DISSERTATIONES GEOLOGICAE UNIVERSITATIS TARTUENSIS

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NATURAL CHEMICAL COMPOSITION OF GROUNDWATER AS A BASIS FOR GROUNDWATER MANAGEMENT IN THE CAMBRIAN-VENDIAN AQUIFER SYSTEM IN ESTONIA

ANDRES MARANDI

TARTU UNIVERSITY
PRESS

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Supervisors: Prof Volli Kalm, University of Tartu
Prof Rein Vaikmäe, Tallinn University of Technology

Opponent: Prof. W. Mike Edmunds, Research Director of the Oxford Centre for Water Research, UK

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AUTHOR'S CONTRIBUTION

Paper I

The author initiated the publication and is fully responsible for the fieldwork, data collection and analysis, as well as manuscript writing. E. Karro is responsible for water-rock interpretation and E. Puura is responsible for geochemical modelling.

Paper II

The author is fully responsible for fieldwork and data collection. The author has performed most of data analyses and is partly responsible for writing the manuscript description of Barium occurrence in Cambrian-Vendian aquifer system. E. Karro initiated the publication, is responsible for manuscript writing and performed studies of occurrence of Arsenic and Fluoride in Cambrian-Vendian aquifer system.

Paper III

The author initiated the publication and is fully responsible for data collection and data processing. The author performed hydro-geochemical analyses that resulted in conclusions about major groundwater chemistry. Isotopic instigations are performed by R. Vaikmäe, and E. Karro is responsible for investigations concerning water-rock interaction.

Paper IV

The author is fully responsible for fieldwork and data collection. The author has performed most of data analyses and is partly responsible for writing the manuscript. The author is responsible for analyses of major ion chemistry, groundwater types and geochemical processes. Isotopic investigations are carried out by other authors.

ABSTRACT

The aim of the present study was to analyse and explain the formation of chemical composition of groundwater in the Cambrian-Vendian aquifer system in order to provide a scientifically grounded base for groundwater quality management.

The Cambrian-Vendian aquifer system is the primary source of public water supply in northern Estonia (up to 75% of groundwater consumption) and is used as a source of mineral water in south-Estonia. Intensive overexploitation of groundwater from the Cambrian-Vendian aquifer system has led to the formation of two extensive depressions of potentiometric level.

The research was carried out in the framework of the FP5 project Baseline and FP6 project Bridge in order to establish the criteria for the baseline concentrations of a wide range of substances that occur naturally in groundwater. The results of the study will be applied in the development of new environmental standards in Europe.

According to new EU legislation, threshold values are applied as environmental quality standards. Threshold values for groundwater define the extent to which the concentration of a certain substance may exceed the natural background level (NBL). Therefore, natural background level (NBL) plays a central role in the derivation of threshold value, as it is the point of departure for the whole process. Furthermore, it is essential to have knowledge of the natural baseline quality so that the impact of imposed environmental change can be measured with an acceptable degree of certainty.

77 new samples for major ion chemistry were analysed from the Cambrian-Vendian aquifer system and were used for interpretation together with 1500 samples from a historical database. The results showed large natural variations in TDS and major ion chemistry in the Cambrian-Vendian aquifer system, but also changes caused by human activity. The latter has caused large variations in TDS in the coastal area of the Cambrian-Vendian aquifer system in northern Estonia.

Based on the investigations, the best monitoring compounds to explain possible future changes in groundwater chemistry are electric conductivity (TDS changes), major ion chemistry and isotopes 18O and 3H (upcoming or sea water intrusion), and barium (leakage from crystalline basement).

1. INTRODUCTION

Natural reactions between the water and rocks give rise to a wide diversity in the mineral character of groundwater, imparting intrinsic properties such as hardness and softness, salinity and even bitterness and sweetness, recognisable by humans since the earliest times. For the purposes of aquifer management, there is a requirement for improved understanding of the controlling processes and, where possible, the natural, geologically controlled baseline chemistry. In order to understand the pollution trends and impacts on an aquifer, it is essential to have knowledge of the natural baseline quality so that imposed environmental change can be measured with an acceptable degree of confidence (Edmunds et al. 2003).

No common approach across Europe for defining the natural quality of groundwater has emerged as yet. At present, different scientific projects are seeking to work out a common approach to defining the baseline quality of groundwater. Such a standard is necessary for scientific assessment of natural variation in groundwater quality and for assessing whether or not anthropogenic pollution is taking place.

The aim of the study was to explain the formation of chemical composition of the Cambrian-Vendian aquifer system in order to provide data for scientifically based methods for groundwater management. In order to make decisions on groundwater monitoring, the following is required:

1. Knowledge of the characteristics of groundwater chemistry (major ion chemistry, water types, TDS, etc.);
2. Knowledge of possible anomalously high concentrations of substances and ability to define whether the origin of anomalies is natural or anthropogenic;
3. Following any recorded trends in changes of groundwater quality and defining the extent and origin of the changes;
4. Explaining major geochemical processes forming the quality of natural groundwater.

The Cambrian-Vendian aquifer system, which is the major source of public water supply in northern Estonia, was selected for the baseline study in Estonia. In the northern and north-eastern region of Estonia, the share of Cambrian-Vendian groundwater consumption is about 75% and in the north-western region the indicator is almost 50% (Savitskaya, 1999). The resources in southern Estonia can be used as mineral water (Karise, 1997). Intensive water extraction has led to the formation of two extensive depressions of potentiometric level.

The Cambrian-Vendian aquifer system is a confined system, whereby direct input of pollutants is not likely. However, as groundwater quality is formed by processes between the water and rocks, and the processes are also dependent on groundwater dynamics, human activity can also have an indirect impact on the quality.

Recently, a great deal of attention has been paid to the environmental condition of groundwater. The main subjects of discussion are natural (physical, chemical, and biological) groundwater environment and best practices in the management of water resources. A major objective of groundwater research is to identify – and communicate to decision-makers – the trends in key environmental signals, especially those warning of impending thresholds and requiring changes to policy institutions and human behaviour (Berger, 1997).

A wide range of environmental policies are based on the monitoring of chemical parameters (Directive 2000/60/EC 2000, Directive 2006/118/EC), which are used to evaluate the environmental status of groundwater with the aim of making appropriate management decisions. The soundness of policy decisions is therefore directly related to the reliability of environmental monitoring programmes. Monitoring reliability in turn is predominantly linked to scientific and technological progress (Quevauviller, 2005).

EU standards for the quality of drinking water impose rigorous controls on water quality management issues but the limits may be breached due to entirely natural processes. Under certain geochemical conditions several potentially harmful elements or their complexes may be mobile and understanding how and where these occur is necessary for effective aquifer management (Edmunds et al, 2003).

According to new EU legislation (Directive 2000/60/EC 2000, Directive 2006/118/EC), threshold values will be used as environmental quality standards. Threshold values for the groundwater define the extent to which the concentration of a certain substance may exceed the natural background level (NBL), without failing good chemical status. Therefore, natural background level (NBL) plays a central role in the derivation of the threshold value, as it is the starting point for the whole process. In general, most organic substances have no NBL, as these have anthropogenic origin, i.e. most organic substances found in groundwater.

The originally proposed method, which has been applied during the BRIDGE project, suggests deriving threshold values on the basis of the ratio between the estimated NBL and a relevant reference value (REF) – e.g. a drinking water standard (DWS) or environmental quality standard (EQS).

The NBL derivation process requires a high level of knowledge of baseline geochemical transfers and processes. It also requires high quality data from the aquifer.

The results of the present study are applied in the development of new environmental standards in Europe.

The papers that are an essential part of this thesis can be viewed as case by case studies starting from one area and one problem and finishing with an explanation of the overall system.

PAPER I

Marandi, A., Karro, E. & Puura, E. 2004. Barium anomaly in the Cambrian-Vendian aquifer system in northern Estonia. Environmental Geology, 47 (1), 132–139.

Barium anomaly with maximum Ba^{2+} content of 6.37 mg/l was studied in the Cm-V aquifer system that is widely used as the source of drinking water in north-Estonian towns. The modelling results show that at low sulphate concentrations (below 3 mg/l), Ba^{2+} contents can exceed the limit values for drinking water (such as 2 mg/l set by US EPA), and bicarbonate ions at their common concentrations in groundwater cannot limit Ba^{2+} at its content below 10 mg/l. The probable natural sources of the anomaly are the crystalline basement and its weathering core. Groundwater in clayey weathering core is hydraulically connected with the overlying Cm-V aquifer system, thus enabling the capturing of deeper-seated groundwater by intensive exploitation of wells. Policy-makers and health organisations have turned their attention to the scientific evidence of barium anomalies. As a result of the investigations, data about the natural occurrence of barium was updated in WHO guidelines for drinking-water quality.

PAPER II

Karro E, **Marandi A** (2003) Mapping of potentially hazardous elements in Cambrian-Vendian aquifer system, northern Estonia. Bull Geol Soc Finland 75: 17–27

The distribution of fluorine, barium and arsenic was studied in north-Estonian water supply wells. The results of hydro-chemical mapping enable delimiting the barium anomaly in the Cambrian-Vendian aquifer system. Vertical distribution of the studied compounds and hydraulic connection between water-bearing Vendian sediments with underlying crystalline basement refers to the weathered basement rocks as the probable source of barium and fluorine in groundwater. The elevated concentrations of barium and fluorine detected in the groundwater of north-Estonian wells may become a source of growing concern in Estonia. The results of the hydro-chemical research must be developed into instructions on how to avoid or eliminate the quality problems in risk areas.

PAPER III
Karro E, **Marandi A**, Vaikmäe R (2004) The origin of increased salinity in the Cambrian-Vendian aquifer system on the Kopli Peninsula, northern Estonia. Hydrogeology Journal 12:424–435.

Long-term monitoring of the confined Cambrian-Vendian aquifer system utilised for industrial water supply at Kopli Peninsula, northern Estonia, reveals remarkable changes in the chemical composition of groundwater. A 1.5 to 3.0-fold increase in TDS and in concentrations of major ions in abstracted groundwater is the consequence of heavy pumping. The main sources of dissolved load in Cambrian-Vendian groundwater are host rock leaching and other geochemical processes that occur in the saturated zone. Underlying crystalline basement, which comprises saline groundwater in its upper weathered and fissured portion and is hydraulically connected to the overlying Cambrian-Vendian aquifer system, is the second important source of ions. Fractured basement and its clayey weathering crust host the Ca-Cl type groundwater, which is characterised by a high TDS value (2–20 g/L). Due to intensive water abstraction, the exchange of groundwater is accelerated, and the influence area of pumping is increased. Chemical and isotopic studies of groundwater indicate an increasing contribution of leakage from the crystalline basement. An intrusion of seawater into the aquifer system with consequent implications on water quality is not evident.

PAPER IV
Vaikmäe R, Kaup E, **Marandi A**, Raidla V, Vallner L (accepted) The Cambrian-Vendian aquifer, Estonia. In: Edmunds W M, Shand P (eds) The Natural Baseline Quality of Groundwater. Blackwell Publishing.

Investigations of natural groundwater quality were also carried out in the Cambrian-Vendian aquifer system in the framework of the Baseline project and other porjects. An essential first step for assessing the natural (baseline) groundwater quality is an understanding of the system within which the groundwater is contained. To define the source terms, the input to the system must be known, i.e. the chemistry of infiltrating water, which in the past resulted mainly from rainfall. To explain the characteristics of groundwater chemistry within the aquifer, information on geology, mineralogy, geochemistry, flow pattern and timescales is required.

2. THEORETICAL BACKGROUND

Groundwater overexploitation and aquifer overexploitation are terms that are becoming common in water-resources management and are increasingly used to point out negative aspects of groundwater development (Custodio 2002).

Intruded saline water may irreversibly change the development of groundwater resources, whether it is seawater encroaching into overexploited aquifers in coastal areas (Chen et al. 1997, Giménez and Morell 1997, Steinich et al. 1998, Yakirevich et al. 1998, Cruz and Silva 2000, Martínez and Bocanegra 2002) or older saline groundwater upconing in response to pumping from an overlying layer of fresh water (Karro 1999). Coastal groundwater aquifers are particularly threatened by salt-water intrusion from both sources (Mitrega and Lahermo 1991, Custodio 2002).

Human action that results in saline groundwater entering into the fresh water aquifer is termed saline water encroachment. Intruded saline water may irreversibly change the development of groundwater resources, whether it is seawater encroaching into effectively exploited aquifers in coastal areas or older saline groundwater upconing in response to pumping of an overlying layer of fresh water.

Salinization is the most widespread form of water contamination, and leads to an increase in the content of certain dissolved chemical species, as well as to the overall change in chemical water composition (Richter and Kreitler 1993).

Barium is a a naturally occurring component of minerals that are found in small but widely distributed amounts in the earth's crust, especially in igneous rocks, sandstone, shale and coal (Kunesh 1978; Miner 1969). Barium enters the environment naturally through the weathering of rocks and minerals. The primary source of naturally occurring barium in drinking water results from the leaching and eroding of rocks into groundwater (Kojola et al. 1978). Although barium occurs naturally in most surface water bodies (Kopp and Kroner 1967), releases of barium to surface waters from natural sources are much lower than those to groundwater (Kojola et al. 1978). However, the concentration of barium in natural waters is very low, because its dissolution is limited by baryte ($BaSO_4$) and witherite ($BaCO_3$) solubility products (Ball and Nordstom 1991).

Under natural conditions barium will form compounds in the +2 oxidation state. Barium does not hydrolyse appreciably except in highly alkaline environments (i.e., at pH levels greater than or equal to 10) (Bodek et al. 1988). Appreciable levels of barium sulphate occur because natural water often contains high sulphate concentrations. The data by Monnin et al. (2001) show an overall symmetrical behaviour between barium and sulphate, suggesting that the sediment pore water barium content is controlled by equilibrium with barium sulphate (baryte). Since the solubility of barium sulphate is low, only trace amounts of barium dissolve in surface water (Bodek et al. 1988; NAS 1977).

For the author, problems with assessing the quality of groundwater arose already during the investigations conducted in Pakri Peninsula in 1995. Although the impact of human activity was clearly visible in changes of water types, there was no environmental standard to force polluters to change their activities.

It was possible to use either the list of hazardous substances, which regulated the maximum allowed amount of heavy metals and organic pollutants, or the drinking water standard (Joogivesi 1995), which regulated major and minor compounds in the drinking water. Both standards were developed on the basis of the effect of the substances to human health and neither of these took account of natural occurrence of substances. This resulted in a situation where pollution was clearly visible in the changes of major compounds (HCO3, SO4, Ca) but there was no limiting factor in the standard for Ca or HCO3 and the limit of SO4 was too high to take any action.

Until now, there is no common methodology in Europe to define natural groundwater quality and possible pollution. Groundwater is still mainly considered as a reservoir for drinking water. About 75% of EU inhabitants depend on groundwater for their water supply (Quevauviller 2005). As a result, in many countries groundwater is assessed according to drinking water quality (Council directive 98/83/EC 1998) and there are no guidelines for considering the natural background as well.

The Water Framework Directive (Directive 2000/60/EC 2000) was the first attempt to start organising the assessment of groundwater quality based on natural variations in groundwater quality. The water framework directive is holistic, incorporating surface water and groundwater and bringing the concept of water cycle into legislation. Groundwater can no longer be taken as a separate source of drinking water – it is now a critical part of aquatic ecosystems.

The Water Framework Directive integrates monitoring inter alia monitoring as a key decision-making tool for evaluating the quantitative and chemical status of ground water (Quevauviller 2005). The Groundwater Directive (Directive 2006/118/EC) was introduced in 2006 in order to establish frames for environmental activities in groundwater. Groundwater directive sets the requirements for new environmental standards in assessing the groundwater quality. It can be either in a good or bad state, and the content of pollutants can be respectively below or above the threshold value (Directive 2006/118/EC). It is the responsibility of the EU member states to ensure that monitoring is representative (both monitoring points and monitoring elements), and all assessments based on monitoring results are scientifically correct.

