ value of −13.8‰ in I- type of waters is the same as the measured weighted mean value for winter precipitation in Tiirikoja, Estonia (Punning et al., 1987) and Espoo, Finland (IAEA/WMO, 2013).

2. The II-type of waters are located mainly in North-western Estonia (Figure 6b) at depths of 25-250 meters (Table 1). The TDS concentrations of these waters are close to those found in the I-type of waters. The II-type watres can be differentiated from the former by the elevated Na^+ and Cl^- concentrations. The waters are characterized by $\delta^{18}O$ and δ^2H values from −14.7‰ to −22.4‰ and from −112‰ to −169‰, respectively. The mean $\delta^{18}O$ and δ^2H values of −18.5‰ and −141‰ are more negative compared to modern precipitation in the research area (Table 2).The mean *d*-excess value of 10.5 is very close to the value in modern precipitation (Table 2).
3. The III-type of waters are located in Southern Estonia at depths of 250-560 meters (Figure 6b; Table 1). The waters in this type are much saltier than those found in former types and are characterized by TDS concentrations of 700-1950 mg/l. The water type differs from the previous types in low concentrations of bicarbonate anion. The Na^+ and Cl^- concentrations dominate the major elemental composition in these waters with values of 10-28 mmol/l and 9.5-31 mmol/l, respectively. The III-type of waters have $\delta^{18}O$ values ranging from −13.6‰ to −15.6‰. The mean $\delta^{18}O$ value in these waters is −14.6‰ and only available δ^2H value for this water type is −100.7‰ (corresponding to $\delta^{18}O$ value of −13.7‰). Thus, the waters of the III-type are characterized by isotope values which lie in between the values found in modern precipitation and more negative values found in waters of the II-type.

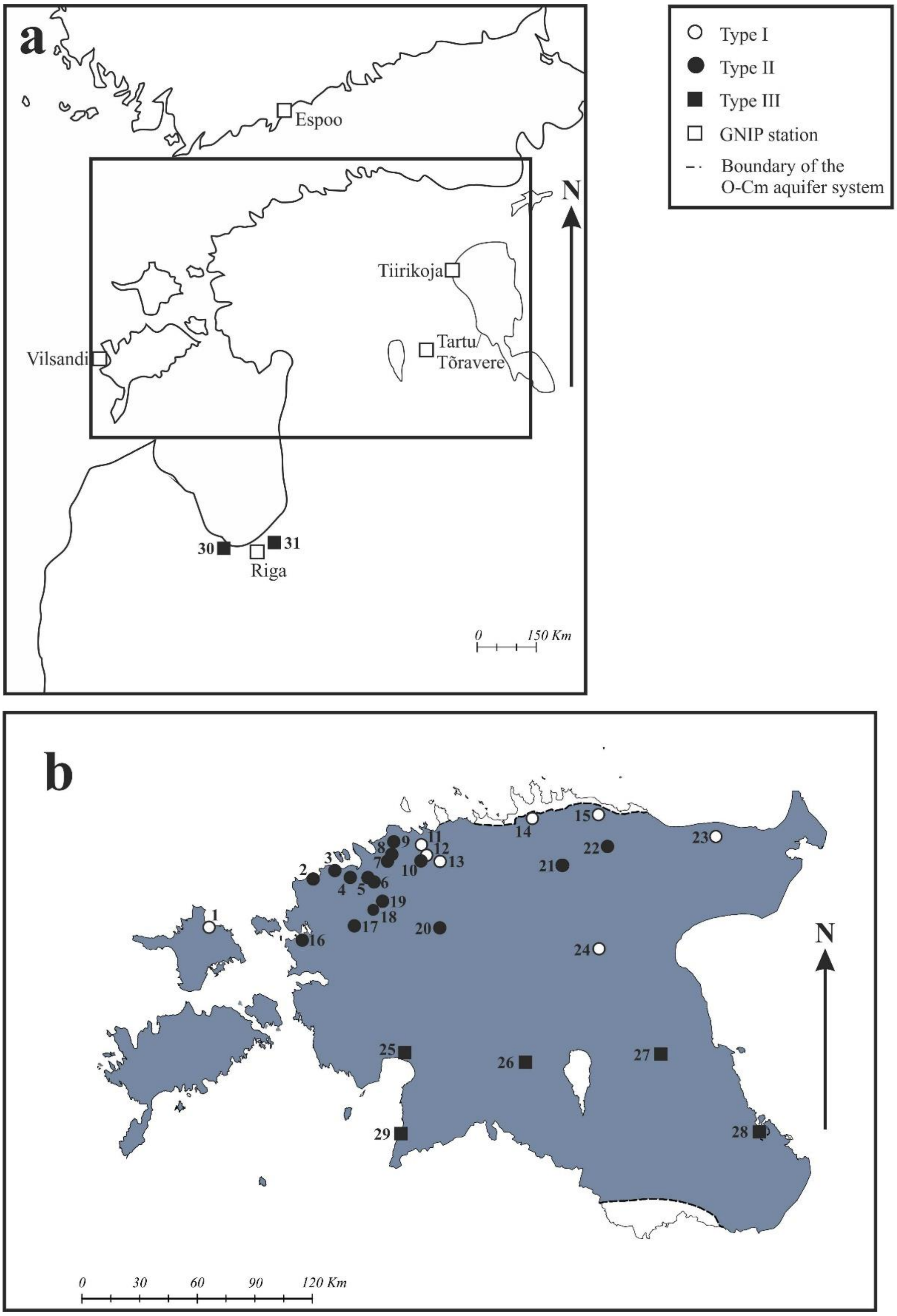

Figure 6. (a) The locations of GNIP stations mentioned in the text together with two sampled wells from the Cambrian aquifer system in Latvia. Numbers indicate the position of the sampled groundwaters in Tables 1 and 2. The rectangle marks the location of the research area in Estonian territory shown in the figure below. (b) The locations of the sampled wells in Ordovician-Cambrian aquifer system in Estonia. The symbols indicate the groundwater type in wells based on the classification given in the text. Numbers indicate the position of the sampled groundwater in Tables 1 and 2.

To clarify the origin of III-type of waters, their isotope and chemical composition is compared with water from deeper wells in the Cambrian aquifer system in Latvia (Figure 6a). The two studied waters are located at the approximate depth of 1000 meters (Table 1). The waters are characterized by high concentrations of Na^+, Ca^{2+}, Cl^- and very low concentrations of HCO_3^- having the TDS concentrations of 114900 mg/l and 116500 mg/l, respectively (Table 2). The Na^+ and Cl^- concentrations range from 1450 to 1570 mmol/l and from 1920 to 1990 mmol/l, respectively. The waters have Ca^{2+} concentrations of 170-210 mmol/l. The HCO_3^- concentrations in the sampled wells are of 0.5-0.7 mmol/l. The mean $\delta^{18}O$ and δ^2H values of −4.6‰ and −42‰ show that these waters are characterized by more positive isotope composition when compared to values found in the O-Cm aquifer system and in modern precipitation. It must be noted that the Cambrian aquifer system can be viewed as an extension of the O-Cm aquifer system in Latvia because the Lontova/Voosi Formation which forms a regional aquitard between the aquifer systems pinches out in the southernmost part of Estonia (Mens and Pirrus, 1997).

Table 2. Major ion chemistry, δ^2H, δ^{18}O and *d*-excess values of the groundwaters in the studied wells. The average chemical and isotope composition of precipitation in the research area is also given for reference. * - chemical analyses performed in Vilnius University; ** - some technical difficulties occurred during sampling.

No.	Well ID	Location	Sampling date	pH	TDS	Ca^{2+}	Mg^{2+}	K^+	Na^+	HCO_3^-	Cl^-	SO_4^{2-}	$\delta^{18}O$	δ^2H	*d*-excess	Type	Publication
					mg/l				*mmol/l*				‰, VSMOW				
		Precipitation: Espoo, Finland											−11.5	−82.0	10.3		IAEA/WMO, 2013
		Precipitation: Tiirikoja, Estonia											−10.4				Punning et al., 1987
		Precipitation: Riga, Latvia											−9.7	−73.3	11.0		IAEA/WMO, 2013
		Modern precipitation: Estonia				0.05	0.01	0.01	0.05		0.06	0.06					Treier et al., 2004
1	13872	Hiiumaa island, Nõmme	03.10.2013	8.5	118	0.54	0.15	0.03	0.23	1.20	0.24	0.04	−11.5	−81.1	10.8	Type I	
2	8104	Nõva commune, Nõva*	26.08.2013	8.2	279	0.55	0.44	0.13	1.65	2.70	0.39	0.26	−22.4	−169.3	9.8	Type II	
3	16413	Padise commune, Vihterpalu*	27.08.2013	8.0	315	0.64	0.50	0.17	1.94	3.00	1.11	0.14	−20.3	−151.9	10.3	Type II	
4	1333	Padise commune, Harju-Risti*	27.08.2013	8.0	362	0.63	0.58	0.17	2.80	2.90	1.66	0.16	−19.8	−148.3	10.4	Type II	
5	1183	Vasalemma commune, Rummu*	27.08.2013	7.8	362	0.62	0.44	0.15	3.00	3.00	1.54	0.10	−19.1	−142.2	10.7	Type II	
6	14109	Vasalemma commune, Rummu	01.10.2010	7.6	399	0.86	0.43	0.21	3.01	2.90	2.02	0.29	−18.7	−139.8	9.8	Type II	
7	15346	Keila commune, Karjaküla	11.10.2013	7.3	359	0.92	0.46	0.15	1.88	3.40	1.19	0.12	−19.3	−142.2	12.1	Type II	
8	574	Keila	26.06.1995	8.0	306	0.64	0.49	0.16	1.74	2.50	1.19	0.21	−19.3			Type II	Savitskaja et al., 1995
9	766	Harku commune, Vääna*	28.08.2013	7.7	479	1.10	0.96	0.19	1.78	5.30	0.67	0.15	−15.3	−112.3	10.5	Type II	
10	213	Saku commune, Saku	05.07.1989	8.0	386	0.77	0.61	0.23	2.21	3.60	1.51	0.08	−18.7			Type II	Kivit et al., 1993
11	218	Tallinn	05.04.2001	8.2	208	0.61	0.44	0.16	0.46	2.40	0.22	0.01	−11.3			Type I	
12	204	Saku commune, Saku*	11.12.2013	7.2	625	1.99	1.29	0.19	1.12	6.65	0.52	0.57	−12.2	−87.8	9.9	Type I	
13	1630	Kiili commune, Kiili*/**	29.08.2013	7.4	583	2.51	0.91	0.12	0.43	6.00	0.50	0.63	−11.5	−82.1	9.6	Type I	
14	1037	Kuusalu commune, Kolgaküla	27.08.2013	7.4	340	1.68	0.35	0.08	0.22	3.60	0.48	0.18	−12.0	−84.8	10.9	Type I	
15	3688	Haljala commune, Aaviku	27.08.2013	7.3	400	1.66	0.81	0.10	0.09	4.90	0.14	0.03	−11.9	−84.7	10.2	Type I	
16	4207	Haapsalu*	26.08.2013	8.2	418	0.28	0.24	0.10	4.24	4.18	1.17	0.02	−19.2	−143.3	10.4	Type II	
17	9483	Lääne-Nigula commune, Risti*	26.08.2013	8.1	439	0.53	0.49	0.16	3.75	4.02	1.90	0.01	−19.0	−140.8	11.2	Type II	
18	1576	Nissi commune, Turba	21.08.1990	8.0	426	0.73	0.56	0.20	3.33	3.10	2.99	0.03	−18.4			Type II	Kivit et al., 1993
19	2063	Nissi commune, Riisipere*/**	30.08.2013	8.0	435	0.66	0.49	0.16	3.51	3.70	2.13	0.07	−17.8	−131.3	10.9	Type II	
20	8365	Rapla	29.06.1995	7.8	428	0.88	0.83	0.23	2.61	3.50	2.23	0.02	−16.1			Type II	Savitskaja et al., 1995