It was recognised that a better understanding of environmental problems requires an improved awareness of multidisciplinary scientific developments, and that better integration of research results is required at various stages of policy development (Quevauviller 2005). Thus, several scientific projects were introduced after the enforcement of the Water Framework Directive.

In order to develop a scientific base for statistical methods for groundwater quality assessments, the project titled WFD-GW (The EU Water Framework Directive: Statistical aspects of the identification of groundwater pollution trends, and aggregation of monitoring results) was initiated in 1999 (WFD GW 1999). The aim of the project was to develop the proposals of algorithms to enable the aggregation of groundwater quality data at the groundwater body level, and trend and trend reversal assessment including proposals for the definition of the starting point and the length of time series.

The project BASELINE was started in 2000 with a view to providing a scientific foundation for the establishment of water quality guidelines under the Water Framework Directive. The aim was to introduce a standard, based on geochemical principles, to enable scientific assessment of natural variations in groundwater quality. To realise the task, a series of reference aquifers across Europe were established in order to illustrate variations in natural groundwater quality.

Natural baseline concentration of a substance in the Baseline project was defined as the concentration of a given element, species or chemical substance presence in a solution, which is derived from natural geological, biological or atmospheric sources. One important outcome from the Baseline project was that groundwater in Europe differs to a large extent, due to which the development of one unified baseline quality standard for Europe is impossible.

In 2005, another EU 6th FP project began, titled "Background criteria for the identification of groundwater thresholds" (BRIDGE), aiming to develop a new methodology for defining environmental standards for groundwater quality. The standard is referred to as threshold value in groundwater directive. Since previous investigations have shown that it is impossible to introduce a single value or even a range of concentration of a given element for all Europe, the purpose of the Bridge project was to develop a unified methodology.

The groundwater directive (Directive 2006/118/EC 2006) requires that threshold values should be established taking into account pollutant origin (including any possible natural occurrence), pollutant toxicology and dispersion tendency, plus pollutant persistence and bioaccumulation potential. According to the Bridge project, threshold values are quality standards for pollutants in groundwater, which need to be set according to individual EU member states, and represent the concentration of pollutants which must not be exceeded in order to protect human health and the environment (Figure 1). This demands a good conceptual understanding of the groundwater system, its environmental setting, and the relationship with and impacts upon the ultimate receptor.

Natural background level (NBL) plays a central role in the derivation of threshold value, as it is the starting point for the whole process. In general, most organic substances have no NBL, as these have anthropogenic origin, i.e. most organic substances found in groundwater. The NBL derivation process requires a high level of knowledge of geochemical transfers and processes. It also requires groundwater monitoring data for the whole country, specific groundwater typologies or for a specific groundwater body. Initial evaluation refers to the natural background level of the investigated element or substance. Hence, the first step towards the derivation of threshold values is to derive the NBL of the investigated substance. (Müller et al. 2006). The second step is focused on possible impacts on receptors (i.e. associated surface waters, dependent terrestrial ecosystems or groundwater itself), and the significance of these impacts, for example significant diminution of the ecological or chemical quality of surface water bodies.

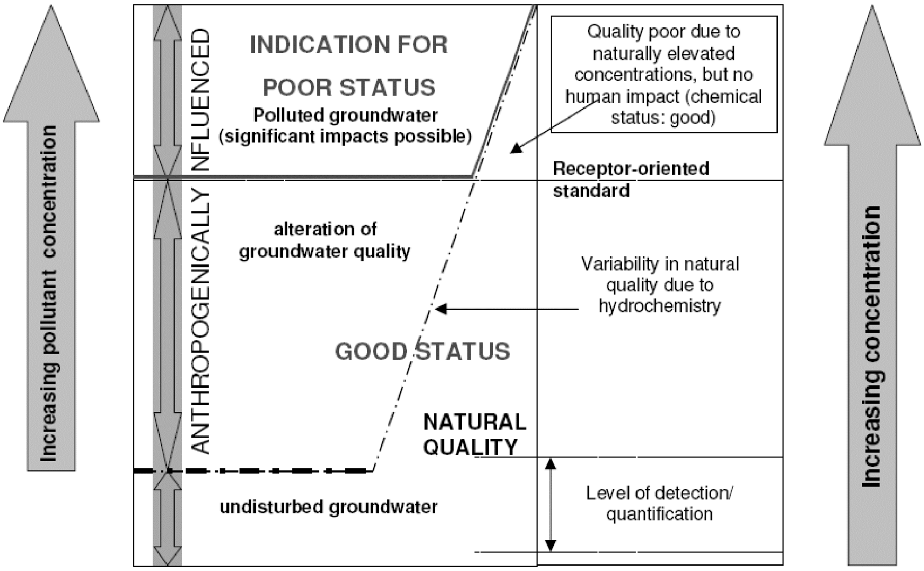


Figure 1. General relationship of groundwater quality and status defined in Bridge project (Müller et al. 2006).

Recent investigations have produced a good basis for the development of new environmental standards, which also consider natural contestations of substances in groundwater.

3. STUDY AREA

3.1. Geology

Estonia is situated in the north-western part of the East-European Platform. Structurally, its sedimentary beds, lying on the southern slope of the Baltic Shield, plunge southwards sloping about 3–4 metres per kilometre.

The crystalline Paleoproterozoic basement is overlain by Vendian, Cambrian, Ordovician, Silurian and Devonian sedimentary rocks, which are covered by Quaternary deposits (Perens & Vallner 1997). In northern Estonia, the Vendian, Cambrian and Ordovician rocks are the only sedimentary rocks covering the crystalline basement, which lies approximately 150 m below the surface (Figure 2).

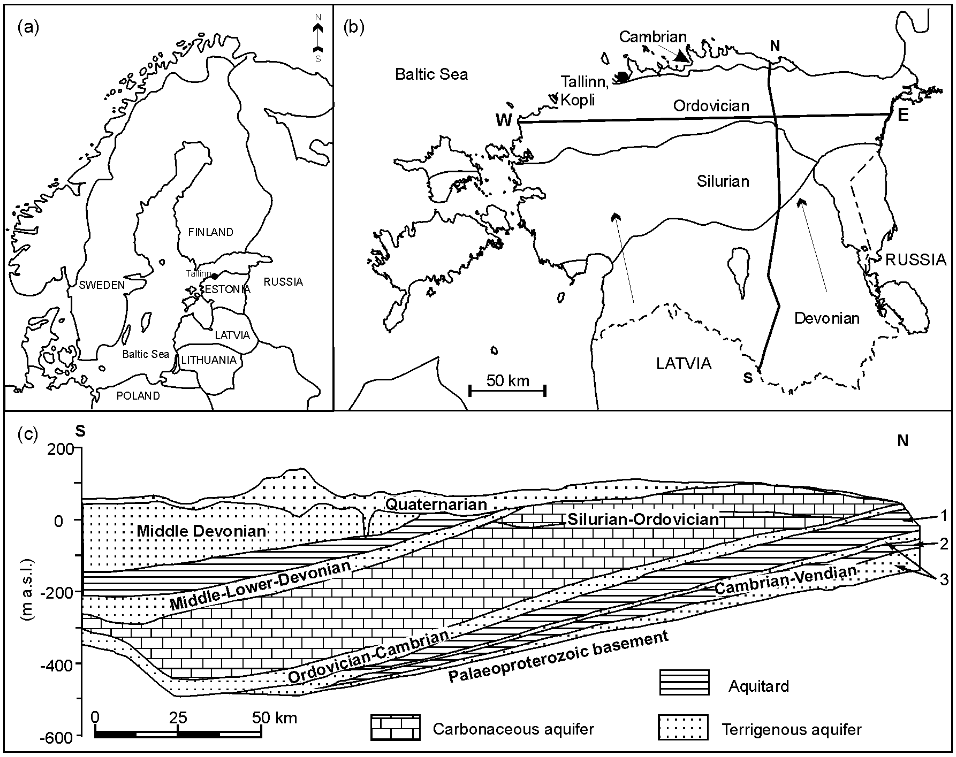


Figure 2. (a) Schematic map showing the location of Estonia; (b) hydrogeological map of Estonia with the position of the line of cross-section; arrows indicate the direction of groundwater flow and (c) the North-South cross-section of major hydrogeological units of Estonia (1-Lontova and 2-Kotlin clays; 3-Voronka (upper) and Gdov (lower) aquifers, confining the Cambrian-Vendian aquifer system) (Paper IV).

The crystalline basement mostly consists of gneisses and biotite gneisses (Koistinen et al. 1996) and its upper part (10–150 m thick) is fractured and weathered. Weathering profiles are predominantly composed of kaolinite, illite, chlorite and montmorillonite, depending on the original bedrock composition and the intensity of weathering.

Weathered basement rocks are overlain by water-bearing Vendian and Cambrian silt- and sandstones (with interlayers of clay), which form the Cambrian-Vendian aquifer system. In the eastern part of Estonia, the Vendian sedimentary rocks are divided by a clay layer of the Kotlin Formation (V_2kt) into the Voronka (V_2vr) and the Gdov (V_2gd) aquifers (Figure 3).

The terrigenous rocks of the Cambrian-Vendian aquifer system (Cm–V) occur all over Estonia, except for the Mõniste-Lokno uplift area in southern Estonia. The aquifer system is overlain by clays and siltstones of the Lükati-Lontova aquitard (Lontova) (Figure2), (Perens & Vallner 1997).

However, in places the aquitard and the water-bearing bedrock formation have been penetrated by a relatively dense set of ancient buried valleys filled with loamy till and, in places, glaciofluvial gravel in lower parts of the valleys (Tavast 1997). The valleys are orientated north-west to south-east, approximately perpendicular to the north-Estonian coastline.

3.2. Hydrogeology of the Cambrian-Vendian aquifer system

There is an obvious difference between the cross-sections of the Cambrian-Vendian aquifer system in western Estonia compared to those in the east. In the eastern part, up to 53 m thick clays of the Kotlin Formation (V_2kt) divide the aquifer system into two aquifers (Figure 3).

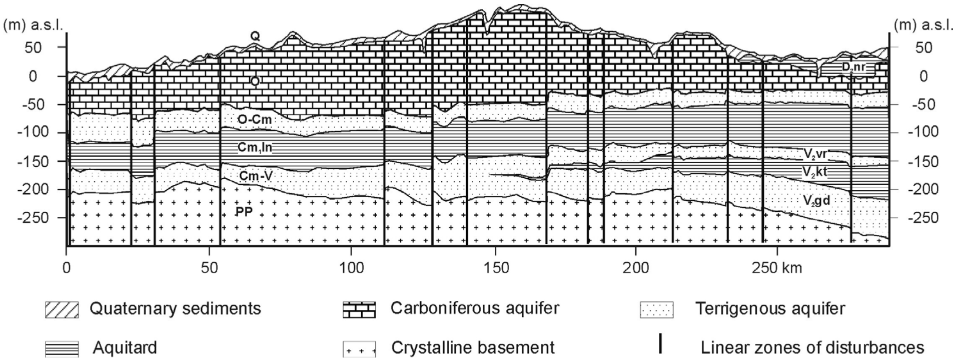


Figure 3. Hydrogeological cross-section (WE) of the Cambrian-Vendian aquifer system in northern Estonia. Line of cross-section shown in Figure 1 (Paper II).

The upper Voronka aquifer (V_2vr) consists of quartzose sandstone and siltstone with a thickness of up to 45 m in north-eastern Estonia. The conductivity of the rocks ranges from 0.6 to 12.5 m/d with an average of 2 to 6 m/d. The transmissivity decreases from 100–150 m^2/d in northern Estonia to 50 m^2/d (and less) in the south. Under natural conditions, the potentiometric levels along the coast of the Gulf of Finland are about 1.5–5.5 m a.s.l.

The lower Gdov (V_2gd) aquifer is formed by an up to 68 m thick complex of mixed sandstone and siltstone. It directly overlies the Precambrian basement and is confined by the overlying clay of the Kotlin Formation. In northern Estonia, the conductivity of water-bearing rocks is 0.5–9.2 m/d with an average of 5–6 m/d. Transmissivities in north-eastern Estonia are in the range of 300–350 m^2/d and decrease in a southerly and westerly direction to 100 m^2/d and less. The potentiometric surface in the coastal area is about 3–5 m a.s.l. under natural conditions.

Westward of the line where the Kotlin clays pinch out (Figure 3), the Cambrian and Vendian water bearing rocks form the Cambrian-Vendian aquifer. The Cambrian-Vendian aquifer system thins out towards southern and western Estonia. In northern Estonia, however, its thickness amounts to 90 m and the aquifer system outcrops along the northern coast in the south of the Gulf of Finland.

In northern Estonia, the aquifer system is mostly confined by 60–90 m thick clays of the Lontova Formation, and the system has a strong isolation capacity due to its low transversal conductivity of 10^{-7} to 10^{-5} m/d. However, as mentioned above, in places the aquitard is penetrated by ancient buried valleys. The Cambrian-Vendian aquifer system is underlain by Lower Proterozoic crystalline basement; its cracks and fissures contain a small amount of water but it is not exploited. The lower portion of the basement serves as an impermeable base layer for all the overlying aquifer systems (Vallner 1997).

3.3. Hydrogeochemistry of the Cambrian-Vendian aquifer system

The Cambrian-Vendian aquifer system recharges in southern Estonia from where it dips towards the discharge areas situated in the depressions of the Baltic Sea and the Gulf of Finland. The length of the deeper branches of the flow system can reach 250 km.

According to earlier studies, in the Cambrian-Vendian aquifer system in northern Estonia, $Cl\text{-}HCO_3\text{-}Na\text{-}Ca$ and $Cl\text{-}HCO_3\text{-}Ca\text{-}Na$ type waters with TDS contents between 0.4–1.0 g l^{-1} predominate.

In north-eastern, south-western and south-eastern Estonia, as well as on the islands of Saaremaa and Ruhnu, Cl-Na, Cl-Na-Ca and Cl-Ca-Na type waters with TDS contents from 2–22 g l^{-1} are widespread (Figure 4)(Karise 1997).

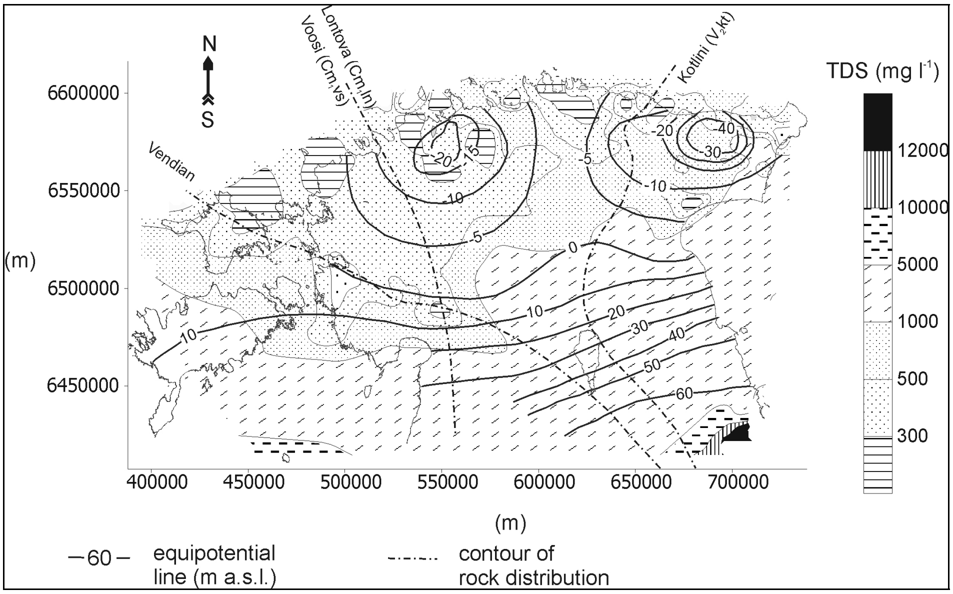


Figure 4. Equipotential lines, TDS content and contours of rock distributions of the Cm-V aquifer system. The equipotential lines are drawn after Perens & Vallner (1997).