21	4107	Tapa	21.08.2013	8.0	377	0.79	0.11	0.17	2.68	4.00	0.85	0.03	−17.2	−128.0	9.4	Type II	
22	2739	Rakvere	19.06.1995	8.0	357	0.66	0.66	0.23	1.94	3.80	0.62	<0.01	−14.7			Type II	Savitskaja et al., 1995
23	2268	Jõhvi	19.06.1995	7.4	514	1.36	1.46	0.20	1.06	5.90	0.21	0.16	−13.8			Type I	Savitskaja et al., 1995
24	10057	Jõgeva commune, Tooma	22.08.2013	7.6	318	1.02	0.89	0.06	0.22	3.70	0.52	0.03	−11.3	−80.4	10.0	Type I	
25	4486	Pärnu	26.06.1995	7.9	1526	0.86	0.73	0.24	21.75	3.50	20.10	0.30	−14.0			Type III	Savitskaja et al., 1995
26	7298	Viljandi	21.06.1995	8.2	978	0.69	0.53	0.19	13.48	1.80	13.37	0.30	−15.6			Type III	Savitskaja et al., 1995
27	1222	Tartu	21.06.1995	8.3	716	0.31	0.27	0.12	10.40	1.50	9.48	0.19	−15.1			Type III	Savitskaja et al., 1995
28	3950	Värska commune, Värska*	03.07.2013	7.9	1940	2.18	1.32	0.40	24.63	3.83	27.81	0.17	−14.4			Type III	
29	8021	Häädemeeste	02.10.2012	7.6	1946	1.65	1.65	0.33	27.84		31.67	0.66	−13.7	−100.7		Type III	
30	50202 LV	Kemeri, Latvia	03.10.2012		114900	170	106	6.81	1458	0.70	1990	12.1	−4.4	−40.6		Type III	
31	50194 LV	Riga, Latvia	03.10.2012		116500	208	101	8.39	1565	0.59	1920	13.7	−4.8	−42.7		Type III	

5.2. Sources of water: oxygen and hydrogen isotopes

Three groundwater types in the O-Cm aquifer system are characterized by wide variety in stable isotope composition. The correlation of $\delta^{18}O$ values with well depth reveals that the shallow part of the aquifer system at depths less than 250 meters contains two groundwater types with different stable isotope composition (Figure 7). In Northern and North-eastern part of Estonia waters of the type I dominate with $\delta^{18}O$ values more positive than −14‰.

The II-type waters with $\delta^{18}O$ values less than −16‰ dominate in North-western Estonia. Some II-type waters with more positive isotope composition are found in both North-western and North-eastern Estonia.

The III-type of waters found at depths greater than 250 meters in Southern Estonia have $\delta^{18}O$ values in the range of −13‰ to −16‰ while the more saline waters in the Cambrian aquifer system at depths of 1000 meters are characterized by a more positive mean $\delta^{18}O$ value of −4.6‰.

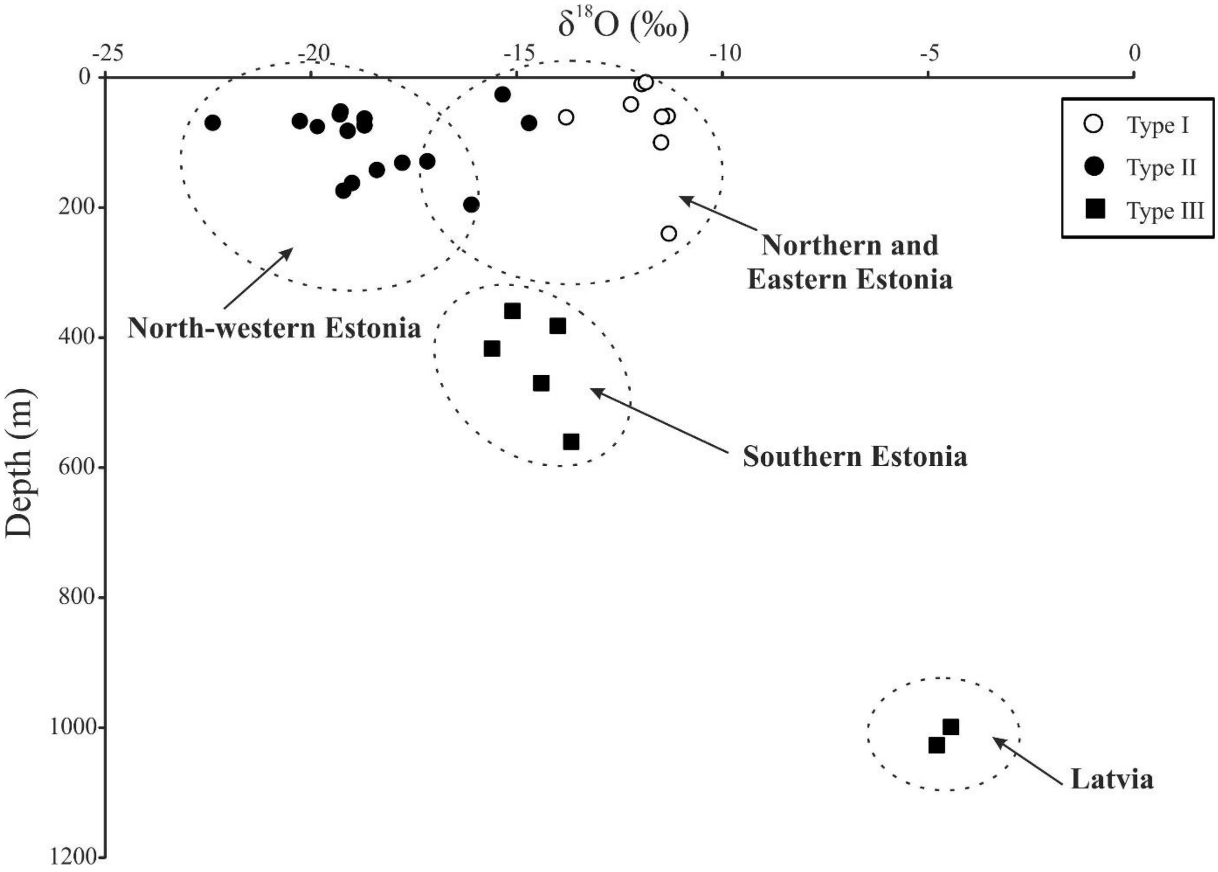

Figure 7. Oxygen isotope composition of various groundwater types in the Ordovician-Cambrian aquifer system versus the depth marking the start of their opened interval. The geographical location of the sampled wells is shown for reference.

Water types I and II have $\delta^{18}O$ and $\delta^{2}H$ values that define a line of $\delta^{2}H = 7.98\delta^{18}O + 9.98$ ($r^2=0.99$) which is almost coincident with the Global Meteoric Water Line (Figure 8). That indicates their origin from meteoric recharge. The $\delta^{18}O$ and $\delta^{2}H$ correlation in waters of the III-type deviates from the GMWL and the correlation between the oxygen and hydrogen values in these waters is $\delta^{2}H = 6.68\delta^{18}O + 10.85$ (Figure 8).