The Cambrian-Vendian aquifer system is situated in the passive water exchange zone where reducing of conditions occur. The groundwater stored in those conditions is usually rich in trace elements.

However, the concentrations of trace elements are the highest at Värska in south-eastern Estonia, where cadmium (Cd), lithium (Li), manganese (Mn) and lead (Pb) concentrations exceed the values set by the EU regulations. In several regions of Estonia, high concentrations of bromide (Br) have been detected in the Cambrian-Vendian aquifer system, for example, values of 13 mg Br l^{-1} were observed in Kuressaare at depths between 540–55 m whilst concentrations in Värska ranged between 16–17 mg Br l^{-1} at 520–35 m and 51–6 mg l^{-1} at 540–600 m (Karise 1997).

3.4. Age of the Cambrian-Vendian aquifer system

The Cambrian Vendian aquifer system belongs to a passive water exchange zone on Estonian monocline (Vallner 2003) and acts as a recharge area of a large arthesian basin lying in the Baltic syneclise. The Masurian-Byelorussian massive acts as the recharge area of this artesian basin (Mokrik 1997).

The piesometric head in the Cm-V aquifer system varies from 60 m a.s.l to 20 m b.s.l (Figure 4). Thus, the natural flow direction is from south to west. Large depression cones in the piesometric head are caused by groundwater overexploitation while the natural level of piesometric head was from 2 to 5 m in the coastal area of north-Estonia (Vallner, 2003).

During the glaciations in Pleistocene, the bedrock of Estonia was heavily eroded and the Cm-V aquifer system became dynamically connected with the melt water below the glacials.

The results of isotope and geochemical investigations as well as noble gas analyses (Vaikmäe et al. 2001) show that the water in the Cambrian-Vendian aquifer system in northern Estonia was recharged during the last glaciation.

It has further been shown that for about 11 ka during the Late Pleistocene, the Scandinavian ice sheet in the Cambrian-Vendian outcrop area was underlain by meltwater (Jõeleht 1998).

During this time the hydraulic head was controlled by the thickness of the ice. Although the Cambrian-Vendian aquifer system itself has relatively high hydraulic conductivity, it is surrounded by areas of low hydraulic conductivity and therefore the hydraulic head in the outcrop area of the aquifer system was probably close to floating point, e.g. about 90% of ice thickness (Piotrowski1997).

Taking into account also the postglacial uplift and the present depth of the Cambrian-Vendian aquifer system (about –100 m below sea level), the hydraulic gradient was around 0.0031 (Jõeleht 1998). Thus, recharge into the Cambrian-Vendian aquifer probably occurred during the glaciation, most likely by sub-glacial drainage through the tunnel valleys (Vaikmae et al. 2001).

In contrast, Mokrik (1997) suggests that the freshwater in the Cambrian-Vendian aquifer complex in north Estonia was formed by cryogenic metamorphism. He proposes that during the Pleistocene glaciation the aquifers went through several freezing-refreezing cycles down to a depth of 200–50 m, which led to the freshening of the originally highly mineralised groundwater in the Cambrian-Vendian aquifer complex. This would imply that a permafrost zone had developed on the surface of the Baltic Shield about 100–50 km from the outcrop of the aquifer (Mokrik 1997).

However, all these works agree in the fact that freshening took place during the last glaciation and that the intruded water has its origins in cold climate.

The oxygen isotope composition in the groundwater of most aquifer systems in Estonia range from –11.0 to –12.2‰ (Figure 5) (Vaikmäe&Vallner 1999).

However, groundwater in the Cambrian-Vendian aquifer system shows a heavily depleted oxygen isotope composition, with $\delta^{18}O$ values varying mainly from –18 to –22‰ (Vaikmäe et al. 2001).

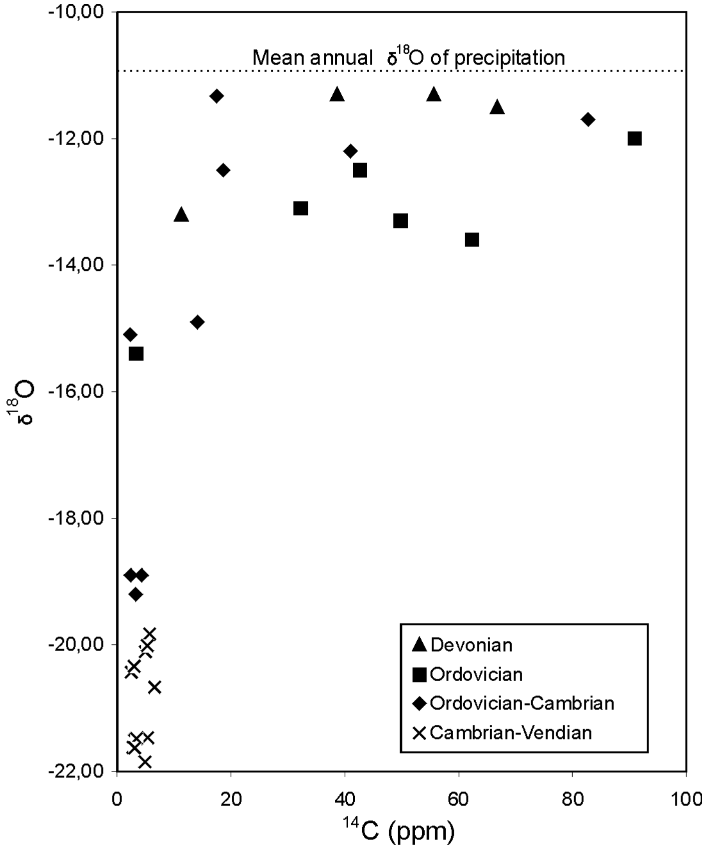


Figure 5. Distribution of $\delta^{18}O$ values of groundwater from different aquifers in Estonia according to their ^{14}C concentrations. $\delta^{18}O$ values from two wells (PK 705 and PK 897) indicate mixing with infiltrated modern water (Paper IV).

In contrast, long term mean annual $\delta^{18}O$ value in contemporary precipitation in Estonia is –10.4‰ (Punning et al. 1987). Low $\delta^{18}O$ values in the Cambrian-Vendian aquifer are indicative of recharge in cold conditions, whilst low ^{14}C concentrations are indicative of long residence time of groundwater (Vaikmäe et al. 2001).

4. MATERIALS AND METHODS

For the studies, the results of which are presented in papers 1 to 4, 77 groundwater samples were collected from the Cambrian-Vendian aquifer system during the period from 2001 to 2003. The sampling points were selected according to the following criteria: 1) assurance of a good areal representation of the aquifer, and 2) sampling of both Gdov and Voronka aquifers at every sampling point, if possible. All sampled wells are water supply wells and under operation at the moment of sampling.

Groundwater samples were taken after the stabilisation of field parameters (redox potential, pH, electrical conductivity and temperature) in the pumped-out water. Most water samples were analysed in Tartu Environmental Research laboratory (Reg. no L100), where Cl^-, SO_4^{2-}, HCO_3^-, Ca^{2+}, Mg^{2+}, K^+, Na^+, Fe and Ba^{2+} were measured. A more detailed analysis was performed during the Baseline study, where 30 samples were analysed for a full range of inorganic species (by ICP MS) and field measurements, including Eh, DO, pH, temperature and SEC, which are used to assist the interpretation. All samples were filtered in the field and acidified with nitric acid (1% v/v) in order to stabilise trace elements in the solution.

Historical data together with new sampling results was used during the present study in order to describe the natural background quality of Cambrian-Vendian groundwater. An extensive data set collected within approximately 55 years exists in the Geological Survey of Estonia (GSE), and contains more than 1500 chemical analyses from 967 wells from the Cambrian-Vendian aquifer system. The database contains information on the main compounds of groundwater chemistry: dry matter, TDS, Na^+, K^+, Na+K, NH_4^+, Ca^{2+}, Mg^{2+}, Fe_2, Fe_3, Fe_{tot}, Cl^-, SO_4^{2-}, NO_2^-, NO_3^-, CO_3^{2-}, HCO_3^-, pH, SIO_2, hardness (Perens et al. 2001). Data is also available from a number of published and unpublished (mainly various reports of GSE) investigations. The Cambrian-Vendian aquifer system has been studied at various times over the last decades (Mokrik & Vaikmäe 1988; Mokrik, 1997; Perens & Vallner 1997; Groundwater state 1998; Vaikmäe et al. 2001). The results of these studies provided extensive information on the hydrogeology, geochemistry and lithology of the aquifer system. All these results were critically analysed for the present study.

Two databases containing the historical and fresh data were compared in order to evaluate the suitability of the historical database. The methods and results of comparison are presented in Paper 4. The summary statistics showed that both databases compare relatively well.

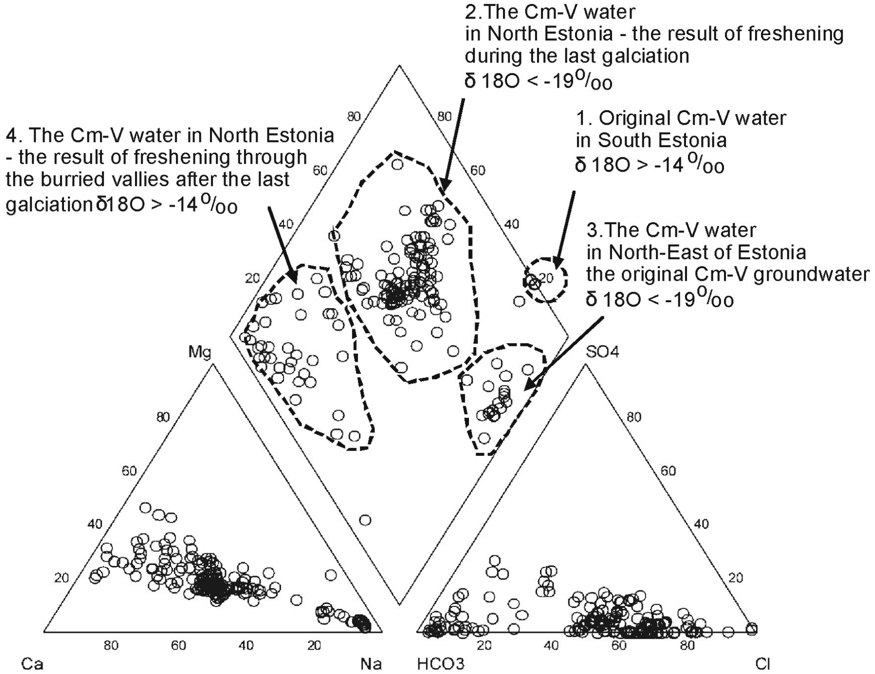
For data processing of all samples, interpretation and hydrogeochemical assessment of the results, MapInfo Professional 6.0 and AquaChem 3.7 were used.

5. RESULTS AND DISCUSSION

5.1. Groundwater chemistry of major ions in the Cambrian-Vendian aquifer system

The chemical evolution of groundwater in aquifers along flow paths depends on the age distribution with depth and distance, geological conditions and the lithological composition of water-bearing rocks and sediments. However, considering the extremely low velocity of groundwater in the Cambrian-Vendian aquifer system and taking into account both the palaeohydrological situation during the Late Pleistocene, as well as the contemporary situation in northern Estonia, where the groundwater geochemistry is influenced by intensive abstraction, the overall picture of the aquifer system is rather complicated and not yet well understood.

All processes described in the previous section have led to a complicated picture of Cambrian-Vendian groundwater chemistry, which can be described by the areal distribution of TDS in groundwater. The TDS ranges from 0,2g/l until 26 g/l in Estonia, while the length of flow line is max 250 km (Figure 4). Therefore, the best way to follow the changes in natural baseline characteristics is to use the Piper diagram (Figure 6).



2.The Cm-V water
in North Estonia - the result of freshening
during the last galciation
δ 18O < -19 ^{0}/oo

1. Original Cm-V water
in South Estonia
δ 18O > -14 ^{0}/oo

4. The Cm-V water in North Estonia
- the result of freshening through
the burried vallies after the last
galciation δ18O > -14 ^{0}/oo

3.The Cm-V water
in North-East of Estonia
the original Cm-V groundwater
δ 18O < -19 ^{0}/oo

Figure 6. The piper plot reflecting major groundwater chemical types in Cm-V aquifer system (Paper IV).

Four major groundwater types can be distinguished in the diagram based on their chemical composition:

The first type is Cl-Na type, which can be interpreted as a saline baseline or relict groundwater of the Cambrian-Vendian aquifer system. It may be very old and probably formed long before the last ice age. TDS concentrations in waters of this type are higher than 2 g l^{-1}, which means that they are mineral waters.

In south-eastern Estonia, TDS concentrations in the groundwater of the deeper part of the Cambrian-Vendian aquifer system even reach values up to 18 g l^{-1}. The $\delta^{18}O$ values of this groundwater type are higher than $-14^{o}/_{oo}$.

Relict groundwater of the Cl-Na type is widely distributed in the Cambrian-Vendian aquifer system in southern and central Estonia but also in Voronka aquifer in north-eastern Estonia.

It is also characterised by a very high Cl^{-} content, ranging from 1083 mg l^{-1} in wells in north-eastern Estonia up to 10919 mg l^{-1} in south-eastern Estonia. The Na^{+} content in these wells is 684 mg l^{-1} and 5222 mg l^{-1}, respectively.

The second type is Ca-Na-HCO_3-Cl or Ca-Na-Cl-HCO_3 water. This is the “fresh baseline” water of glacial origin, recharged during the last glaciation (Vaikmäe et al. 2001).

The chemical composition of this type of water is formed through the water-rock interaction during the last more than 10 ka. This water type has the largest spatial distribution, spreading from the northern coast to central Estonia, and also shows mixing with other water types (except with type 1) on the Piper diagram.

The TDS concentrations vary from 300 mg l^{-1} to several g l^{-1}. Due to lack of sampling wells in central Estonia, the exact border between the “saline baseline” waters and “fresh baseline” waters cannot be defined. This is also reflected in the Piper diagram, which shows mixture zones between the different water types, although mixing with type-1 water is not apparent. The relative proportions of HCO_3^{-} and Cl^{-} control different chemical water types. Thus, some waters are classified as different water types even though the actual differences in their chemical concentrations are small.

However, the most characteristic feature of this groundwater type is its strongly depleted stable isotope composition. The $\delta^{18}O$ values range between $-19^{o}/_{oo}$ and $-22^{o}/_{oo,,}$ indicating the formation of the water under cold climatic conditions (Figure 6).

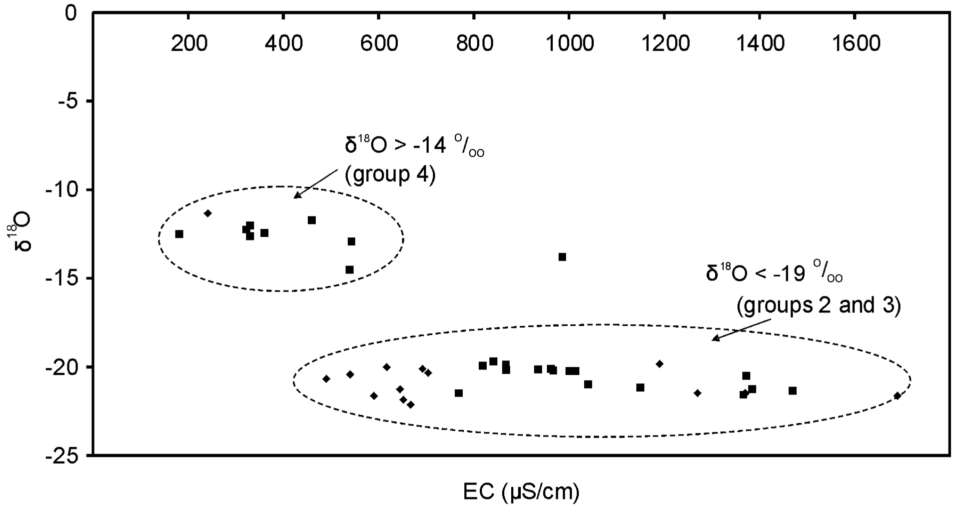


Figure 7. $\delta^{18}O$ versus EC values of the Cambrium-Vendian groundwater (Paper IV).