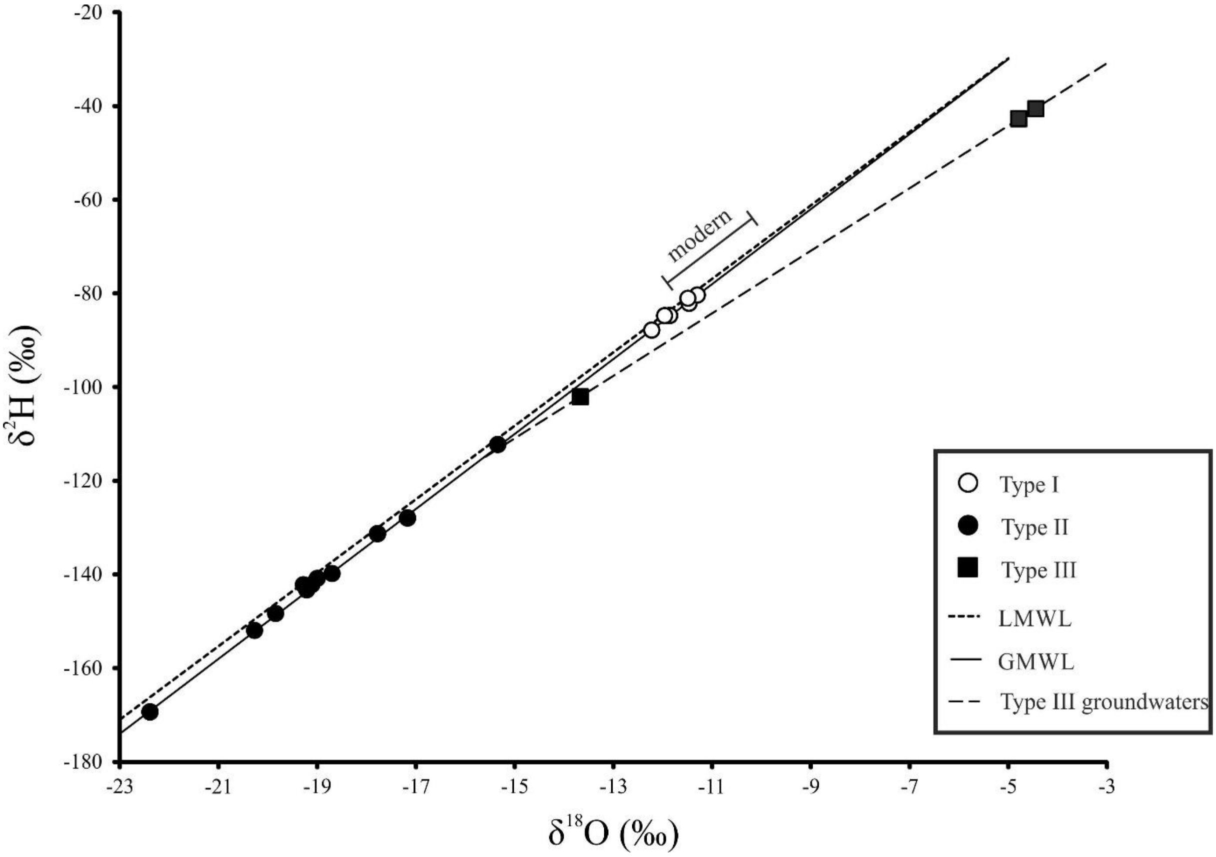

Figure 8. The oxygen and hydrogen isotope composition for groundwaters in the Ordovician-Cambrian aquifer system. The dashed line shows the LMWL from Espoo, Finland which is described by the equation $\delta^{2}H = 7.84\delta^{18}O + 9.35$ (Kortilainen and Karhu, 2004). The continuous line shows the GMWL defined by Craig (1961a) as $\delta^{2}H = 8\delta^{18}O + 10$. The range of annual weighted mean isotope composition found in modern precipitation in the research area is shown for reference.

The waters of the I-type plot close to the $\delta^{2}H$ and $\delta^{18}O$ values found in annual mean values of modern precipitation in the research area. The groundwater in the O-Cm aquifer system is recharged mainly from Pandivere Uplands in Northern Estonia (Figure 5; Perens and Vallner, 1997). Thus, the occurrence of the I-type of waters in Northern and North-eastern Estonia can be explained by the close proximity of the recharge area. In addition, the modern precipitation can also enter the aquifer system through the ancient buried valleys located in the area (Savitskaja et al., 1995) that are also responsible for the freshening of groundwater in the underlying Cambrian-Vendian aquifer system (e.g. Marandi, 2007; Vaikmäe et al., 2008).

Waters of the II-type have stable isotope compositions more negative compared to modern precipitation showing that meteoric water with a more negative isotope composition than the modern annual mean of precipitation in the research area has been the source of groundwater in this water type.

The II-type of waters are characterized by $\delta^{18}O$ and $\delta^{2}H$ mean values of −18.5‰ and −141‰, respectively (chapter 5.1). The only possible modern meteoric source with $\delta^{18}O$ values in the same range with the given values is snow. The most negative monthly isotope composition of snow measured in Espoo, Southern Finland has the $\delta^{18}O$ value of −21.6‰ (IAEA/WMO, 2013). However, the isotope composition of groundwater in a large area cannot be effected by such onetime extreme events. The measured weighted mean $\delta^{18}O$ values of precipitation for winter months range from −13.8‰ to −14.0‰ in the research area (Punning et al., 1987; IAEA/WMO, 2013). This means that waters characterized with $\delta^{18}O$ values less than −14‰ cannot originate from snowmelt. Furthermore, the chemical composition of groundwaters of the II-type is characterized by high sodium and chloride concentrations relative to modern precipitation (Table 2) which also excludes the possibility that the water originates from snowmelt.

Another hypothesis used to explain the negative isotope composition found in groundwaters is that of *in situ* ice formation during permafrost growth (Stotler et al., 2012). In this instance this possibility can be excluded, because the $\delta^{18}O$ and $\delta^{2}H$ values in this type of ice and residual fluids do not fall on the GMWL (Stotler et al., 2012).

The negative $\delta^{18}O$ values of less than −19‰ in the underlying Cambrian-Vendian aquifer system have been associated with isotopically light subglacial recharge from the Scandinavian Ice Sheet during last glaciation (Vaikmäe et al., 2001). This hypothesis could also be used to explain the origin of II-type water in the O-Cm aquifer system and is concordant with the altered chemical composition of water relative to groundwater originating from modern recharge (type I). Vaikmäe et al. (2001) showed that the more negative oxygen isotope values of less than −14‰ in the O-Cm aquifer system were associated with ^{14}C content of less than 5 pmC. The ^{14}C measurements available from the O-Cm aquifer system indicate that the more negative isotope composition is associated with older waters.

The II-type of waters in North-western Estonia are located further away from the recharge area and are characterized by lower absolute heights of the water table (Figure 6). Due to low actual mean groundwater velocity of 0.005 m/d in Cambrian sandstones the groundwater could have moved only for about 20-40 km during the last ~10000 years (Vallner, 1997). This could have made possible the preservation of glacial meltwater in this part of the aquifer system and provide enough time for groundwater to mix with older more saline waters and for the alternation of its chemical composition through water-rock interactions.

This type of preservation has been helped by the greater thickness of the Lower Ordovician aquitard overlying the O-Cm aquifer system in North-western Estonia. The transversal conductivity of the Lower Ordovician aquitard ranges from 10^{-7} to 10^{-5} m/d (Perens and Vallner, 1997). The main part of this aquitard consists of graptolite argillite of the Lower Ordovician age which has the greatest thickness of up to 7.7 meters in North-western Estonia (Hade and Soesoo, 2014). The greatest thickness of the overlying aquitard correlates with most negative $\delta^{18}O$ values found in the O-Cm aquifer system (Figure 9a, b).

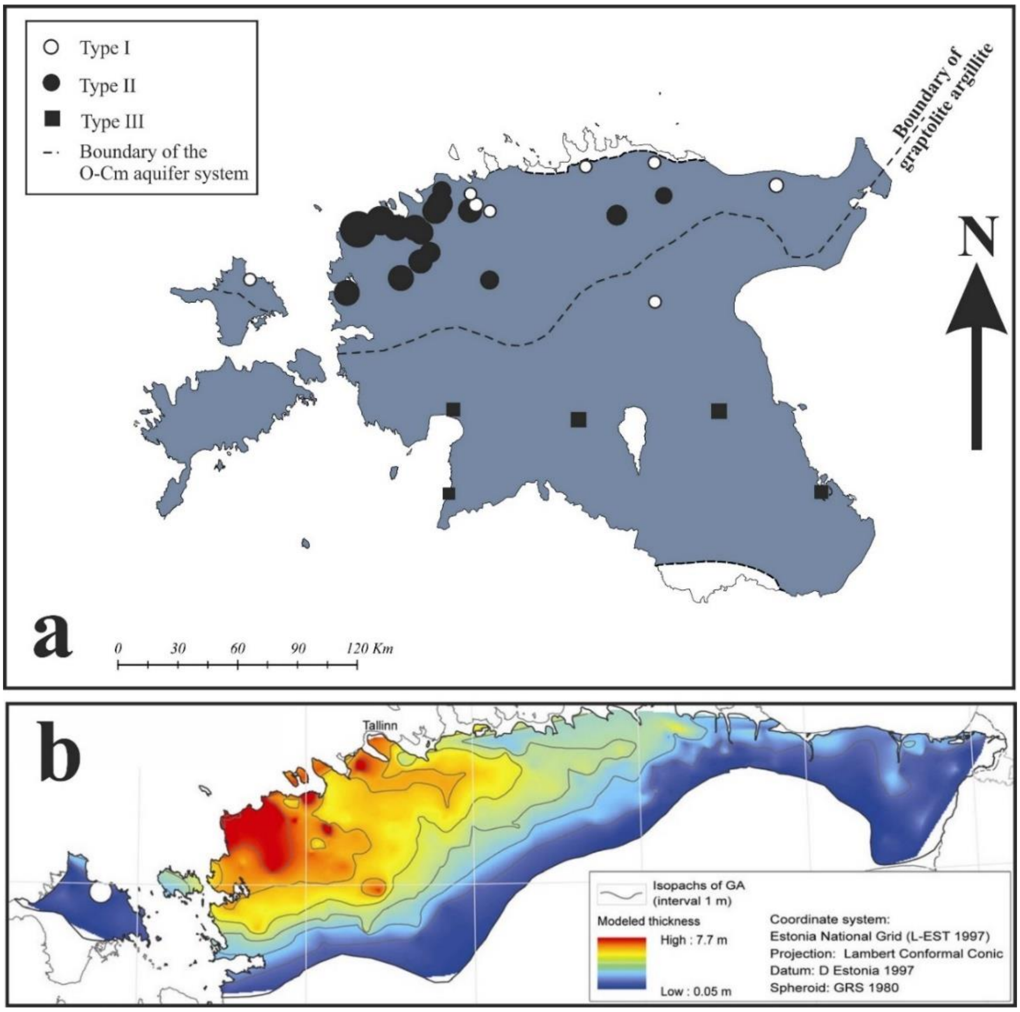

Figure 9. (a) The $\delta^{18}O$ isotope composition of different groundwater types in the Ordovician-Cambrian aquifer system. The size of the symbols are proportional to measured $\delta^{18}O$ values in groundwater with larger symbols indicating more negative values. (b) The occurrence and modelled thickness of graptolite argillite in Estonia (from: Hade and Soesoo, 2014).

The groundwaters of the III-type deviate from the GMWL in their isotope composition (Figure 9). This indicates that they do not originate directly from meteoric waters. They also differ from previous water types in their chemical composition, most notably in chloride and sodium concentrations.

The main sources of chloride in groundwaters have been associated with various processes such as the dissolution of the late stage evaporates (e.g. NaCl), the mixing with saline waters retained in sediments since deposition and the intrusion of sea-water (Hem, 1985; Richter and Kreitler, 1991). There is no evidence for the occurrence of evaporate minerals in the Lower Ordovician and Cambrian sedimentary rocks in the Baltic Artesian Basin. In the absence of evaporates in the rocks of the aquifer system the high chloride concentrations found in the III-type of waters suggest that they most likely originate from saline waters retained in sediments since deposition. The waters are enriched with respect to Ca^{2+} and depleted in Mg^{2+} and SO_4^{2-}. Lowenstein et al. (2003) have proposed that high Ca^{2+} and low SO_4^{2-} concentrations found in basinal brines in Phanerozoic sedimentary basins can be explained by their origin from paleoseawaters from geological time when the world ocean was Ca^{2+} rich and SO_4^{2-} poor. In many sedimentary basins, the chemical studies of brines have inferred the presence of remnant evaporated seawater. For example, Stueber and Walter (1991) have shown that remnant evaporated seawater has been preserved in Silurian-Devonian strata in the Illinois Basin in North America and that this type of water has evolved to NaCaCl-type brine through water-rock interactions.

The groundwaters of the III-type found in southern parts of the O-Cm aquifer system have a positive isotope composition compared to modern precipitation and their $\delta^{18}O$ and $\delta^{2}H$ correlation plots below the GMWL. This characteristic deviation from the GMWL for sedimentary basin brines has been attributed to number of processes such as the ^{18}O exchange with carbonate minerals at elevated temperatures; the ^{2}H exchange with hydrocarbon, H_2S and hydrated minerals; dewatering of clays during compaction; the hydration of anhydrite and the mixing with meteoric waters (Clark and Fritz, 1997). While this deviation is mostly attributed to water-rock interactions (Hiscock, 2005) Stueber and Walter (1991) have argued that the deviation of the $\delta^{18}O$ - $\delta^{2}H$ covariance from GMWL in waters of the Illinois Basin is due to infiltration of meteoric waters which have mixed with remnant evaporated seawater. This process was manifested in the increases of $\delta^{18}O$ and $\delta^{2}H$ values with water salinity. The isotope exchange reactions with surrounding rock matrix were thought to have played only a limited role.

The positive mean $\delta^{18}O$ value of −4.6‰ found in III-type of waters in southern parts of the aquifer system is a characteristic feature for formation waters which should lie close to the value of 0±2‰ reported by Muehlenbachs (1998) for the ice-free Palaeozoic ocean water. Furthermore, there is a distinct depletion in stable isotope composition and most notably in the $\delta^{18}O$ values in northerly directions in the aquifer system. The $\delta^{18}O$ values decrease from a mean value of −4.6‰ in Latvia to values up to −15.6‰ in Southern Estonia. Thus, the III-type of waters found in the O-Cm aquifer system have most likely originated from remnant evaporated sea-water found in more southern parts of the aquifer system. Their chemical and isotope composition has been altered by mixing with more dilute meteoric waters.

To explain the formation of brine waters in Cambrian and Ediacaran rocks in the Baltic Artesian Basin Mokrik (1997) has suggested that meteoric waters replaced the original syngenetic seawater within the sediments during the Middle-Late Cambrian uplift of the area and the seawater intruded the sediments during Ordovician-Devonian when the basin was considerably subsidised.

5.3. Geochemical evolution of groundwaters in the Ordovician-Cambrian aquifer system

There are distinct differences in hydrochemical state of three groundwater types in the O-Cm aquifer system. To describe the transition of fresh waters in the active water exchange zone to highly mineralized waters in the stagnant water exchange zones Mokrik (1997) proposed a coefficient of $(Na^{+} + Cl^{-})/HCO_3^{-}$ called groundwater metamorphic degree (GMD). Values of GMD show the decreasing HCO_3^{-} concentration and increasing Na^{+} and Cl^{-} concentration during the transition from the meteoric to saline deep groundwater (Mokrik, 2009). When GMD in the O-Cm aquifer system is plotted against depth, it can be shown that in the shallow part (less than 250 m) of the aquifer system two groundwater types with different GMD values are found (Figure 10). Groundwaters of the I-type have mean GMD value of 0.2, showing the dominance of HCO_3^{-} over other ions in the coefficient as can be expected from the chemical composition of these waters. Groundwaters of the II-type have a mean GMD value of 1.2, which shows that these waters are chemically more altered than the groundwaters of the I-type. The III-type waters found in Southern Estonia are characterized by the mean GMD value of 13.5. This value is concordant with the values found in other deep sodium and chloride dominated groundwaters in the Baltic Artesian Basin (Mokrik 1997). Thus, the GMD values show that the three major groundwater types in the O-Cm aquifer system in Estonia are in different stages in their geochemical development. Despite their location at similar depths the chemical composition of the II-type waters has experienced more alteration compared to the waters of the I-type. The GMD values for III-type of waters found in Latvia exceed 10000 and are too high to plot together with other water types. This further confirms the old age of these brines.

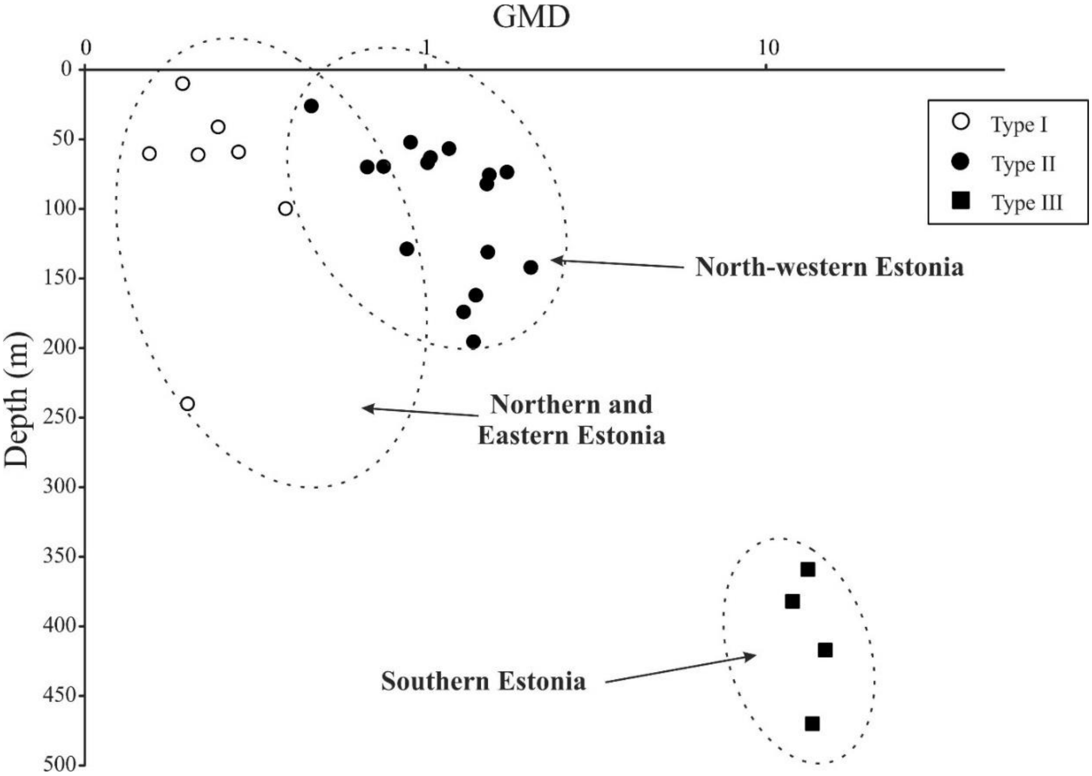

Figure 10. The values of groundwater metamorphic degree (GMD) in the Ordovician-Cambrian aquifer system versus depth marking the start of the opened interval of the sampled wells. The geographical location of the sampled wells is shown for reference.

The chemical composition of groundwater in the O-Cm aquifer system has been influenced by mixing between groundwater originating from different end-members. The mixing between waters from those end-members can be illustrated using conservative geochemical tracers $\delta^{18}O$ and Cl^-. The $\delta^{18}O$ composition of groundwater in low-temperature systems can be viewed as a conservative tracer, which has a direct link to water recharging the saturated zone (Geyh, 2000). More than three-quarters of chloride found in Earth's outer crust, atmosphere and hydrosphere is contained in a solution as Cl^- in the oceans (Hem, 1985). Thus chloride is a very conservative ion that once in a solution is not easily removed by the processes other than precipitation in very late evaporation stages (Richter and Kreitler, 1991). The chloride concentrations found in different groundwater types are probably derived from brines found in southern part of the O-Cm aquifer system. This assumption is supported by the study of Raidla et al. (2009) who conclude that a simple seawater dilution-concentration mechanism is responsible for the chloride concentrations found in the Cambrian-Vendian aquifer system.

The three mixing end-members are defined as:

1. Recent meteoric water, with annual weighted mean $\delta^{18}O$ value of −10.4‰ (Punning et al., 1987) and low salinity (Cl^{-}<0.06 mmol/l) (Treier et al., 2004);
2. Brine water, with more positive isotope composition compared to modern precipitation and high salinity. The end-member is represented by groundwaters of the type III found in Cambrian aquifer system in Latvia with generalized $\delta^{18}O$ value of −4.6‰ and Cl^{-} concentration of 2000 mmol/l;
3. The end-member representing glacial melt-water. The values characterizing this end-member are the most uncertain due to large variability in both $\delta^{18}O$ values and Cl^{-} concentrations that probably existed between different parts of the Scandinavian Ice Sheet. The $\delta^{18}O$ values of the Pleistocene continental ice sheets have been reported to have been −30‰ and less (Dansgaard and Tauber, 1969). The $\delta^{18}O$ values of the Pleistocene aged glacial recharge waters from the Laurentian Ice Sheet in North America have been estimated to have values close to −25‰ (Remenda, 1994). The groundwaters in the Cambrian-Vendian aquifer system which is thought to have formed from isotopically light subglacial recharge from the Scandinavian Ice Sheet are characterized by $\delta^{18}O$ values from −19‰ to −22‰ (Vaikmäe et al., 2001). The Cl^{-} concentrations found in the melt-waters of the modern continental ice sheets of Antarctica and Greenland range from 0.01 to 1 mmol/l (Brown 2002; Yde et al., 2005). Taking into account this large variability the chosen end-member represents the mean values of the expected variability in concentrations found in continental ice sheets with $\delta^{18}O$ value of −25‰ and Cl^{-} concentration of 0.1 mmol/l.

The $\delta^{18}O$ values and Cl^{-} concentrations indicate a three-component mixing trend between modern precipitation, recharge water of glacial origin and brine water in the aquifer system (Figure 11). This trend is similar to same type of mixing reported in the underlying Cambrian-Vendian aquifer system by Raidla et al. (2009) as well as in the groundwaters from the Canadian Shield by Douglas et al. (2000).