The third, Cl-HCO$_3$-Na groundwater type is interpreted as a mixture of glacial melt water with some remains of relict saline groundwater. This groundwater type is distributed predominately in the north-eastern part of Estonia, where the Kotlin clays divide the Cambrian-Vendian aquifer system into two aquifers and where the overlying clays reach their maximum thickness in Estonia (Figure 3).

Therefore, intrusion of fresh melt water into the aquifer during the last glaciation probably occurred to a lesser extent in this area than in the western part of north-Estonia.

However, TDS is decreased to 1g/l. A freshening effect by glacial melt water is also reflected in the ^{18}O content, which here is below –19 $^{o}/_{oo}$ (Figure 7).

The fourth, Ca-HCO$_3$ groundwater type is found in northern Estonia, in areas around the ancient buried valleys, where the intrusion of fresh groundwater from overlying aquifers and/or rainwater occur. The intensity of such fresh water intrusions varies spatially and temporally, depending on the extent of groundwater exploitation near the valleys. In areas where groundwater draw-down is significant, freshwater intrusions occurred into the aquifer through the buried valleys and caused the groundwater chemistry and in its isotopic composition to change (Figure 7). The $\delta^{18}O$ values are usually higher than 15$^{o}/_{oo}$ due to freshwater intrusions and the TDS contents are low (200–500 mg l^{-1}).

5.2. Changes in groundwater chemistry in the Cambrian-Vendian aquifer system

The most serious consequence of intensive groundwater use in northern Estonia is the formation of regional depressions in potentiometric levels around Tallinn and Kohtla-Järve (an industrial area in north-eastern Estonia). A basin-wide model simulation showed that overexploitation has caused changes in the direction and velocity of groundwater flow (Vallner 2003). As a result, lateral and vertically rising groundwater flows support the transport of connate brackish water from the deeper parts of the aquifer system and from the underlying crystalline basement to the groundwater intakes and also promote seawater intrusion (Yezhova et al. 1996; Vallner & Savitskaja 1997; Mokrik 1997; Savitski 2001).

In order to investigate the impact of intensive use of groundwater on groundwater quality, a study was performed in Kopli area in north-Estonia (Paper III). Overexploitation of fresh-water resources of the Cambrian-Vendian aquifer system at Kopli Peninsula has resulted in a rise in TDS content and concentration of major ions in groundwater.

Three main theories were analysed as the source of salinity of Cambrian–Vendian groundwater at Kopli Peninsula: 1) intrusion of present-day seawater; 2) pumping-induced upconing of salt water from below the freshwater; 3) a combination of the two. The purpose of this study is to evaluate the possible causes of the increase in the content of dissolved solids in groundwater.

The lateral seawater intrusion into water intakes can take place at Kopli Peninsula where production wells are located close to the sea (Paper III). Taking into consideration the good screening properties of the overlying Lontova aquitard, vertical penetration of the seawater from above is hardly realistic. The large-scale variation of TDS and major ion concentrations in the water of the production wells is clearly visible during 1978–2002 (Figure 4, Paper III). Permissible concentrations of the major components in water set by the Estonian drinking water standard (Regulation 2001) and Drinking Water Directive of the European Union (98/83/EEC) have been exceeded.

Major ion chemistry of the sampled groundwater is examined as a whole using the Piper diagram (Figure 8). It shows slight variations in relations between the main cations and anions in the aquifer system. A change towards more Ca-Cl-dominated groundwater is visible. Water types (I–III) on the diagram represent an attempt to systematise the chemistry of groundwater. In reality, there are no sharp boundaries between water types, and the progression from group I to III represents the evolution of waters with an increasing degree of water-rock interaction and mixing with brackish water from crystalline basement.

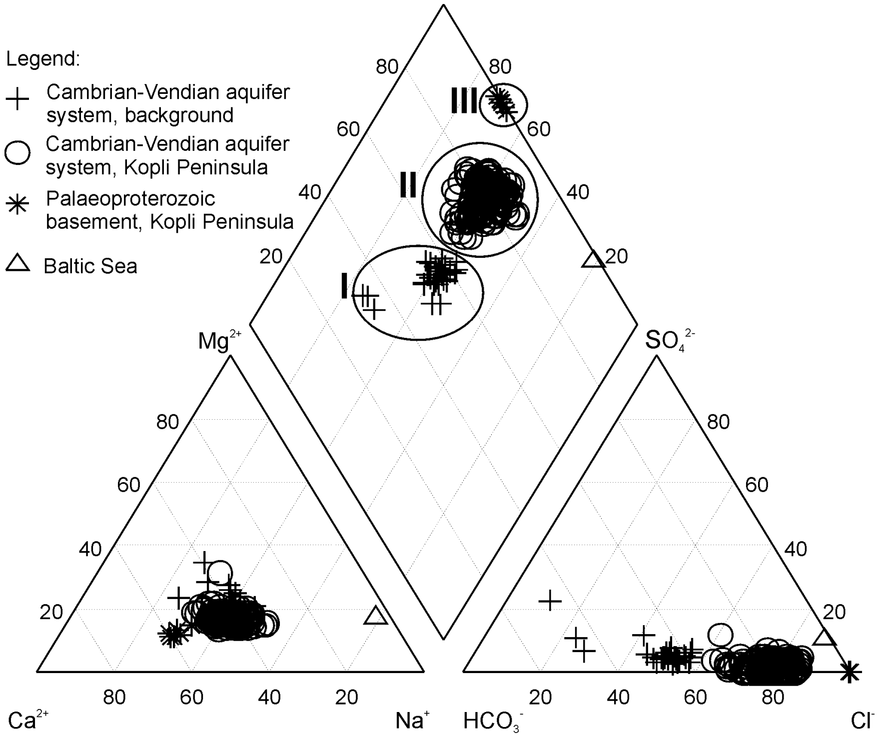


Figure 8. Piper diagram showing the ionic composition of Cambrian-Vendian groundwater from wells in northern Estonia (Group I), at Kopli Peninsula (Group II) and in Palaeoproterozoic basement (Group III). For reference, data of the Baltic Sea are presented (Paper III).

Abstracted groundwater is depleted in sodium relative to seawater, and the abundance of calcium, potassium and bromide in groundwater relative to seawater (Figure 9) points rather to the upconing of saline deep-seated groundwater than to lateral seawater intrusion.

The changes in water chemistry can be explained by the mineralogical and chemical characteristics of the reservoir rocks and water exchange with underlying water bearing weathering core of fractured crystalline basement, which hosts brackish Ca-Cl type water (Paper III).

The theory of upconing of saline deep-seated groundwater is also supported by the result of isotope investigations carried out in the Kopli area (Paper III). The oxygen isotope composition of groundwater in most of aquifer systems in Estonia ranges from –11.0 to –12.2‰ (Vaikmäe et al. 2001). However, the groundwater in the Cambrian-Vendian aquifer system has a heavily depleted oxygen isotope composition. The values of $\delta^{18}O$ vary mainly from –18.1 to –22.0 ‰ in northern Estonia (Vaikmäe et al. 2001, Mokrik and Mažeika 2002).

At the same time, the long term mean annual δ^{18}O values in contemporary precipitation in Estonia are –10.4 ‰ (Punning et al. 1987).

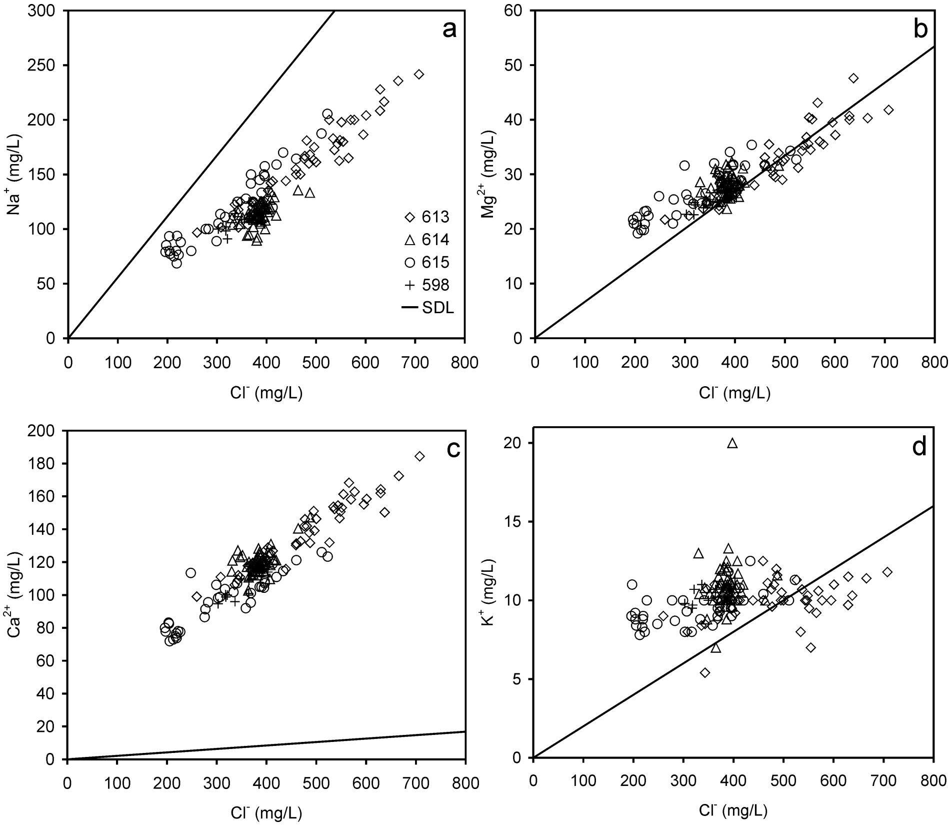


Figure 9. The concentrations of various ions plotted against chloride concentration. SDL – seawater dilution line (Paper III).

In 2001, groundwater samples from six wells at Kopli Peninsula were analysed for their isotopic composition (Paper III). The δ^{18}O values obtained are typical to Cambrian-Vendian groundwater. Low δ^{18}O values in the Cambrian-Vendian aquifer system (from –19 to $-22^{0}/_{00}$) are indicative of recharge in cold conditions, whilst low ^{14}C concentrations (from 2 to 5 pmc) are indicative of long residence time of groundwater.

Mokrik (1997) has concluded that the corrected absolute age of Cambrian-Vendian groundwater in northern Estonia averages from 23 to 33 ka BP. In places where deep erosional valleys are developed, owing to the infiltration of meteoric water caused by intensive exploitation, the age of groundwater is considerably younger, ranging from 7 to 19 ka BP. According to δ^{18}O and ^{14}C determinations from the Kopli Peninsula, detectable intrusion of modern water (including seawater) into the Cambrian-Vendian aquifer system as a consequence of heavy pumping has not been occurred. This conclusion is confirmed also by the absence of ^3H in most of the sampled wells in the costal areas of northern Estonia (Vaikmäe et al. 2001).

5.3. Barium anomaly in the Cambrian-Vendian aquifer system

Several studies have indicated a low content of micro-compounds in the Cambrian-Vendian aquifer system. However, an anomalously high content of barium was discovered during investigations in the north-eastern area.

In the water of the deep wells of the north-Estonian water supply system, anomalously high concentrations of dissolved barium were first recorded in 1996 (Otsa and Tamm 1997; Tamm 1998), as only by that year laboratory techniques had developed to the level that application of routine controls could be accomplished. A study of micro-compounds in the Cambrian-Vendian aquifer system was also performed in 1994, but did not include barium (Savitskaja and Viigand 1994). According to the findings in 1996, the barium concentration exceeded the limit value of the previous Estonian drinking water standard –0.7 mg/l – (Joogivesi 1995) 2–13 times in several sampling locations.

A comprehensive study with a view to explaining the barium anomaly was performed between 2001 and 2002 (Paper I and II). The aim of the study was to provide scientific evidence for the barium anomaly in north-Estonian groundwater, to map the territory of the anomaly, to provide a hydrogeochemical analysis to explain the occurrence of the anomalies.

Groundwater was sampled systematically from west to south in northern Estonia in order to follow any lateral geochemical changes in groundwater composition. In every sampling, location analyses from both Gdov and Voronka aquifer were sampled in order to follow any vertical changes (Paper I).

The results showed that general lateral changes in the chemical composition as well as in the type of groundwater are remarkably bigger than those in vertical direction in certain sampling points.

The prevailing of Ca and HCO_3 ions in groundwater decreases eastwards where Na and Cl ions become dominant (Figure 10) (Paper I Table 2, Figure 4). The content of Na^+ and Cl^- in the Cm-V aquifer system varies from 26 to 405 mg/l and 46 to 700 mg/l, respectively, exhibiting the highest values in the eastern part of the country. The concentrations of Ca^{2+} (6–188 mg/l) and HCO_3^- (103–264 mg/l) show somewhat higher values in the western part of the studied area. The highest SO_4^{2-} values are also detected from the western margin of the area (Paper I, Table 2). The content of total dissolved solids (TDS) in the analysed groundwater samples varies from 0.2 to 1.5 g/l.

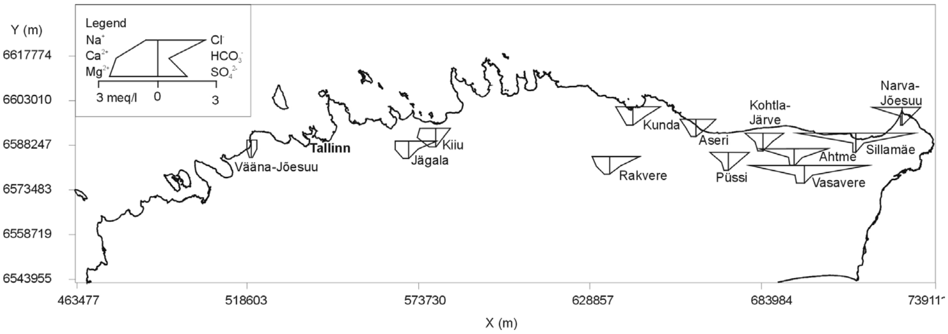


Figure 10. Stiff diagram showing lateral changes in the chemical composition of groundwater in Gdov aquifer in north-Estonia (Paper I)

The content of barium in the analysed water samples varies from 0.07 to 6.37 mg/l. Territorially, an evident pattern in the distribution of barium can be observed. Marginal parts of the studied area are characterised by low barium content while high barium values (0.41–6.37 mg/l, median 2.41 mg/l) concentrate in the Kunda-Rakvere-Kohtla-Järve region, which can be outlined as a Ba-anomaly in the aquifer system (Figure 11)

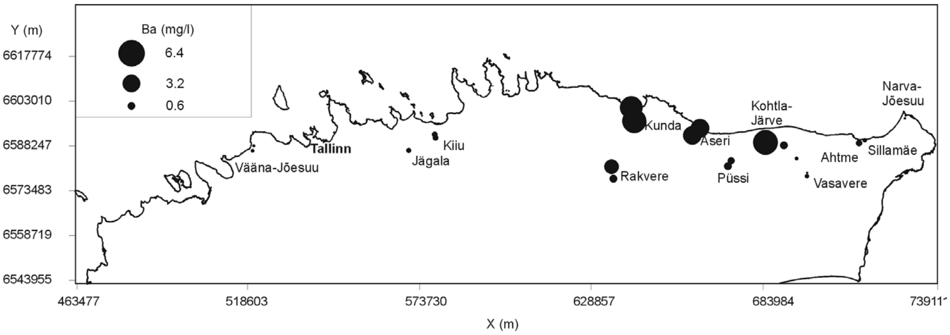


Figure 11. The content of Ba^{2+} in the Cambrian-Vendian aquifer system in north-Estonia (Paper I).