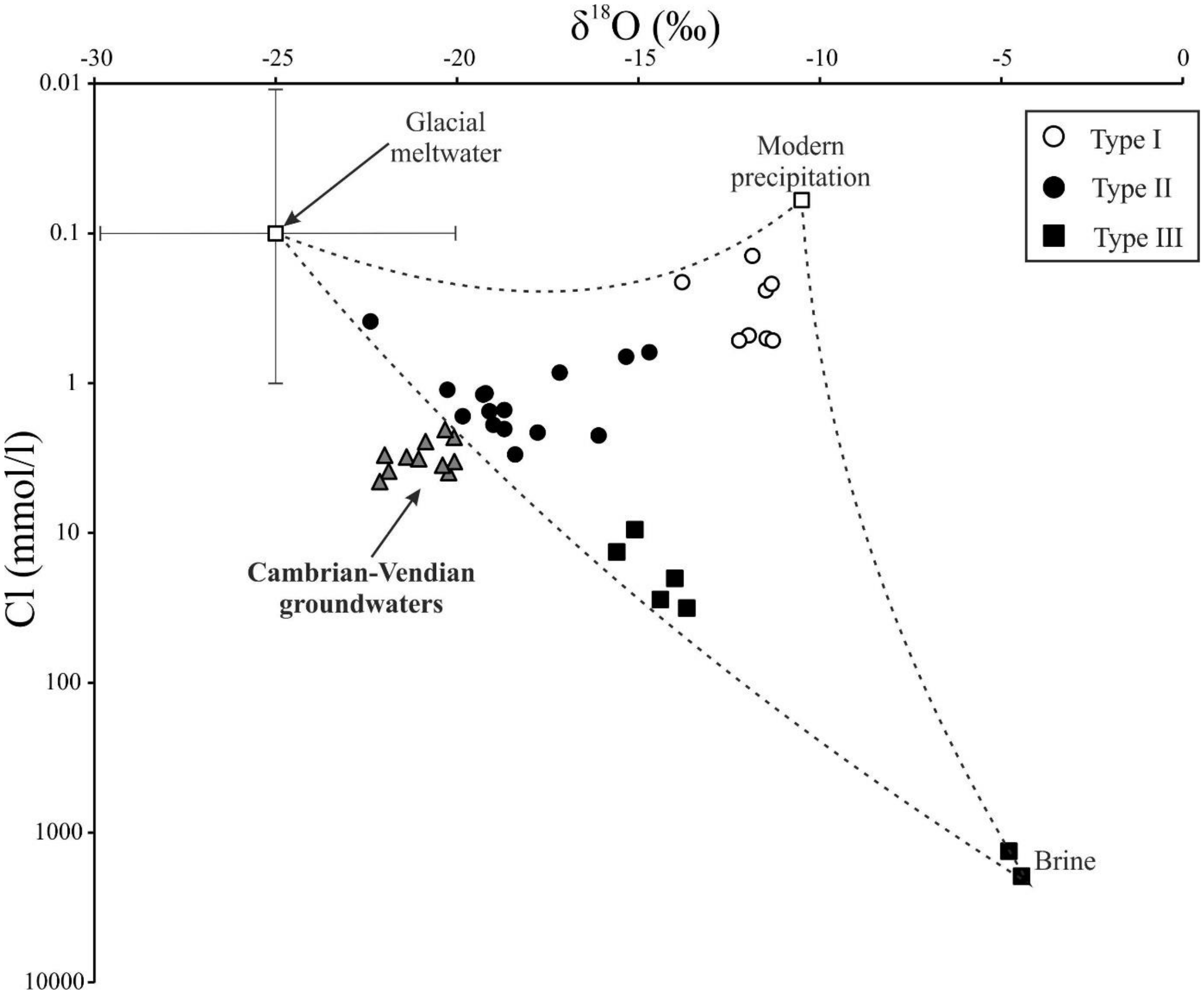

Figure 11. $\delta^{18}O$ and Cl^- variation in different groundwater types in Ordovician-Cambrian aquifer system. The end-members representing modern precipitation, glacial meltwater and brine water are shown. The definitions of the end-members are given in the text. The $\delta^{18}O$ and Cl^- error bars are shown for end-member representing glacial meltwater based on the discussion in the text. For reference the figure shows the $\delta^{18}O$ and Cl^- variation in Cambrian-Vendian waters in North-western Estonia.

The groundwaters of the I-type plot close to the modern precipitation end-member. The groundwaters of the II-type plot closer to the glacial meltwater end-member. The III-type of waters plot closer to the brine end-member.

The groundwaters of the I-type have thus originated mainly from precipitation infiltrated in the recharge areas and have only been minorly altered by mixing with waters from the II- and the III-type.

The II-type waters in North-western Estonia and the III-type waters in Southern Estonia plot close to a mixing line between glacial meltwater and brine end-members. This indicates a replacement of original NaCl-type waters with more dilute glacial meltwater. The latter have since then been chemically altered by water-rock interactions and mixing with original NaCl water type. The waters of the III-type have not been significantly affected by mixing with modern meteoric recharge waters due to the lack of great deviations from the observed linear relationship. The position of some II-type waters indicates mixing with modern recharge waters (Figure 11).

Figure 11 also shows the position of Cambrian-Vendian groundwaters from North-western Estonia in the described mixing plot. The similarities between possible glacial meltwater in the Cambrian-Vendian aquifer system and groundwater with negative isotope composition in O-Cm aquifer system lead to a possibility that the groundwater with negative isotope composition may have leaked from the Cambrian-Vendian to the O-Cm aquifer system in North-western Estonia. During this process these waters could have become more dilute due to the mixing with modern recharge waters. In North-western Estonia the Lükati-Lontova aquitard separating the two aquifer systems becomes thinner and its permeability increases from 10^{-7} m/d to 10^{-5} m/d (Perens and Vallner, 1997).

Groundwaters from the Cambrian-Vendian aquifer system plot below the II-type of waters in the North-western part of the O-Cm aquifer system as they are described by more negative $\delta^{18}O$ values and larger Cl^- concentrations. Groundwaters from the Cambrian-Vendian aquifer system differ from the II-type of waters in the O-Cm aquifer system in their chemical composition. In the Cambrian-Vendian aquifer system the dominant anion in the waters is the chloride ion, whereas in the O-Cm aquifer system the anion proportion of the groundwater is dominated by the bicarbonate ion. Figure 11 shows that the II-type of groundwaters do not plot on the mixing line between modern precipitation and Cambrian-Vendian groundwaters.

However, the possibility of groundwater leakage from Cambrian-Vendian aquifer system to the O-Cm aquifer system is still plausible, when one takes into account the height of the potentiometric surface of the Cambrian-Vendian gorundwaters in North-western Estonia. The height of the roof of the O-Cm aquifer system in Northern Estonia is in the range of 20-100 m b.s.l. (Perens and Vallner, 1997). The modern potentiometric surface of the Cambrian-Vendian groundwaters in Northern Estonia is located at the heights of 0-40 m b.s.l. (Marandi, 2010). Thus, one cannot completely exclude the hypothesis of Cambrian-Vendian groundwater leaking into the O-Cm aquifer system.

In addition to mixing processes the water-rock interactions have also played an important role in the formation of the chemical composition of different groundwater types. To trace the sources of salinity in the O-Cm aquifer system the relationships of Cl^- with the major cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) are utilized (Figure 12a-d).

The SDL (Sea Water Dilution Line) represents the ratios of major cations with chloride in the open ocean water. The values for Na^+/Cl^-, K^+/Cl^-, Mg^{2+}/Cl^- and Ca^{2+}/Cl^- in the open ocean water are 0.55, 0.02, 0.07 and 0.02, respectively (Cox and Culkin, 1966). It must be noted that the Na^+/Cl^-, K^+/Cl^-, Mg^{2+}/Cl^- and Ca^{2+}/Cl^- in the Baltic Sea are almost coincident with the same values in the open ocean water (Kremling, 1969).

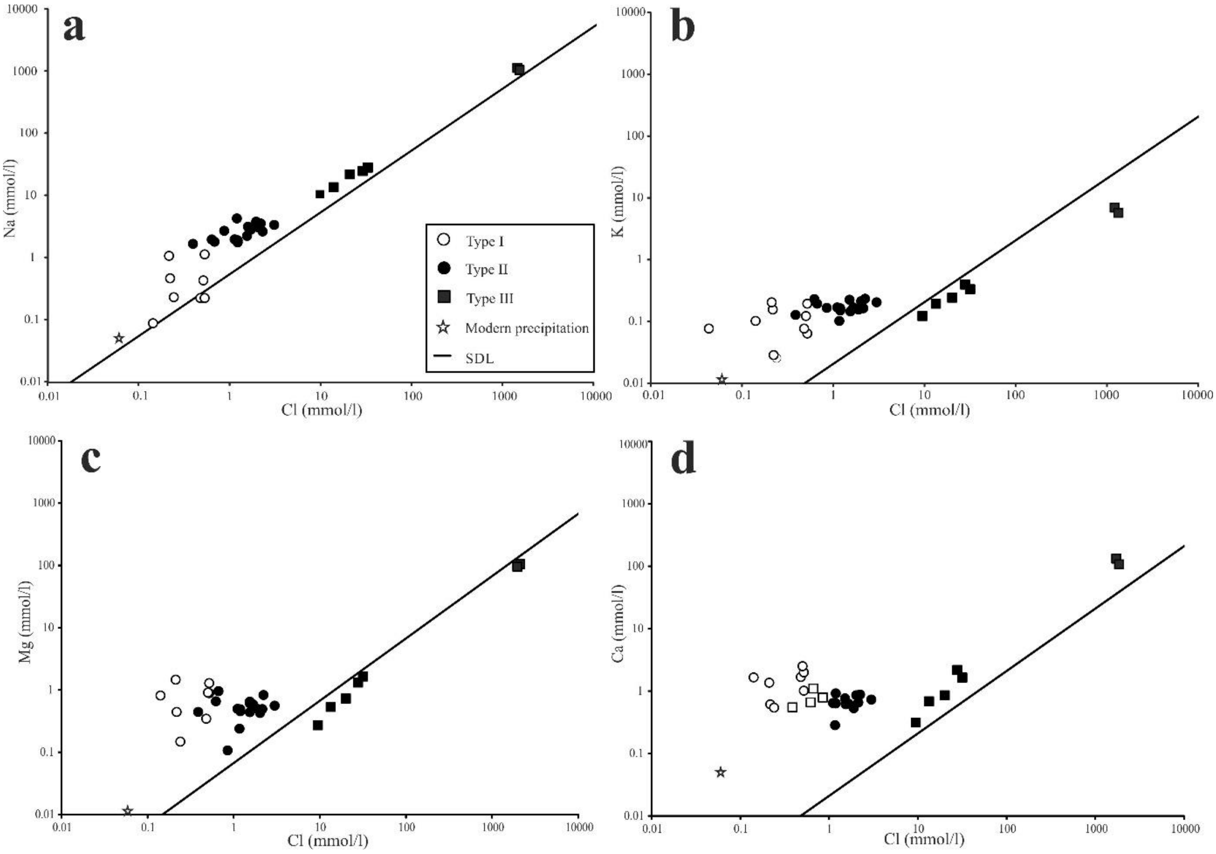

Figure 12. The concentrations of various ions plotted against chloride concentration in groundwater. SDL represents a seawater dilution line for a.) Na^+/Cl^-, b.) K^+/Cl^-, c.) Mg^{2+}/Cl^- and d.) Ca^{2+}/Cl^- relationships in the open ocean water (Cox and Culkin, 1966). The open star describes the position of modern precipitation in the research area (Treier et al., 2004).