Generally, the deep-seated Gdov aquifer is enriched in barium compared to the overlying Voronka aquifer (Figure 12). All high Ba^{2+} values (>2 mg/l) in the Gdov aquifer are associated with the anomaly. Furthermore, some groundwater production wells opening the Cambrian-Vendian aquifer system in its full thickness (both Voronka and Gdov aquifer) exhibit elevated barium concentrations. The highest barium value (3,77 mg/l) is analysed from a well which reaches 3 metres into the crystalline basement.

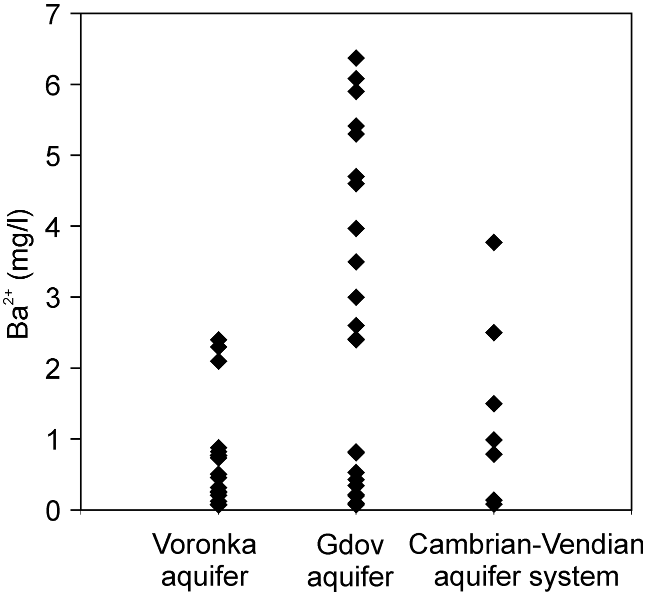


Figure 12. Concentration of Ba^{2+} in different hydrogeological units (Paper II)

According to Klein et al. (1983), the content of barium in gneisses of Estonian crystalline basement is 700 ppm. The highest average barium content (1000 ppm) of the north-east Estonian bedrock has been detected in silicate marbles (Koppelmaa and Kivisilla 1997), which are associated with hydrothermal pyrrhotite-pyrite ore mineralisations at magnetic anomalies in north-eastern Estonia.

Therefore, one potential source of barium is ion exchange between the water bearing underlying weathering core. Besides, the working intervals of groundwater abstraction wells opening the Gdov aquifer are often located close to the weathered basement, and as the influence area of pumping increases, an increasing contribution of leakage from the underlying bedrock may affect the quality of groundwater.

The major ion chemistry of groundwater also plays an important role in generating high concentration of barium in groundwater. The modelling, performed in Paper I showed that sulphate and bicarbonate ions are the main compounds that precipitate barium ion out from solute, although bicarbonate ion has practically no influence when barium ion concentrations are low (<10 mg/l). The content of chloride ion, on the contrary, contributes to an increased solubility of barium ion.

The results also showed that in case of a low (< 3 mg/l) concentration of sulphate ion, the barium ion content in Cm-V aquifer system can be higher than the limit value (2 mg/l) set for drinking water by EPA (1995)(Figure 13).

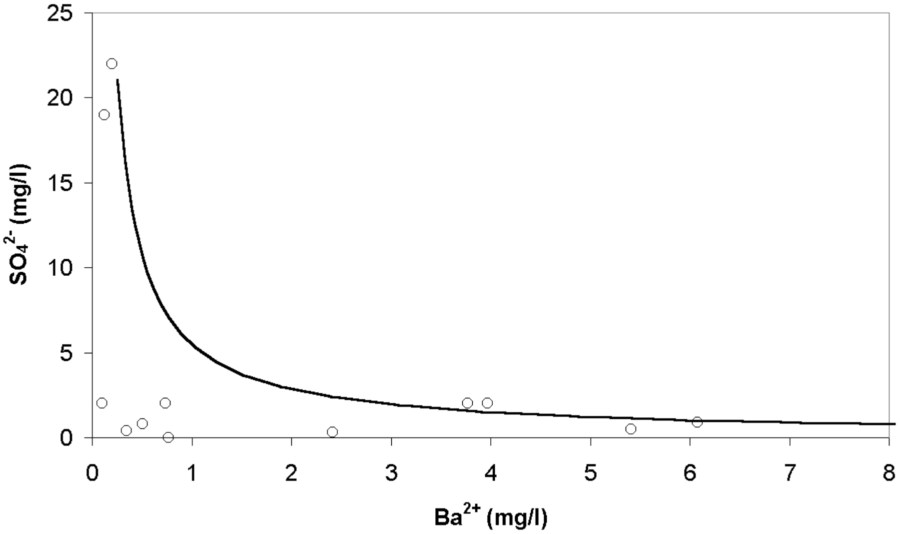


Figure 13. The Ba^{2+} and SO_4^{2-} content in groundwater of the Cambrian- Vendian aquifer system and the equilibrium line of baryte solubility modelled by PHREEQC (Paper I).

5.4. Processes defining the quality of groundwater in the Cambrian-Vendian aquiver system

Several assumptions can be made on the basis of geochemical studies (Paper I–IV).

In southern and central Estonia, the Cambrian-Vendian aquifer system contains relict saline groundwater of marine origin with total dissolved solids (TDS) up to 22 g l-1. Chloride and Na predominate over all other ions in this zone.

In northern Estonia the Cambrian-Vendian aquifer system contains palaeogroundwater, which recharged during the last glaciation. This is fresh water with TDS values mainly below 1.0 g l-1. The baseline chemical composition of the water is formed through the water-rock interaction during the last 10 ka. In northern Estonia, the most characteristic feature of the Cambrian-Vendian aquifer system is the very light oxygen isotopic composition (δ18O values of c. –22‰) of the groundwater, which provides an ideal tracer for the detection of possible changes in groundwater baseline quality.

Fresh groundwater of the Na-Ca-HCO_3-Cl type characterise the upper part of the Cambrian-Vendian aquifer system in north-Estonia (Perens et al. 2001) owing to the hydrochemical differentiation and to stratification due to density differences of water types. The lower part of the Cambrian-Vendian aquifer system and the weathered crystalline basement are characterised by groundwater of Na-Ca-Cl-HCO_3 and Ca-Na-Cl types with TDS content of 1.4 to 5.0 g/l.

Long-term pumping has induced the upward movement of salty deep-seated groundwater into wells. A relatively fast 1.5 to 3.0-fold increase in TDS and in concentrations of major ions in abstracted groundwater is the consequence of heavy pumping. The aquifer is not in hydraulic continuity with seawater, and the simple upconing of saltwater-freshwater interface does not take place on the Kopli Peninsula in Tallinn (Karro et al. 2004).

Excessive pumping of the fresh water aquifer may result in the development of depressions of potentiometric levels and in deterioration in the quality of groundwater through overall salinisation of abstracted water as well as the introduction of potentially toxic chemical elements. A barium anomaly with the maximum Ba^{2+} concentration of 6.37 mg/l was distinguished in the Cambrian-Vendian aquifer system, which is widely used as a drinking water source in north-Estonia. The probable natural sources of the anomaly are the crystalline basement and its weathering zone. Groundwater in the clayey weathering core is hydraulically connected to overlying the Cambrian-Vendian aquifer system, thus the upconing of deeper-seated groundwater, caused by intensive exploitation of wells, is possible (Marandi et al 2004).

6. CONCLUSIONS

Based on the results of investigations carried out in the Cambrian-Vendian aquifer system, the following summary conclusions on the formation of natural chemical composition of Cm-V groundwater can be drawn.

In southern and central Estonia, the Cambrian-Vendian aquifer system contains relict saline groundwater of marine origin with total dissolved solids (TDS) up to 22 g l-1. Chloride and Na predominate over all other ions in this zone.

In northern Estonia the Cambrian- Vendian aquifer system contains palaeo-groundwater, which recharged during the last glaciation. This is fresh water with TDS values mainly below 1.0 g l-1. The baseline chemical composition of the water is formed through the water-rock interaction during the last 10 ka.

In northern Estonia, the most characteristic feature of the Cambrian-Vendian aquifer system is a very light oxygen isotopic composition (δ18O values of c. – 22‰) of groundwater, which provides an ideal tracer for the detection of possible changes in groundwater baseline quality.

The Cambrian-Vendian aquifer system provides high quality drinking water for communities and towns in northern Estonia (including the capital city of Tallinn) but is also important as an industrial water supply. This, in turn, has caused changes in the direction and velocity of the groundwater flow and has led to a 1.5 to 3-fold rise in TDS contents and major ion concentrations in the groundwater.

The main sources of the dissolved load in the Cambrian- Vendian groundwater are leaching from the host rock as well as geochemical processes in the saturated soil zone. Leakage from the underlying crystalline basement, which comprises saline groundwater in its upper weathered and fissured portion and is hydraulically connected to the overlying Cambrian-Vendian aquifer system, is the second important source of ions which results in high TDS values or high content of barium.

At present, a seawater intrusion into the aquifer system is not evident but may occur in future decades, and possible impacts on the quality of groundwater should be considered.

Based on the investigations, the best monitoring compounds to explain possible future changes in groundwater chemistry are electric conductivity (TDS changes), main chemical compound ^{18}O and ^{3}H (upcoming or sea water intrusion), barium (leakage from crystalline basement).

Since the Cambrian-Vendian aquifer system presents a non-renewable resource of fresh palaeowater and, as such, is limited, special regulations are required to ensure sustainable consumption of its water.

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SUMMARY IN ESTONIAN

Põhjavee looduslik keemiline koostis kui põhjavee kasutamise alus Kambriumi-Vendi põhjaveekompleksis Eestis

Käesoleva töö eesmärk oli selgitada Kambriumi-Vendi põhjaveeladestiku loodusliku keemilise koostise kujunemise põhifaktoreid.

Kambriumi-Vendi põhjaveeladestik on Põhja-Eesti linnades ja asulates peamiseks joogiveeallikaks, moodustades kuni 75% kogu piirkonna põhjavee tarbimisest. Tulenevalt suurest põhjavee tarbimisest on Kambriumi-Vendi põhjaveeladestikus moodustunud kaks suurt depressioonilehtrit, mille üks kese on Kirde-Eestis ja teine Tallinnas. Seoses põhjavee tarbimisega ning asjaoluga, et kõrgekvaliteediline Kambriumi-Vendi põhjavesi on praktiliselt taastumatu maavara, on põhjavee otstarbekas kasutamine nimetatud piirkonnas määrava tähtsusega.

Antud töö viidi läbi peamiselt kahe Euroopa Liidu Teaduse ja Tehnoloogilise Arendustegevuse Raamprogrammi (RP) projekti käigus, milles osales ka autor ning mille raames uuriti Kambriumi-Vendi põhjaveelastiku vee keemilist koostist. RP5 projekti Baseline eesmärgiks oli välja selgitada põhjavee looduslik koostis reas Euroopa põhjavee kihtides ning töötada selle abil välja kriteeriumid põhjavee loodusliku koostise kirjeldamiseks. Kambriumi-Vendi põhjaveeladestiku puhul selgitati antud projekti raames välja põhjavee makrokomponentide looduslik sisaldus, põhjavee tüübid ning peamised protsessid, mis on kujundanud ja kujundavad ka tänapäeval Kambriumi-Vendi põhjaveeladestiku põhjavee loodulikku koostist. Tööde tulemusena selgus, et Lõuna- ja Kesk-Eestis levivad Kambriumi-Vendi põhjaveeladestikus reliktsed Cl-Na tüüpi soolased veed soolsusega kuni 22 g/l. Põhja-Eestis levivad Kambriumi-Vendi põhjaveeladestikus viimase jäätumise ajal infiltreerunud jääliustike sulaveed, mille soolsus jääb reeglina alla 1 g/l. Lisaks on Põhja-Eestis veel ka tänapäeval ürgorgude kaudu toituva põhjaveega alad, kus põhjavee soolsus on tavaliselt alla 0,5 g/l. Kesk-Eestis jääb kahe – soolase ja mageda – põhjavee vahele üleminekupiir, kuid seda ei ole andmete puudumise tõttu võimalik täpselt paika panna.

Kambriumi-Vendi põhjavee keemiline koostis on kujunenud pikaajaliste vee ja kivimite vaheliste protsesside mõjul ning tänapäeval võib põhjavee keemilist koostist muuta põhjavee tarbimisest tulenev veevahetuse intensiivsus. Viimane võib tingida muu kvaliteediga põhjavee sissetungi kristalliinsest aluskorrast või merevee sissetungi rannikualadel. Hetkel merevee sissetungi Kambriumi-Vendi põhjaveeladestikku veel täheldatud ei ole, kuid tänu lekkele aluskorrast on mõnedes piirkondades (Kopli ps) tõusnud mineraalsus kuni kolm korda või tekkinud mikroelementide (baarium) kõrgenenud sisalduste anomaalsed alad (Kirde-Eesti).

Eelnenud anomaaliate ning keemilise koostise muutuste põhjuseks on suur põhjavee väljapumpamine ning regionaalsete depressioonilehtrite teke.

RP6 projekti Bridge eesmärk oli projekti Baseline ja teiste samalaadsete projektide tulemusi kasutades töötada välja konkreetsed metoodikad põhjavee loodusliku koostise kirjeldamise kriteeriumide – keskkonnastandardite – arvutamiseks. Uued keskkonnastandardid saavad olema põhjavee säästliku majandamise ning muutuste jälgimise aluseks. Põhjavee kasutamine toob alati kaasa teatud muutusi põhjavee loodulikus koostises ning seetõttu ei saa keskkonnastandardiks olla vaid looduslik koostis. Bridge metoodika järgi põhineb keskkonnastandard peamiselt põhjavee looduslikul koostisel, kuid sellel on lubatud varieeruda teatud piirini, mis on kirjeldatud ökotoksikoloogiliste piiridega. Seega võib põhjavee kvaliteet varieeruda loodusliku koostise ning ökotoksikoloogilise normi vahel olevas alas. Loodavat metoodikat saab siiski kasutada vaid juhul, kui eelnevalt on teada põhjavee looduslik koostis, ning normid on otstarbekas määrata vaid kõige tundlikumatele põhjavee koostise komponentidele, mis inimtegevusele kõige kiiremini reageerivad. Kuna Baseline uuringute käigus selgus, et kõige paremini iseloomustavad põhjavee muutusi põhjavee elektrijuhtivus ja põhikomponendid, siis on otstarbekas kehtestada keskkonnanormid just neile. Juurde lekkiva põhjavee päritolu iseloomustamiseks on parimad komponendid Kambriumi-Vendi põhjaveeladestiku puhul ^{18}O ja ^{3}H isotoobid, mis võimaldavad hinnata nii võimalikku pinna- või merevee sissetungi kui ka leket aluskorrast. Seetõttu on soovitatav kaaluda nende komponentide kasutamist põhjaveeseireprogrammides.

Töö tulemusi on võimalik rakendada Kambriumi-Vendi põhjavee säästva kasutamise ülesehitamiseks, mille tulemusena saavad loodetavasti ka tulevased põlvkonnad kvaliteetset põhjavett joogiveena kasutada.

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PAPERS I–IV

I

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II

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III

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IV

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THE CAMBRIAN-VENDIAN AQUIFER, ESTONIA

Rein Vaikmäe[1], Enn Kaup[1], Andres Marandi[1,2], Valle Raidla[1], Leo Vallner[1]

[1] Institute of Geology at Tallinn University of Technology, Ehitajate tee 5,
19086 Tallinn, Estonia (e-mail: rein.vaikmae@ttu.ee)
[2] University of Tartu, Institute of Geology, Vanemuise 46, 51014 Tartu, Estonia

ABSTRACT

In southern and central Estonia the Cambrian-Vendian aquifer system contains relict saline groundwater of marine origin with TDS up to 22 g/l. Cl^- and Na^+ predominate over all other ions in this zone. In northern Estonia the Cambrian-Vendian aquifer system contains palaeogroundwater, which recharged during the last glaciation. This is fresh water with total dissolved solids mainly below 1.0 g/l. The baseline chemical composition of the water is formed through the water-rock interaction during the last more than 10 ka. Generally, the groundwater is of good quality, but in some areas problems are associated with elevated Fe and Mn contents. Groundwater does not always fulfil the requirements of drinking water standards in respect of Cl^- and Na^+ content. The most characteristic feature of the baseline quality of groundwater of the Cambrian-Vendian aquifer system in Northern Estonia is its lightest known oxygen isotopic composition ($\delta^{18}O$ values of c. –22‰) in Europe. This gives the possibility to use the isotopic composition of groundwater as an ideal tracer of possible changes in groundwater baseline quality.

In northern Estonia the groundwater of the Cambrian-Vendian aquifer system provides high quality drinking water for communities and towns (including the capital city of Tallinn) but its industrial use is also important. The supply is very significant, amounting to 10–13% of the Estonian groundwater consumption. Overexploitation of freshwater groundwater resources in Tallinn and mine dewatering in northeast Estonia have resulted in the development of two basin-wide cones of depression. In turn, it has caused the changes in the direction and velocity of groundwater flow, which has led to 1.5 to 3.0-fold rise in the total dissolved solids content and concentration of major ions in groundwater. The main sources of dissolved load in the Cambrian-Vendian groundwater are the leaching of host rock and various geochemical processes

that occur in the saturated zone. Leakage of saline water from underlying crystalline basement, is the second most important source of mineralisation. Intrusion of seawater with consequent implications for groundwater quality is at present time still not evident but should be considered in coming decades.

BACKGROUND TO UNDERSTANDING OF BASELINE GROUNDWATER QUALITY IN ESTONIA

Introduction

Estonia is a flat country with an area of 45,000 km^2, where plateau-like areas and regions of small hills alternate with lowlands. The average altitude is 50 m and only 10% of the territory has an elevation between 100–250 m above sea level. The Baltic Sea with the Gulf of Finland forms the main drainage basin. The climate is moderately cool and humid. Average annual precipitation ranges from 500–700 mm. The mean surface runoff from Estonia is 270 mm per year (Perens and Vallner 1997).

An essential first step for assessing the natural (baseline) groundwater quality is an understanding of the hydrogeology. To define the source terms the input to the system must be known i.e. the chemistry of infiltrating water, derived mainly from rainfall. To explain the characteristics of groundwater chemistry within the aquifer, information on the geology, mineralogy, geochemistry, flow patterns and timescales are required.

Geological setting

Structure

Estonia is situated in the north-western part of the East-European Platform. Structurally, the main sedimentary basins, situated on the southern slope of the Baltic Shield, plunge southwards, sloping about 3–4 metres per kilometre (Figure 1c). The crystalline Lower-Proterozoic basement is overlain by Upper-Proterozoic (Vendian) and Paleozoic (Cambrian, Ordovician, Silurian and Devonian) sedimentary rocks which are covered by Quaternary deposits (Perens & Vallner 1997).

In northern Estonia, the Vendian, Cambrian and Ordovician rocks are the only sedimentary rocks covering the crystalline basement, which lies approximately 150 m below the surface (Fig.16.1c). The crystalline basement comprises mainly gneisses and biotite gneisses (Koistinen et al. 1996) and its upper part (10–150 m thick) is fractured and weathered. Weathering profiles are predominantly composed of kaolinite, illite, chlorite and montmorillonite, depending on the original bedrock composition and the intensity of weathering.

Stratigraphy

Weathered basement rocks are overlain by water-bearing Vendian and Cambrian silt- and sandstones (with interlayers of clay), which form the Cambrian-Vendian aquifer system. In the east of Estonia, the Vendian sedimentary rocks are divided by a clay layer, the Kotlin Formation, into the Voronka and Gdov aquifers (Figure 1b, c).

The terrigeneous rocks of the Cambrian-Vendian aquifer system occur all over Estonia, except in the Mõniste-Lokno uplift area in southern Estonia. The aquifer system is overlain by clays and siltstones of the Lükati-Lontova aquitard (Figure 1c), which has a strong isolation capacity due to its low conductivity of 10^{-7}–10^{-5} m d^{-1} (Perens and Vallner, 1997). However, in places the aquitard and water-bearing bedrock formation have been penetrated by a relatively dense set of ancient buried valleys filled with loamy till and, in places, glaciofluvial gravel in the lower parts of the valleys (Tavast 1997). These valleys are orientated north-west to south-east, approximately perpendicular to the north Estonian coastline.

Hydrogeology

There is an obvious difference between the cross-sections of the Cambrian-Vendian aquifer system in western Estonia compared to those in the east. In the east, up to 53 m thick clays of the Kotlin Formation divide the aquifer system into two aquifers (Figure 1c). The upper, Voronka aquifer, consists of quartzose sandstone and siltstone with a thickness of up to 45 m in north-eastern Estonia. The hydraulic conductivity of the rocks ranges from 0.6–12.5 m d^{-1} with an average 2.6 m d^{-1}. The transmissivity decreases from 100–150 m^2 d^{-1} in northern Estonia to 50 m^2 d^{-1} (or less) in the south. Under natural conditions, the potentiometric levels along the coast of the Gulf of Finland are about 1.5–5.5 m a.s.l. The lower Gdov aquifer is formed by a complex of mixed sandstone and siltstone up to 68m thick. It directly overlies the Pre-Cambrian basement and is confined by the overlying clay of the Kotlin Formation. In northern Estonia, the hydraulic conductivity of the water-bearing rocks is 0.5–9.2 m d^{-1} with an average of 5–6 m d^{-1}. Transmissivities in north-eastern Estonia are in the range of 300–350 m^2 d^{-1} and decrease in a southerly and westerly direction to 100 m^2 d^{-1} or less. The potentiometric surface in the coastal area is about 3–5 m a.s.l. under natural conditions. West of the line where the Kotlin clays pinch out, the Cambrian and Vendian water bearing rocks form the Lontova-Gdov aquifer. The Cambrian-Vendian aquifer system thins out towards the south and west. In northern Estonia, however, its thickness amounts to 90 m outcropping along the northern coast in the south of the Gulf of Finland. In northern Estonia, the aquifer system is mostly confined by 60–90 m thick clays of the Lontova Formation. However, in places the aquitard is penetrated by ancient buried valleys.

The Cambrian-Vendian aquifer system is underlain by Lower Proterozoic crystalline basement, whose fractures contain a small amount of water but is not exploited. The lower portion of basement serves as an impermeable base layer for all the overlying aquifer systems.

The Cambrian-Vendian aquifer system forms part of the regional flow system that recharges in southern Estonia, in the Haanja and Otepää heights, where groundwater levels are 180–280 m a.s.l. In these locations, the head declines with depth, indicating the existence of downward groundwater flow. On reaching the impermeable portion of the crystalline basement, this flow is directed towards the discharge areas in the depressions of the Baltic Sea and the Gulf of Finland. The length of deeper branches of the regional flow system can reach 250 km.

The Cambrian-Vendian aquifer system north of the recharge area belongs to a slow flow subzone (Vallner 1997). The calculated velocities of deep groundwater movement lie between $5x10^{-4}$ and $5x10^{-3}$ m d^{-1}. This indicates that during the last ~10 ka the deep groundwater could only have progressed several tens of kilometers and complete water exchange along flow branches would not have been possible. Therefore it appears that, under natural conditions, groundwater recharged during the last glaciation has been preserved in the aquifer . This has been confirmed using isotopic tracers (Vaikmäe et al. 2001).

Palaeohydrological conditions during the Late Pleistocene

During the late glacial maximum (LGM) around 18 ka BP (21 calendar ka), the whole Baltic Sea area and northern Poland were covered by the Fennoscandian ice sheet. Different reconstructions of the ice sheet have yielded different results. According to the ice model proposed by Denton and Hughes (1981), the ice thickness over the Baltic States area at that time was about 800–2500 m . A modified ice sheet model by Lambeck (1999) shows that the ice sheet thickness over the area at 18 ka BP was only about 600–800 m. The final ice recession from the south-western Baltic Basin occurred 13.5–13 ka BP and Estonia became ice-free between 13.6–12.5 ka BP (Berglund 1979; Rinterkneht et al. 2006). The rapid deglaciation produced huge volumes of meltwater as well as icebergs. Therefore, practically the whole area in front of the ice margin was covered with vast ice-dammed lakes during the last stages of ice sheet retreat. Starting around the Palivere stage, at about 11 ka BP, these lakes formed the eastern part of the Baltic Ice Lake.

Due to the stadial-oscillatory character of deglaciation, the level of the Baltic Ice Lake changed rapidly several times. At the end of the Younger Dryas cold stage the amelioration of the climate caused rapid retreat of the ice margin, and the Baltic Ice Lake drained catastrophically into the North Sea via the Öresund Strait. Its surface was lowered by 26–28 m within only a few years (Björck 1995). An open sound north of Billingen provided direct connection between the Baltic basin and the North Sea. According to Björck (1995) the final drainage is dated at ca 10.3 ka BP.

In the context of groundwater formation, it is important to note that the main discharge area of the Cambrian-Vendian aquifers into the Gulf of Finland was submerged during all stages of the Baltic Sea in spite of both the several drastic changes in the Baltic Sea level and the high glacio-isostatic uplift rate in northern Estonia during and after the last deglaciation.

In contrast to the coastal areas of north-west Europe and the Mediterranean, where groundwater circulation during the LGM was in many cases activated by evolving shorelines due to sea level lowering, the groundwater recharge and circulation in the Baltic region ceased or was strongly inhibited at this time due to ice cover and/or permafrost.

The results of isotope and geochemical investigations as well as noble gas analyses (Vaikmäe et al. 2001*)* showed that the water in the Cambrian-Vendian aquifer system in northern Estonia was recharged during the last glaciation. It has further been shown that for about 11 ka during the Late Pleistocene, the Scandinavian ice sheet in the outcrop area was underlain by melt-water (Jõeleht 1998). During this time the hydraulic head was controlled by the thickness of the ice. Although the aquifer has relatively high hydraulic conductivity, areas of low hydraulic conductivity surround it and therefore the hydraulic head in the outcrop area of aquifer system was probably close to floating point e.g. about 90% of ice thickness (Piotrowski 1997). Taking into account also the postglacial uplift and the present depth of the Cambrian-Vendian aquifer system (about –100 m below sea level), the hydraulic gradient was around 0.0031 (Jõeleht 1998). Thus, recharge probably occurred during the glaciation, most likely by sub-glacial drainage through the tunnel valleys (Vaikmae et al. 2001).

Hydrochemistry

Earlier studies showed that Na-Ca-Cl-HCO_3 and Ca-Na-Cl-HCO_3 type waters with TDS contents between 0.4–1 g l^{-1} dominate the Cambrian-Vendian aquifer system in northern Estonia. In north-eastern, south-western and south-eastern Estonia, as well as on the islands of Saaremaa and Ruhnu, Na-Cl, Na-Ca-Cl and Ca-Na-Cl type waters with TDS contents from 2–22 g l^{-1} are widespread (Karise 1997). The aquifer has predominantly reducing conditions occur (Vallner 1997) and is usually rich in trace elements with concentrations increasing towards the east. East of Tallinn, for example, concentrations of iodide reach values between 120–280 mg l^{-1}. In some wells in north eastern Estonia, the concentrations of cadmium (Cd), lead (Pb) and lithium (Li) are slightly in excess of the EU drinking water standards. However, the concentrations of trace elements are highest at Värska in south-eastern Estonia, where cadmium (Cd), lithium (Li), manganese (Mn) and lead (Pb) concentrations exceed the EU regulations for drinking water. In several regions of Estonia, high concentrations of bromide (Br) have been detected in the Cambrian-Vendian aquifer system, for example, values of 13 mg l^{-1} Br were observed in Kuressaare at depths between 540–555 m whilst concentrations in Värska ranged between 16–17 mg l^{-1} at 520–535 m and 51–56 mg l^{-1} at 540–600 m (Karise 1997).

The oxygen isotope compositions in the groundwater of most aquifer systems in Estonia range from –11.0 to –12.2‰ (Vaikmäe and Vallner 1989). However, groundwater in the Cambrian-Vendian aquifer system shows a heavily depleted oxygen isotope composition, with $\delta^{18}O$ values varying mainly from –18 to –22‰ (Vaikmäe et al. 2001).

In contrast, long term mean annual $\delta^{18}O$ value in contemporary precipitation in Estonia is –10.4‰ (Punning et al. 1987). Low (highly negative) $\delta^{18}O$ values in the Cambrian-Vendian aquifer are indicative of recharge in cold conditions, whilst low ^{14}C concentrations are indicative of long residence time of groundwater (Figure.2.). Low ^{3}H concentrations (< 2 TU) in most of the studied well waters confirm that no detectable intrusion of modern water (including sea water) into the Cambrian-Vendian aquifer has occurred during the past ~45 years (Vaikmäe et al. 2001).

Data for the Cambrian-Vendian aquifer and interpretation

Historical and recent data on water quality

Extensive data collected during the last 55 years exists in the Geological Survey of Estonia (GSE), contains more than 1500 analyses from 967 wells for the Cambrian-Vendian aquifer system. The database contains information on the main components : TDS, Na^{+}, K^{+}, Na+K, NH_4^{+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Fe_{tot}, Cl^{-}, SO_4^{2-}, NO_2^{-}, NO_3^{-}, CO_3^{2-}, HCO_3^{-}, pH, SiO_2, hardness (Perens et al. 2001). Data are also available from a number of published and unpublished (mainly various reports of the Geological Survey of Estonia) investigations. The aquifer has been studied at various times over the past decades (Mokrik and Vaikmäe 1988; Mokrik 1997; Perens and Vallner 1997; Groundwater State 1998; Vaikmäe et al. 2001). The results of these studies provide extensive information on the hydrogeology, geochemistry and lithology of the aquifer system. All these results were critically analysed for this study.

During 2001–2003 new samples were collected from representative sites of the Cambrian-Vendian aquifer system in order to assess the major groundwater chemistry as well as the trace elements. The samples were analysed for a wide range of inorganic species, and field measurements including Eh, DO, pH, temperature and SEC, which are used to assist interpretation. All samples were filtered in the field and acidified with nitric acid (1% v/v) in order to stabilise the trace elements in solution.

Data handling

The two databases containing the historical and the new data were compared in order to evaluate the suitability of the historical database in the context of a baseline study. Where concentrations were below the detection limit of the method, half the value of the detection limit was used for the statistical data analysis and interpretation. Since the historical database goes back to the 1950`s, the quality of the database had to be proved, using one of the following approaches: (1) check and evaluate the extreme values of different species by comparing the dry solid residue contents measured in the laboratory; (2) where the total dissolved solids were calculated (rather than measured), the cation-anion balance was used to assess the quality of sample. Where samples contained only a few measured major ions with extreme values, it was decided that, without knowledge of the background concentrations, it was better to omit these values from further calculations.

For data processing, interpretation and hydrogeochemical assessment of the results, MapInfo Professional 6.0 and AquaChem 3.7 were used. The summary statistics (maxima, minima, median and standard deviation values) showed that the ranges of major ion concentrations in the Cambrian-Vendian aquifer system for the samples from the historical GSE database and the new samples compare relatively well. The cumulative frequency plots were derived from those data showing the concentration ranges for selected elements/species (Figure 3). The median (50%) values and the 97.7th percentiles are used as reference values. These values are useful for comparison between different areas as well as for regulatory purposes. For the majority of elements, the range of distributions represents the geological and geochemical controls on the groundwater compositions whereby the slope and the shape of the plots are indicative of the different hydrogeochemical processes.