The III-type of waters mostly plot parallel to the SDL and have similar values for Na^+/Cl^-, K^+/Cl^-, Mg^{2+}/Cl^- and Ca^{2+}/Cl^-. The slight differences from the SDL found in these waters may be attributed to the fact that Palaeozoic seawater had slightly different chemical composition when compared to modern ocean water (e.g. Lowenstein et al., 2003). Water types I and II have different values of the same ratios and are characterized by enrichment in calcium, magnesium and potassium over chloride when compared to values found in III-type waters (Figure 12b-d).

This indicates that the simple dilution-concentration mechanism is not sufficient to explain the formation of chemical composition of these groundwater types.

The relationship between sodium and chloride concentrations in water types I-III show similarities to the dilution-concentration mechanism. Waters from type III have similar values of Na/Cl ratios. The most diluted I type waters show sodium Na/Cl values close to those found in modern precipitation. Waters of the II-type show a gradual enrichment in sodium concentrations over chloride (Figure 12a). This indicates an additional Na^+ source to the Na^+ found in III-type of waters. Sodium is mostly derived from weathering of the silicate minerals such as feldspars (e.g. albite, anorthite), cation exchange processes with clays and the decomposition of sodium salts (Hem, 1985; Richter and Kreitler, 1991). The latter have not been found in the sedimentary rocks forming the aquifer system.

The additional sodium concentrations found in groundwaters can originate from silicate weathering processes. Raidla et al. (2006) report that subordinate amounts of albite are present in the Cambrian sandstones of Tiskre and Paala Formations. Since not enough data about SiO_2 concentrations is available for groundwaters in the O-Cm aquifer system the observed enrichment of sodium over chloride found in some waters of the I- and II-type cannot be solely attributed to the process of silicate weathering.

Another possible explanation to the elevated sodium concentrations in some I- and II-type of waters involves cation exchange reactions. When fresh water flushes the salt water aquifer, where cation exchangers in contact with water have absorbed Na^+, Ca^{2+} is taken up from water in return for Na^+ (Appelo and Postma, 1999). This process leads to the formation of $NaHCO_3$ water type similar to the II-type of waters in the O-Cm aquifer system. Figure 13 shows that in some I- and II- type of waters the Na^+/Cl^- ratio is increased while the Cl^- concentrations remain stable. This change is followed by the subsequent decrease in Na^+/Cl^- ratios towards III-type of waters together with increasing Cl^- concentrations. The first process has been related to Ca^{2+}/Na^+ exchange while the decrease in Na^+/Cl^- ratios towards more saline waters has been attributed to the mixing processes between different water types (Walraevens and van Camp, 2005).

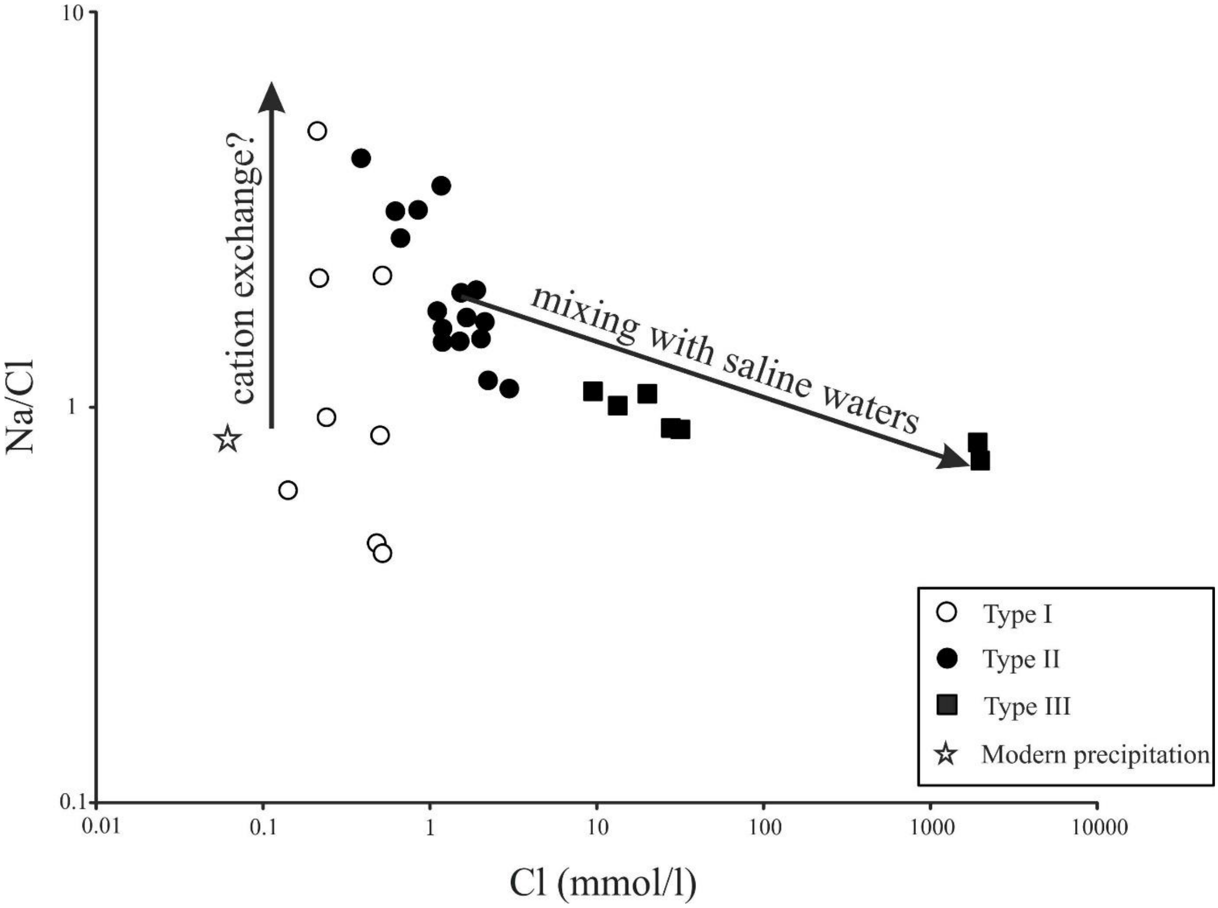

Figure 13. Na^+/Cl^- ratio versus Cl^- concentration in the groundwaters of the Ordovician-Cambrian aquifer system. The position of modern precipitation in the research area is shown for reference.

The potassium versus chloride relationship (Figure 12b) shows a distinct enrichment of potassium over chloride in the water types I and II when compared to III-type of waters. This indicates the alteration of original K^+ concentrations originating from dilute recharge waters or saline brine through water-rock interactions. Potassium is mainly added to groundwater from the weathering of feldspars and clay minerals (e.g. illite) (Hem, 1985; Richter and Kreitler, 1991). The possible potassium source could be the K-feldspar found in both Cambrian sandstones and also in the graptolite argillite that overlies the O-Cm aquifer system (see also chapter 3.4). It must be noted that K-feldspar is more resistant to weathering compared to other silicate minerals which makes such reactions very slow (Appelo and Postma, 1999). As for Na^+ the K^+ concentrations can also be influenced by the processes of cation exchange (Walraevens and van Camp, 2005).

Both calcium and magnesium concentrations in water types I and II show distinct enrichment over chloride when compared to with modern precipitation and waters of the III-type (Figure 12c, d). This indicates that water-rock interactions have modified the original chemical composition of the recharge waters. Both magnesium and calcium in groundwater are mostly derived from dissolution of carbonate minerals (e.g. calcite, dolomite).

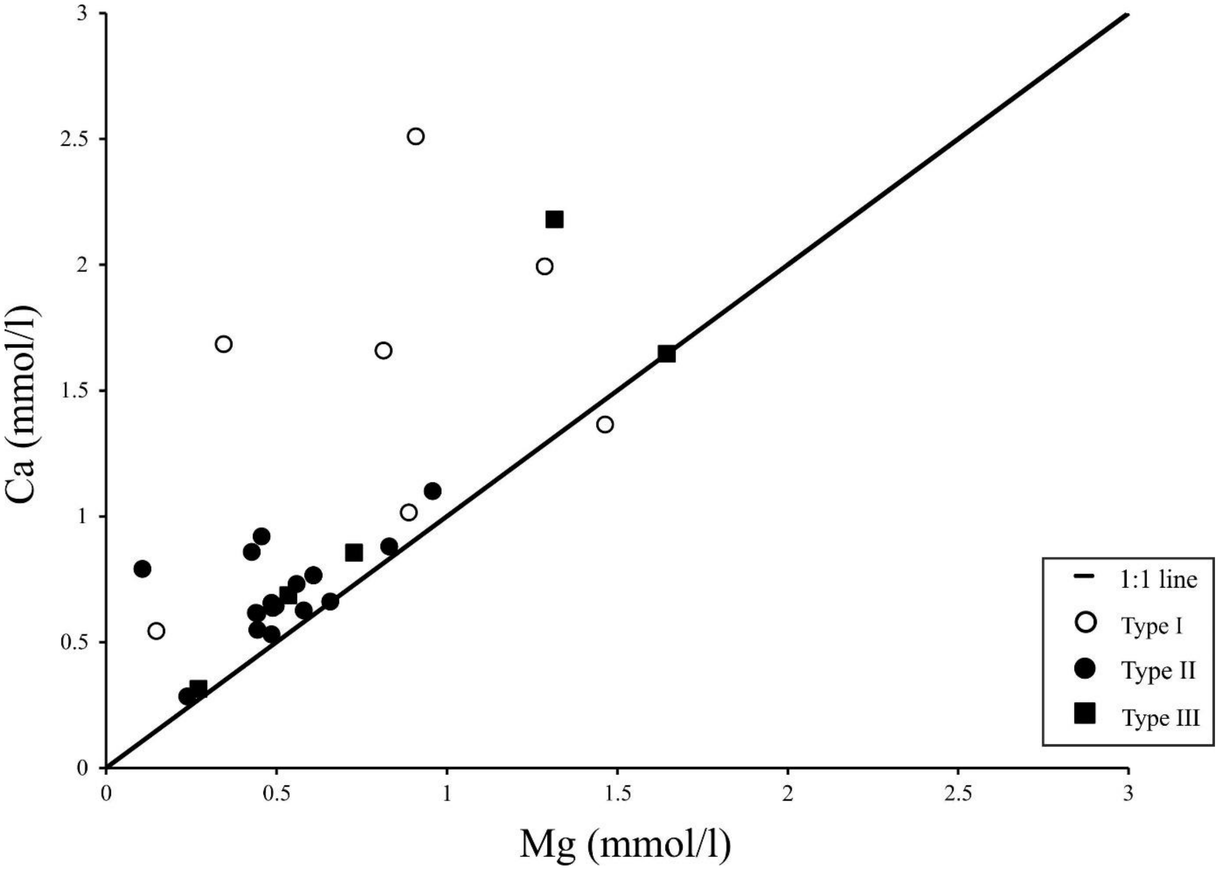

Figure 14. Ca^{2+} and Mg^{2+} concentrations of groundwaters in the Ordovician-Cambrian aquifer system. The 1:1 line for Ca^{2+}:Mg^{2+} ratios is shown for reference. The Ca^{2+} concentrations found in waters from the southern part of the aquifer system in Latvia are too high to plot together with other water types.