The cumulative frequency plots (Figure 3) show that HCO_3, Ca and Mg concentrations vary within a small range and only about 10% of the data have values greater or smaller than the median. In the case of Na and Cl, about 20% of the samples have values greater or smaller than the median, but there are only a few samples with extremely high values. This is probably due to the small number of wells in the Cambrian-Vendian aquifer in South Estonia.

Geochemical controls and regional characteristics

Major element controls

The chemical type of groundwater in the Cambrian-Vendian aquifer system is determined by Na, Ca, Cl and HCO_3, with Na and Cl the most abundant ions in the water. Magnesium is present at relatively low concentrations (3.2–36.0 mg l^{-1}) and the SO_4 concentration is mostly below the detection limit. The highest SO_4 concentrations are usually detected in wells located close to buried valleys, where groundwater freshening has contributed to the development of oxidising conditions.

The main source of dissolved solutes is leaching of the host rock as well as geochemical processes in the saturated zone. The underlying crystalline basement comprises saline groundwater in its upper weathered and fissured part and is hydraulically connected with the overlying Cambrian-Vendian aquifer system, forming a second important source of ions. The fractured basement and its clayey weathering crust contain Ca-Cl type groundwater, which is characterised by high TDS values (2–20 g l^{-1}). Intensive water abstraction in northern Estonia accelerates the groundwater exchange and also increases the area influenced by pumping. Chemical and isotopic groundwater studies indicate an increasing contribution of the leakage from the crystalline basement to the groundwater chemistry (Karro et al. 2004).

Downgradient evolution

The chemical evolution of groundwater in aquifers along flow paths depends on the age distribution with depth and distance, on geological conditions and the lithological composition of the water-bearing rocks and sediments. However, considering the very low velocity of groundwater in the Cambrian-Vendian aquifer system and taking into account both the palaeohydrological situation during the Late Pleistocene as well as the contemporary situation in northern Estonia, where the groundwater geochemistry is influenced by intensive abstraction, the overall picture of the aquifer system is rather complicated and not yet well understood.

It is practically impossible to follow the evolution of the groundwater chemistry all the way back to the recharge area in Southern Estonia, because there are only three wells drilled in the aquifer in southern and central Estonia. Groundwater with high TDS values is pumped and used as a mineral water at two to three localities. In northern Estonia, however, the freshwater of the Cambrian-Vendian aquifer system provides the main source of public water supply and the evolution of groundwater chemistry can by followed through many wells drilled within a distance of about 50 km south of the coastline. As a result of intensive groundwater abstraction, two extensive depression cones have formed in this area with centres around the capital city Tallinn and around the Kohtla-Järve mining industry region in northeast Estonia (Vallner 2003). The natural baseline characteristics of the aquifer can be further explained using a Piper diagram (Figure 4).

Four major groundwater types can be distinguished in the diagram based on their chemical composition:

1) Na-Cl type, can be interpreted as a “saline baseline” or relict formation groundwater of the Cambrian-Vendian aquifer system. It may be very old and probably formed long before the last ice age. TDS concentrations in waters of this type are higher that 2 g l^{-1}, and they are considered as mineral waters. In

Värska (south-east Estonia), TDS concentrations in the groundwater of the deeper part of the aquifer system reach concentrations up to 18 g l^{-1}. The $\delta^{18}O$ values of this groundwater type are around $-14^{o}/_{oo}$. Relict groundwater of Na-Cl type is widely distributed in the Cambrian-Vendian aquifer system in southern and central Estonia but also in the Voronka aquifer in north-east Estonia at Narva-Jõesuu. It is also characterized by a very high Cl^{-} content, ranging from 1083 mg l^{-1} in wells at Narva-Jõesuu up to 10919 mg l^{-1} at Värska. The Na^{+} concentrations in these wells are 684 mg l^{-1} and 5222 mg l^{-1}, respectively. These characteristic features of the Na-Cl type groundwater are also well reflected in the cumulative probability plots (Figure 3).

2) Ca-Na-HCO_3-Cl or Ca-Na-Cl-HCO_3 water. This is the "fresh baseline" water of glacial origin, recharged during the last glaciation (Vaikmäe et al. 2001). The chemical composition has been formed through water-rock interaction during the last 10 ka or more. This water type has the largest spatial distribution, spreading from the north coast to central Estonia, and also shows mixing with other water types (except with type 1) on the Piper diagram. The TDS concentrations vary from 300 mg l^{-1} to several g l^{-1}. Because of the lack of sampling wells in central Estonia, the exact border between the "saline baseline" waters and "fresh baseline" waters cannot be defined. The relative proportions of HCO_3^{-} and Cl^{-} define the different chemical water types. Thus, some waters are classified as different water types even though the actual differences in their chemical concentrations are small. In the probability plots, this group is represented by low variations in HCO_3^{-}, Ca^{2+} and Mg^{2+} concentrations and continuously increasing Cl^{-} and Na^{+} concentrations (Figure 3).

However, the most characteristic feature of this groundwater type is its strongly depleted stable isotope composition. The $\delta^{18}O$ values range between –19‰ and –22‰, indicating the formation of the water under cold climatic conditions (Figure 5).

3) Na-Cl-HCO_3 groundwater type is interpreted as a mixture of glacial melt water with some relict saline groundwater. This groundwater type is distributed predominately in north-eastern Estonia, where the Kotlin clays divide the Cambrian-Vendian aquifer system into two aquifers and where the overlying clays reach their maximum thickness (Figure 1). Therefore, intrusion of fresh melt-water into the aquifer during the last glaciation was probably lower in this area compared to the western part of north Estonia. However, freshening of the original, relict groundwater, by glacial melt water is still evident from the $\delta^{18}O$ values of this water type, which range between –19‰ and –22‰. Moreover, the TDS values are lower (~1 g l^{-1}) compared to those of the relict saline water (Figure 5).

4) Ca-HCO_3 type groundwater is found in northern Estonia, in areas around the ancient buried valleys, where intrusion of fresh groundwater from overlying aquifers and/or rainwater occurs. The intensity of such fresh water intrusion varies spatially and temporally, depending on the extent of groundwater exploitation near the valleys. The intensive groundwater abstraction in the late 1970`s, for example, caused extensive cones of depression to develop around Tallinn and Kohtla-Järve (Vallner 2003). In these areas, the groundwater drawdown of 25m and 35m, respectively, resulted in intensive freshwater intrusion into the aquifer through the buried valleys and caused the groundwater chemistry and its isotopic composition to change (Figure 5.). In the cumulative probability plots, this water type is represented by Ca^{2+}, Mg^{2+} and HCO_3^- values above average and by Na^+ and Cl^- values lower than average (Figure 3.). Due to the freshwater intrusion, the $\delta^{18}O$ values of this water type have been changed from values around –20‰ in early 80's towards more positive values and today are around –15‰. (Figure 5). In parallel the TDS concentrations have also diminished and today are between 200 and 500 mg l^{-1}.

The age of water in the Cambrian-Vendian aquifer

The aquifer system in southern and central Estonia contains relict groundwater with TDS concentrations up to 22 g l^{-1}. There are problems in determining the age of this groundwater, and age estimations have to rely on the data obtained from a groundwater flow model. The model shows that the lateral water movement in this area is directed predominantly towards the north at a velocity of 0.5–1 m a^{-1} (Vallner 2003). This indicates that the groundwater in this part of the aquifer may be very old, probably in excess than 100 ka.

The situation is much different in the northern part of the Cambrian-Vendian aquifer. Consideration of the data collected during the present study together with results from earlier studies lead to the convincing conclusion that the isotopically depleted groundwater in northern Estonia is of glacial origin (Vaikmäe et al. 2001). Results from radiocarbon dating and from noble gas analyses point toward the Fennoscandian ice sheet as a probable source for the groundwater in Estonia. This water is heavily depleted in ^{18}O. This ties in well with the palaeoclimatic and palaeoenvironmental situation in the study area during the late Weichselian glaciation. However, so far there is no convincing answer to the question of how and when the meltwater of the ice sheet reached the aquifer system. Earlier studies have indicated that meltwater recharge into the Cambrian-Vendian aquifer system occurred at about 11–12 ka BP, after the retreat of the continental ice from Estonia and during the formation of the Baltic Ice Lake (Yezhova et al. 1996*)*. However, the low ^{14}C concentrations (< 5pmc) suggests an age of the water of about 15–30 ka BP, which in turn implies that the meltwater intrusion took place much earlier, whilst Estonia was still covered by ice.

In contrast, Mokrik (1997) suggests that the freshwater in the Cambrian-Vendian aquifer complex in the north of Estonia was formed by cryogenic metamorphism. He proposes that during the Pleistocene glaciation the aquifers went through several freezing-refreezing cycles down to depths of 50–200 m, which led to the freshening of the originally highly mineralized groundwater in the Cambrian-Vendian aquifer complex. This would imply that a permafrost zone had developed on the surface of the Baltic Shield about 50–100 km from the outcrop of the aquifer (Mokrik 1997). However, the existence of a thick permafrost layer under the Fennoscandian ice sheet in the region around Estonia seems unrealistic. According to Kleman and Borgström (1994), frozen conditions only existed in the central area of the Fennoscandian ice sheet, whilst most of sub-glacial areas reached melting temperatures due to frictional strain and geothermal heating. Thus, recharge of the aquifers by sub-glacial meltwater seems to be a more realistic explanation for the formation of isotopically light freshwater in the Estonian aquifers and this interpretation also agrees with the recent work of Boulton et al. (1995,1996) and Piotrowski (1994, 1997). During the Late Weichselian, the base of the ice sheet in the Cambrian-Vendian outcrop area in Estonia was probably in a liquid state for about 11 ka (Jõeleht 1998) and the hydraulic head was controlled by the thickness of ice. Whilst the aquifer system has high hydraulic conductivity, areas of low hydraulic conductivity surround it and, therefore, the hydraulic head in the outcrop area of the aquifer system was probably close to floating point e.g. about 90% of ice thickness (Piotrowski, 1997). Taking into account the postglacial uplift as well as the present depth of the Cambrian-Vendian aquifer system of about 100 m bsl, it appears that the hydraulic gradient was around 0.0031 (Jõeleht 1998). Thus, groundwater recharge to the aquifer probably occurred during the glaciation, presumably by sub-glacial recharge through the tunnel valleys.

Trends in water quality and changes with depth

Water quality parameters were investigated in northern Estonia (Karro and Marandi 2003; Karro et al. 2004; Marandi et al. 2004) where the Cambrian-Vendian aquifer system is major source of public water supply. In general, lateral changes in chemical composition and groundwater type are significantly larger than those in the vertical direction. In the Gdov aquifer (the deeper part of the aquifer system), the concentrations of Ca and HCO_3 in the groundwater decrease eastwards where Na and Cl ions dominate (Marandi et al. 2004). A similar trend was observed in the overlying Voronka aquifer (the upper part of the aquifer system). The content of Na and Cl varies from 26–405 mg l^{-1} and 46–700 mg l^{-1}, respectively, exhibiting the highest values in the eastern part of the country. The concentrations of Ca (6–188 mg l^{-1}) and HCO_3 (103–264 mg l^{-1}) show highest concentrations in the western part of the study area. The highest SO_4 concentrations were measured along the western margin of the area with concentrations between 19 and 22 mg l^{-1}. The TDS content in the analysed groundwater samples ranged from 0.1 to 1.5 g l^{-1} (Marandi et al. 2004).

Generally, the groundwater is of good quality in accordance with the limits set by the Estonian Drinking Water Standards (2001). However, in some areas, problems associated with elevated Fe and Mn concentrations occur. Highest Fe concentrations reach concentrations up to 6–7 mg l^{-1}, exceeding the drinking water limits by factor of 5–30 Groundwater does not always fulfil the requirements of drinking water standard also in respect of Cl and Na contents (Marandi et al. 2004).

Barium is the only toxic element that occurs in concentrations much higher than those permitted in water abstracted for drinking purposes. The modelling results of Marandi et al. (2004) showed that SO_4 and HCO_3 are the main anions that may control Ba precipitation, although HCO_3 has practically no influence when Ba concentrations are low (<10 mg l^{-1}). Increasing concentrations of Cl, in contrast, contribute to an increased solubility of Ba. The results also show that in the case of low SO_4 concentrations (<3 mg l^{-1}), the Ba content in the Cambrian-Vendian aquifer system can be higher than limit value of 2 mg l^{-1} set for drinking water.

The most serious consequence of intensive groundwater use in north Estonia is the formation of regional cones of depression around the capital Tallinn and Kohtla-Järve (North-East Estonian industrial area). A basin-wide model simulation showed that over-exploitation has caused the changes in the direction and velocity of groundwater flow (Vallner 2003). As a result, lateral and vertically rising groundwater flows support the transport of connate brackish water from the deeper parts of the aquifer system and from the underlying crystalline basement to the groundwater intakes and also promotes seawater intrusion (Yezhova et al. 1996; Mokrik 1997; Vallner 1999; Savitski, 2001).

A case study was conducted on the Kopli peninsula in Tallinn in order to assess the possible causes for the increase in TDS (Karro et al. 2004). Groundwater production wells trapping the Cambrian-Vendian aquifer system on the Kopli Peninsula are situated close to the sea. The production wells in the pumping stations have depths between 40 and 107 m and drilled, more or less, through the full thickness of the aquifer system. For comparison, a groundwater monitoring well penetrating into the fractured basement, and two wells opening Lontova aquitard were included in the study.

Groundwater abstraction varied between years, ranging from 10–1300 m^3 d^{-1} during 1978–2002 and in 1992 resulted in a drop of the potentiometric surface by 17 m. At about the same time, groundwater extraction decreased due to declining industrial and agricultural production on the one hand and more sustainable groundwater use on the other. As a direct result, the potentiometric surface level of the aquifer system has steadily risen during the last 10 years and is now at –4.0 m.a.s.l (Savitski 2001).

Fresh groundwaters of Na-Ca-HCO_3-Cl type are characteristic of the upper part of the Cambrian-Vendian aquifer complex in the Tallinn region (Perens et al. 2001). In the deeper part of the aquifer and in the crust of the weathered crystalline basement, groundwaters of Na-Ca-Cl-HCO_3 and Ca-Na-Cl type and with TDS content of 1.4–5.0 g l^{-1} are common. In the upper part (–50 m.a.s.l.) of the aquifer system, the groundwater has chloride concentrations of 100 mg l^{-1}, which increase with depth to 350 and 2500 mg l^{-1} at 100 and 130 m, respectively (Savitski 2001; Boldõreva et al. 2002).

The large-scale variations in TDS (0.49–4.6 g l^{-1}) and major element concentrations in the water of production wells are evident from data collected during 1978–2002 (Table 1). The maximum concentrations presented in Table 1 describe the water chemistry during 1994–96, which clearly exceeded the permissible concentrations in major components as set by the Estonian Drinking Water Standard (2001) and by the Drinking Water Directive of the EU (Directive, 1998). During subsequent years the TDS content of the groundwater decreased slightly. The most distinct temporal changes in water chemistry occurred in well 613 (Figure 6), where the TDS reached concentrations of up to 1.5 g l^{-1} increasing by a rate of 50 mg l^{-1} per year. In the other wells of the Kopli peninsula, a less dramatic increase in TDS was observed.

Since major ions constitute the bulk of the mineral matter contributing to the TDS, most major elements (Na, K, Ca, Mg, SO_4, Cl) display the same trends as TDS (Table 1) with the exception of HCO_3. In comparison to other major ions, HCO_3 shows the smallest concentration range, and these relatively stable HCO_3 concentrations explain why, at high TDS values, bicarbonate remains insignificant in determining the groundwater chemical type. When TDS exceeds 0.9 g l^{-1}, Cl type waters dominate.