All studied groundwaters in the O-Cm aquifer system plot above or near to the 1:1 line of Ca^{2+}/Mg^{2+} molar ratios indicating that the dissolution of carbonate minerals is a major source of Ca^{2+} and Mg^{2+} in groundwaters of the aquifer system (Figure 14).

The Ca^{2+}/Mg^{2+}molar ratios in I-type of waters plot above the 1:1 line. Most II type waters plot close to the 1:1 line which can be explained by the higher proportion of Fe-dolomite in authigenic carbonate minerals found in Cambrian sandstones when compared to calcite (Raidla et al., 2006). The III-type of waters found in Estonia also plot above the 1:1 line indicating that the authigenic dolomite and calcite found in Cambrian sandstones is the main source of Ca^{2+} and Mg^{2+} in those waters.

The groundwaters of the I-type found close to the recharge area have Ca^{2+} + Mg^{2+} versus alkalinity molar ratios of 1:2 (Figure 15). This is indicative of the carbonate mineral dissolution according to the stoichiometry of the following reactions (Appelo and Postma, 1999):

$$CaCO_3 + H_2O + CO_{2(g)} \leftrightarrow Ca^{2+} + 2HCO_3^{-} \quad (5)$$

$$CaMg(CO_3)_2 + H_2O + CO_{2(g)} \leftrightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^{-} \quad (6)$$

This further confirms their origin from modern recharge as their chemical composition is mainly influenced by the carbonate dissolution by CO_2 rich dilute rainwater (Hiscock, 2005).

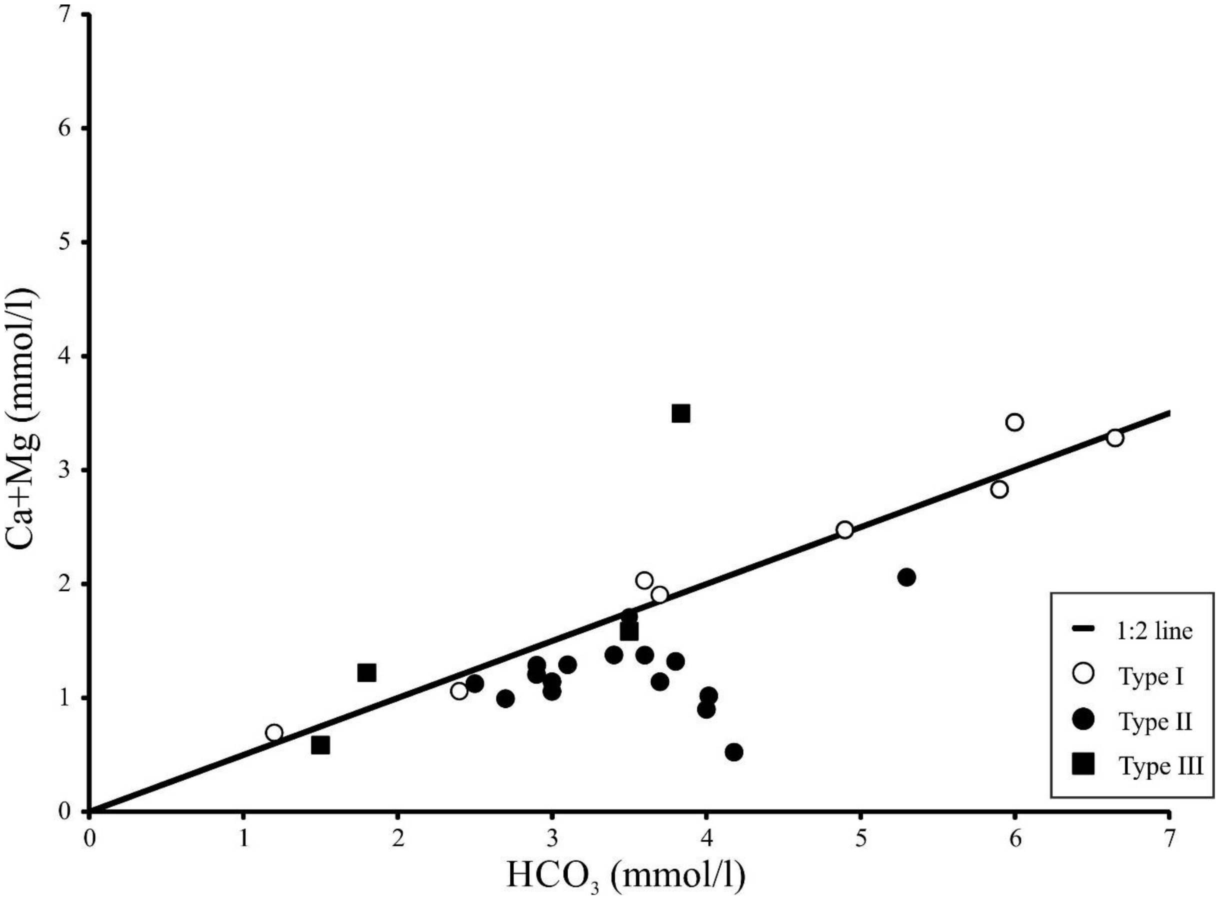

Figure 15. Ca^{2+}+Mg^{2+} versus HCO_3^{-} (alkalinity) concentrations for groundwaters in the Ordovician-Cambrian aquifer system. The HCO_3^{-} concentrations can be used as a measure of alkalinity, because at pH values of less than 8.3 less than 1% of the carbonic acid is present as CO_3^{2-} (Appelo and Postma, 1999). The 1:2 line for Ca^{2+}+Mg^{2+} versus alkalinity is shown for reference.

The groundwaters of the II-type mainly plot below the 1:2 line showing HCO_3^{-} excess over calcium and magnesium concentrations. Coetsiers and Walraevens (2004) have shown that the formation of $NaHCO_3$ water type that is enriched in sodium over calcium and has high HCO_3^{-} concentrations, can be explained by processes of cation exchange. The increase in HCO_3^{-}

concentrations during this process can be attributed to additional carbonate mineral dissolution that occurs when Ca^{2+} is removed from water by cation exchange with Na^+ (Appelo and Postma, 1999). The II-type groundwaters in the O-Cm aquifer system have elevated Na^+ concentrations compared to I-type of waters and show attributes that refer to cation exchange as shown in previous section.

Other possibility is to explain the enrichment of HCO_3^- using the process of sulphate reduction (Figure 16). Sulphate reduction by organic matter in anaerobic conditions is catalysed by bacteria and can be described by the overall reaction (Appelo and Postma, 1999):

$$2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S \quad (7)$$

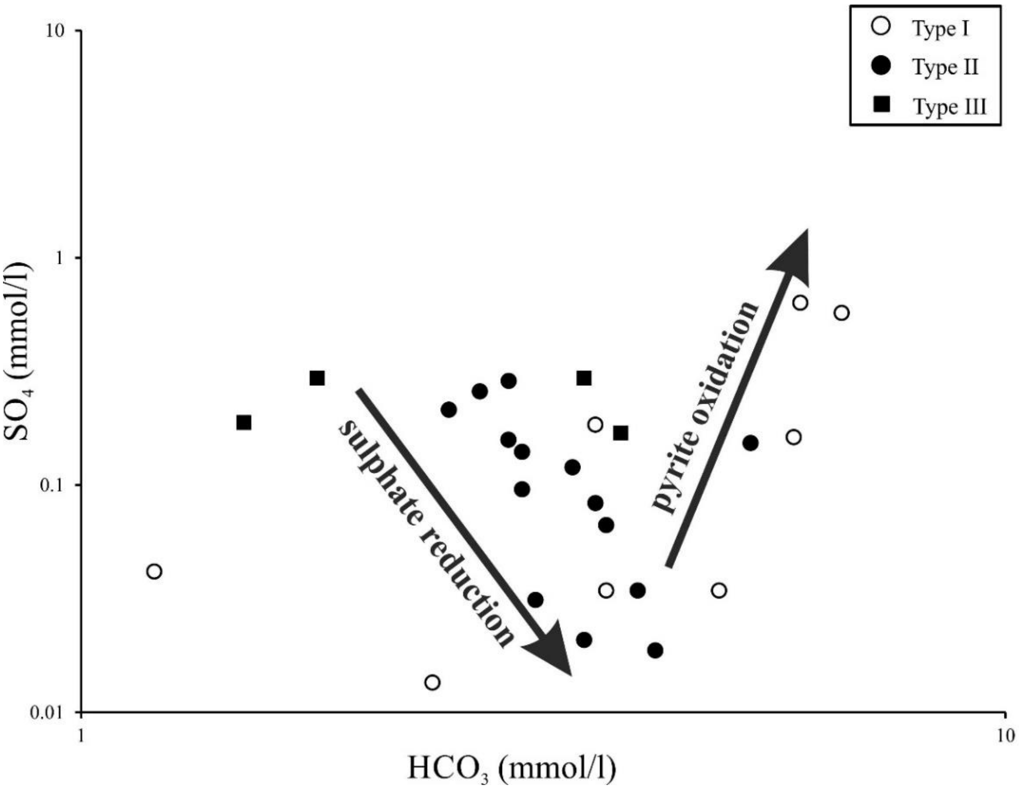

Figure 16. SO_4^{2-} versus HCO_3^- concentrations for different groundwater types in the Ordovician-Cambrian aquifer system in Estonia.

The organic matter necessary for this reaction can be found in Lükati and Lontova/Voosi Formations and in even greater concentrations in the overlying graptolite argillite of the Türisalu Formation. Some organic matter may have flushed in to the O-Cm aquifer system together with recharging glacial melt-waters. Raidla et al. (2012) suggest that glacial meltwater that penetrated to the underlying Cambrian-Vendian aquifer system could have been enriched with easily degradable organic matter from the depression of the Gulf of Finland. Raidla et al.

(submitted data) have shown that sulphate reduction is an important process that has altered the chemical composition of groundwater in the Cambrian-Vendian aquifer system. This process could also be used to explain the SO_4^{2-} and HCO_3^- anomalies found in the O-Cm aquifer system.

Groundwaters from the II-type together with some groundwaters from the III-type show mainly the trend of decreasing SO_4^{2-} concentrations with increasing HCO_3^- concentrations which is characteristic to sulphate reduction (Figure 16). A trend of increasing HCO_3^- and SO_4^{2-} concentrations observed in some groundwaters from I- and II-type can be attributed to the process of pyrite oxidation which adds SO_4^{2-} to solution through the reaction of pyrite with oxygen rich waters (Appelo and Postma, 1999). Pyrite oxidation contrary to sulphate reduction takes place in aerobic conditions and is described by the reaction (Stumm and Morgan, 1996):

$$2FeS_2 + 3.5O_2 + H_2O \leftrightarrow 2Fe(OH)_3 + 2SO_4^{2-} + 2H^+ \qquad (8)$$

The oxidation of pyrite lowers the pH of the solution which in turn increases the dissolution of carbonate minerals together with high concentrations of CO_2 found in fresh oxygen rich waters. This process releases additional HCO_3^- to the solution. Raidla et al. (2006) have shown the occurrence of pyrite in the Cambrian sandstones. In addition Voolma et al. (2013) have also reported the high concentration (2.4-6.0%) of pyrite in the graptolite argillite of the Türisalu Formation overlying the aquifer system.

It is clear from the previous discussion that the precise roles of cation exchange and sulphate reduction in the geochemical evolution of groundwaters in the O-Cm aquifer system needs clarification by future studies both through investigating isotopic signatures in SO_4^{2-} and using geochemical modelling.

The analysis of the geochemical evolution of groundwater in the O-Cm aquifer system shows distinct differences between I- and II-type groundwaters compared to groundwaters of the III-type. The latter mainly show that a dilution-concentration mechanism is responsible for major cation (Na^+, K^+, Mg^{2+}, Ca^{2+}) concentrations found in groundwater. The II-type of waters deviate from this relationship in their chemical composition. This suggests that water from a different source may have recharged the northern part of the aquifer system thus interrupting the dilution-concentration evolution pathway of the waters previously in the aquifer system. The differences in isotope composition between II- and III-type of waters support this assumption. On the basis of the latter this recharging water could have originated from the glacial meltwaters associated with Quaternary glaciations in the research area. To explain the formation of waters with negative isotope composition in Cambrian-Vendian aquifer system Raidla et al., (2009) proposed that during the Pleistocene the melting of 500 to 1500 m thick Scandinavian ice sheet increased hydraulic pressure at the base of the glacier which reversed the regional groundwater flow. The inflow of diluted glacial melt-water into the aquifer system occurred along the outcrop areas at the basin margin and the flow distances were at least 150–200 km. The same model explains the occurrence of isotopically light groundwater in the North-western part of the O-Cm aquifer system (Figure 17). Here the overlying graptolite argillite of the Türisalu Formation acted as an aquitard under which the glacial meltwater could recharge the aquifer system. This aquitard forced glacial meltwater to flow into the deeper parts of the aquifer system where it mixed with older more saline waters. The aquitard also offered favourable conditions for the preservation of the recharged glacial meltwater (Raidla et al., 2009).

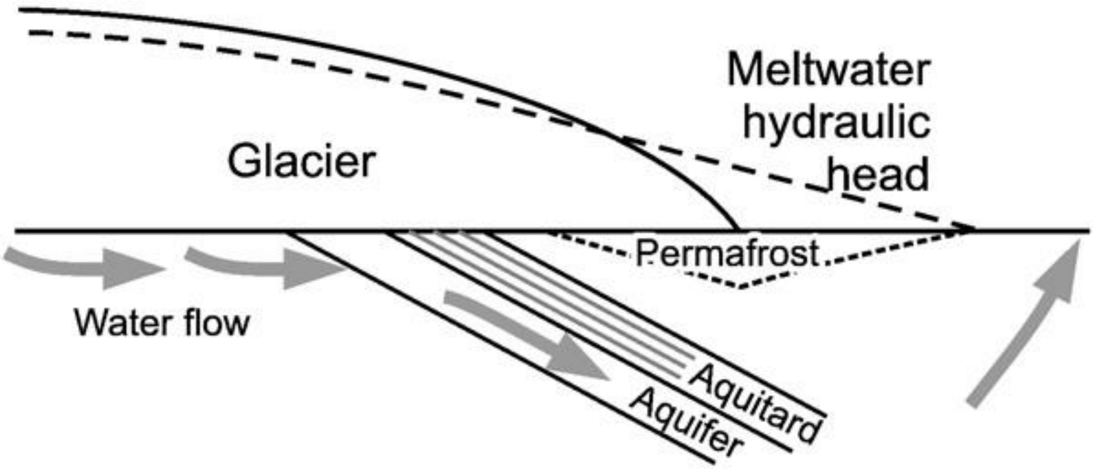

Figure 17. A schematic section illustrating the recharge mechanism and groundwater flow in subglacial conditions. (from: Raidla et al., 2009)

At present second type of mixing occurs by the intrusion of meteoric waters into the O-Cm aquifer system in the recharge area of Pandivere Uplands and deep buried valley systems in Northern and North-eastern Estonia. The more recent meteoric waters are represented by I-type of waters in the O-Cm aquifer system. The chemical composition of these waters is mainly influenced by carbonate mineral dissolution and they are chemically less altered when compared to II-type of waters. The isotope composition of I-type of waters is similar to that found in modern precipitation in the research area.

It must be noted that these conclusions need further clarification in the future. Mainly additions of new sampling sites to the available geochemical database is needed to improve the spatial coverage of data characterizing the O-Cm aquifer system. To test the proposed hypotheses the estimations of residence times for waters in the O-Cm aquifer system are also needed.

6. Conclusions

1. The studied groundwaters in the O-Cm aquifer system show wide variety in isotope and chemical composition;
2. On the basis of these observed variations the groundwaters in the O-Cm aquifer system were divided into three groundwater types: groundwaters originating from modern precipitation located in the northern and north-eastern part of the aquifer system (type I); groundwaters of glacial origin located in the north-western part of the aquifer system (type II); groundwaters originating from brine waters located in the southern part of the aquifer system (type III);
3. The isotope and chemical composition of the three types of groundwater has been influenced by three-component mixing processes between glacial meltwater, modern precipitation and brine end-members;
4. The chemical composition of groundwater has also been influenced by different water-rock interactions (i.e. carbonate mineral dissolution, cation exchange, silicate weathering, sulphate reduction and pyrite oxidation);
5. The isotope and chemical composition of groundwater indicates shorter groundwater residence times in the northern and north-western part of the aquifer system and longer residence times in the north-western and southern part of the aquifer system. This should be taken into account in future decisions concerning the management of groundwater in the aquifer system;
6. To clarify the infiltration mechanism and the residence times of different groundwater types in the aquifer system additional stable isotope tracers (e.g. $\delta^{13}C$, $\delta^{34}S$) and dating methods (e.g. ^{3}H, ^{14}C, noble gases) should be applied in the future studies.

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8. Summary in Estonian

Magistritöös uuriti Ordoviitsium-Kambriumi (O-Cm) põhjaveekompleksi põhjavete kujunemist. O-Cm põhjaveekompleks paikneb Balti Arteesiabasseinis, Ida - Euroopa platvormi põhja- ja loodeosas. Põhjaveekompleksi põhjavete kujunemise selgitamiseks uuriti põhjavete keemilist koostist koos vete hapniku ja vesiniku isotoopkoostisega. Selleks kasutati 31 põhjaveeproovist koosnevat andmebaasi, mis sisaldas nii 2013. aasta käigus kogutud uute põhjaveeproovide tulemusi kui ka ajavahemikus 1989 – 2010 kogutud varem avaldatud ja avaldamata tulemusi. O-Cm põhjaveekompleksi põhjavett iseloomustab suur muutlikkus põhjavee isotoop- ja keemilises koostises. Nendest erinevustest lähtuvalt jaotati uuritud põhjaveed kolme tüüpi.

Esimest tüüpi põhjaveed pärinevad sademetest ja paiknevad valdavalt põhjaveekompleksi põhja- ja idaosas selle toiteala (Pandivere kõrgustiku) lähedal. Keemiliselt koostiselt on need $CaMgHCO_3$-tüüpi veed, mida iseloomustab madal Na^+ ja Cl^- sisaldus ja väike soolsus. Seda tüüpi põhjavee keemilise koostise kujunemist on enim mõjutanud karbonaatsete mineraalide lahustumine. Teist tüüpi põhjaveed paiknevad põhjaveekompleksi loodeosas ja on glatsiaalse päritoluga. Nende vete isotoopkoostis langeb sademetest pärinevat vett iseloomustavale joonele (GMWL), kuid selle väärtused ($\delta^{18}O = -16$ kuni $-22.5‰$) on tänapäevaste sademetega võrreldes palju negatiivsemad. Põhjaveed on oma keemiliselt koostiselt $NaCaMgHCO_3Cl$-tüüpi ja neid iseloomustab väike soolsus, mille väärtused on sarnased esimesele veetüübile. Sellesse tüüpi kuuluvate põhjavete keemilise koostise kujunemist on lisaks karbonaatsete mineraalide lahustumisele mõjutanud ka katioonvahetuse ning sulfaadi redutseerimise protsessid. Kolmanda veetüübi moodustavad soolased põhjaveed, mis paikenvad O-Cm põhjaveekompleksi lõunapoolses sügavamas osas. Seda tüüpi põhjavete isotoopkoostis hälbib GMWL joonelt erinevalt esimest ja teist tüüpi vetest. Põhjavete isotoopkoostis koos nende keemilise koostisega (NaCl- ja NaCaCl-tüüpi) lubab oletada, et tegemist on põhjaveekompleksis paikneva reliktse põhjaveega, mis pärineb arteesiabasseini lõunaosast.

Võttes arvesse O-Cm põhjaveekompleksi vete keemilise ja isotoopse koostise muutlikkust pakuti magistritöös välja skeem põhjavete geokeemilise arengu seletamiseks. Selle järgi asendus põhjaveekompleksis algselt paiknenud NaCl-tüüpi vesi selle põhjaosas Pleistotseenis Eesti ala katnud mandriliustike sulavetega. Pärast Holotseeni jäävaheaja algust algas sademevee sissetung põhjaveekompleksi põhja- ja idaosas paiknevatelt toitealadelt. Selle tulemusena toimub tänapäeval veekompleksi põhjaosas olevate glatsiaalset päritolu vete asendumine nooremate sademetest pärinevate vetega.

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