The Cambrian-Vendian aquifer system at Kopli peninsula is confined by the Lontova aquitard ($k=10^{-7}$ to 10^{-5} m d^{-1}), which protects the aquifer from infiltrating modern water. Thus, human impacts are unlikely to have any effect on the groundwater chemistry.

Considering the hydrogeological situation in the study area, there are three major processes which can be responsible for the increase in TDS values: (1) intrusion of present–day seawater, (2) pumping-induced upwards migration of deeper saline water from areas below the freshwater and (3) a combination of these two processes.

Characteristic ion ratios and scatter diagrams for the most significant chemical components (Figure 7) were used to explore the importance of individual components.

One of the main indicators of seawater intrusion into drilled wells is usually the increase in the conservative elements, especially Cl in the groundwater. However, within the Cambrian-Vendian aquifer system, the use of the Na/Cl ratio to identify modern seawater intrusion is somewhat limited as the original relict groundwater at least in southern and central Estonia has may have a marine origin with a corresponding Na/Cl ratio. Therefore, even in the fresh groundwater of glacial origin northern Estonia the Na/Cl ratio is very close to that of seawater.

The concomitatnt increase of Na and Cl in wells in the Kopli peninsula is quite clear (Table 1). However, the Na/Cl plot shows that the groundwater in the Kopli peninsula water works is depleted in Na relative to seawater (Figure 7a) and that the values fall below the seawater dilution line (SDL). In well 615, the depletion of Na relative to seawater becomes more evident at higher Cl concentrations. The distribution of data below the SDL suggest mixing more saline water with dilute water.

Magnesium concentrations in Kopli lie approximately on the SDL when plotted against Cl, with small deviations to either side (Figure 7b). This indicates that Mg may have a marine component, modified to some extent (mainly at lower Cl values) by dissolution/weathering reactions. Calcium and K are enriched in the groundwater relative to seawater. K concentrations are fairly independent of Cl concentrations as shown in Figure 7c, while Ca exhibits a clear increase at high Cl values (Figure 7d).

Karro et al. (2004) showed that leaching from the host rock and element release resulting from geochemical processes in the saturated zone provide the major sources of dissolved load in the Cambrian-Vendian groundwater of the Kopli peninsula. A second important source of elements is the underlying crystalline basement, which is hydraulically connected with the overlying Cambrian-Vendian aquifer system and its upper weathered and fractured zone, contains saline groundwater. The fractured basement and its clayey weathering crust also host the Ca-Cl type groundwater, which is characterised by high TDS value (2–20 g l^{-1}). Intensive water abstraction in northern Estonia has accelerated the leakage from the crystalline basement as is seen in the results from chemical and isotopic groundwater studies (Karro et al. 2003; Vaikmäe et al. 2001).

Due to its glacial origin, the groundwater in the Cambrian-Vendian aquifer system in northern Estonia has a unique isotopic composition. Thus, the $\delta^{18}O$ values of the groundwater, as well as as the ^{14}C and ^{3}H signature provide the most sensitive indicators of modern seawater intrusion into aquifer system. The, $\delta^{18}O$ values in the palaeogroundwaters vary between –19‰ to –22‰, while ^{14}C concentrations are lower than 5pmc and ^{3}H concentrations lie typically below the detection limit (< 1TU) (Vaikmäe et al. 2001). According to Punning et al. (1991) the annual mean $\delta^{18}O$ value of water in the Gulf of Finland is about –7‰, the ^{14}C concentrations in Baltic Sea are close to 100 pmc and ^{3}H concentrations range between 5–10 TU.

In 2001, groundwater samples from six wells of the Kopli peninsula were analysed for their isotopic composition, and a set of selected $\delta^{18}O$ and ^{14}C values as well as Br/Cl ratios are presented in Table 2 and in Figure 2.

The $\delta^{18}O$ and ^{14}C values are typical for Cambrian-Vendian groundwater in northern Estonia, indicating the glacial origin of the water. Based on these results, it appears that intrusion of modern water (including seawater) into the aquifer as a consequence of heavy pumping has not occurred. This conclusion is also confirmed by the absence of ^{3}H in sampled wells in the costal areas of northern Estonia (Vaikmäe et al. 2001). The Br/Cl ratios (Table 2) are almost double those in sea water (0.0035) and suggest that older formation water (without traces of Cl from modern sea water) is present.

Summary

The groundwater in the Cambrian-Vendian aquifer system is generally not affected by present-day infiltration and the main controls on the baseline chemistry are the geochemistry of the bedrock sediment and processes of water-rock interaction. However, in places, the Lontova aquitard and water-bearing bedrock formation have been eroded forming a set of ancient buried valleys, filled mostly with loamy tills, although glaciofluvial gravels also occur in the lower parts of the valleys. Where groundwater is intensively abstracted, these erosional valleys can provide the Cambrian-Vendian aquifer system with recharge of fresh meteoric water.

The aquifer can be divided in two main zones, which contain groundwater of totally different origin and contrasting baseline chemical composition. In southern and central Estonia, the aquifer system contains relict saline groundwater of marine origin with TDS values up to 22 g l^{-1}. The dominating solutes in this zone are Cl and Na and the age of the groundwater probably exceeds 100 ka.

In northern Estonia, the aquifer system contains palaeogroundwater, which was recharged during the last glaciation, more than 10 ka ago, by sub-glacial drainage through the aquifers. The groundwater in this area is fresh with TDS mainly below 1.0 g l^{-1} with baseline chemical composition resulting from water-rock interaction during about the last 10 ka. Generally, the groundwater quality is good, although problems associated with elevated Fe and Mn concentrations are reported in some areas. However, the most characteristic feature of the baseline chemistry in northern Estonia is the oxygen isotopic composition of the groundwater, with the $\delta^{18}O$ values around c. –22‰ being the lightest signature reported anywhere in Europe. For comparison the long-term mean annual $\delta^{18}O$ values in contemporary meteoric water in Estonia are –10.4‰. Thus, the isotopic composition of the groundwater provides an ideal tracer for possible changes in the groundwater baseline quality.

The principal economic role of the Cambrian-Vendian groundwater in northern Estonia is the provision of high quality drinking water for communities and towns (including the capital city of Tallinn) as well as to supply water for industrial use. The supply is very significant, amounting to 10–13% of Estonian groundwater consumption. Anthropogenic impacts on the aquifer are mainly related to over-exploitation of freshwater resources in northern Estonia and mine dewatering in northeast Estonia and have resulted in the development of two basin-wide cones of depression, around Tallinn and Kohtla-Järve areas. This, in turn, has caused changes in the direction and velocity of groundwater flow and resulted in an increase in TDS and major ion concentrations in the groundwater. Where production wells are situated near the sea, lateral seawater intrusion into the groundwater intakes may occur. The long-term monitoring of the Cambrian-Vendian aquifer system, utilised for industrial water supply at the Kopli Peninsula in Tallinn, showed remarkable changes in the chemical composition of groundwater. The 1.5- to 3-fold increase in TDS and major element concentrations in the abstracted groundwater is probably a consequence of heavy pumping. The main sources of TDS in the Cambrian-Vendian groundwater are leaching from the host rock and release by different geochemical processes in the saturated zone. The second important source of ions is the underlying crystalline basement, which comprises saline groundwater in its upper weathered and fractured zone and is hydraulically connected with the overlying Cambrian-Vendian aquifer system. The fractured basement and its clayey weathering crust host Ca-Cl type groundwater, which is characterised by high TDS values (2–20 g l^{-1}). Intensive water abstraction accelerated the groundwater exchange and also increased the area influenced by pumping, resulting in an increasing contribution from up-coning from the underlying crystalline basement, observed by chemical and isotopic studies of the groundwater. At present, there is no evidence for seawater intrusion into the aquifer system but it may occur in coming decades.

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Tables

Table 1. Statistical summary (range and mean values) of concentrations (mg l) of major chemical compounds and TDS in studied wells, Kopli Peninsula. Analyses from 1978 to 2002 (Karro et al. 2004).

Well no	TDS	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
598	707–	91.0–	8.9–	94.6–	22.6–	302.8–	2.0–	146.4–
	1120	142.9	15.0	117.8	28.1	413.0	17.7	176.9
	804	114.0	10.7	110.4	25.6	364.1	3.7	158.6
613	624–	96.8–	5.4–	99.0–	21.7–	259.9–	2.0–	146.4–
	1545	241.7	13.3	184.4	47.6	707.6	55.6	238.0
	1010	160.6	10.0	138.5	31.7	481.6	21.8	170.8
614	724–	89.6–	7.0–	102.8–	23.7–	330.1–	0.0–	121.9–
	1100	172.2	20.0	149.2	33.0	546.7	19.4	189.2
	832	115.2	10.8	119.6	27.8	387.6	0.0	152.5
615	488–	68.6–	7.8–	71.9–	19.2–	196.1–	0.0–	61.0–
	1170	222.2	15.0	127.3	40.1	546.7	56.4	189.2
	820	122.5	9.8	101.2	28.6	358.4	24.7	167.8
798	3616–	400.0–	16.0–	676.8–	80.4–	2109.5–	0.0–	6.1–18.3
	4587	525.0	22.5	836.7	114.4	2552.6	3.7	
	4347	469.6	20.5	805.1	104.2	2439.7	2.0	12.2

Table 2. Selected isotopic and chemical parameters in studied wells at Kopli peninsula, Tallinn.

Well no	$\delta^{18}O$ (‰)	^{14}C (pmc)	Br^- (mg/L)	Cl^- (mg/L)	Br^-/Cl^-
599	–20,4	2,5	0.63	99	0,0064
600	–19,8	5,7	2.15	494	0,0044
598	–21,5	3,4	3.62	403	0,0090
613	–21,5	3,0	3.84	481	0,0080
615	–21,6	2,8	3.18	521	0,0061
614	–21,5	5,4	3.96	409	0,0097

Figures

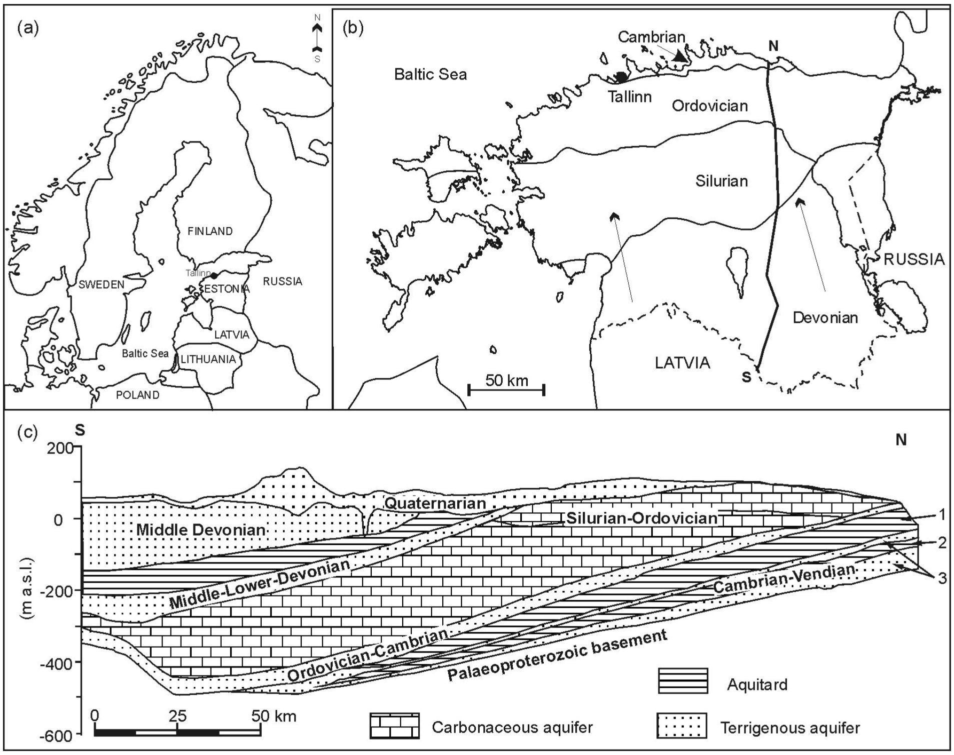

Figure 1 (a) Schematic map showing the location of Estonia; (b) hydrogeological map of Estonia with the position of the line of cross-section; arrows indicate the direction of groundwater flow and (c) the North-South cross-section of major hydrogeological units of Estonia (1–Lontova and 2–Kotlin clays; 3–Voronka (upper) and Gdov (lower) aquifers, confining the Cambrian-Vendian aquifer system).

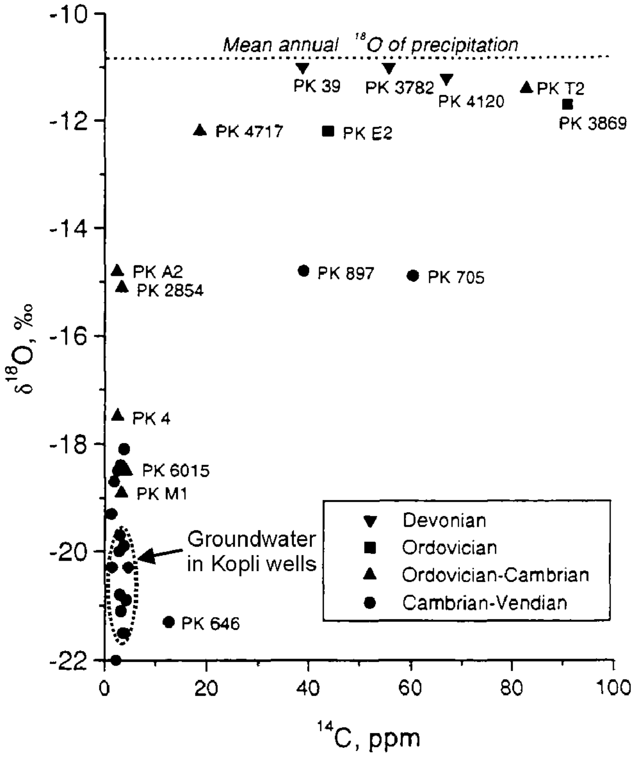

Figure 2. Distribution of $\delta^{18}O$ values of groundwater from different aquifers in Estonia according to their ^{14}C concentrations. $\delta^{18}O$ values from two wells (PK 705 and PK 897) indicate the mixing with infiltrated modern water.

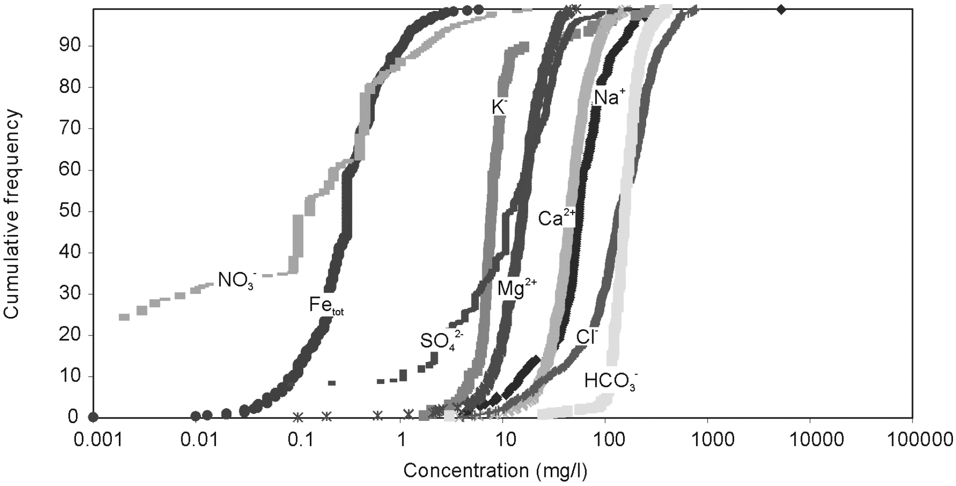

Figure 3. Cumulative frequency diagrams of major ions in the Cambrian-Vendian aquifer.

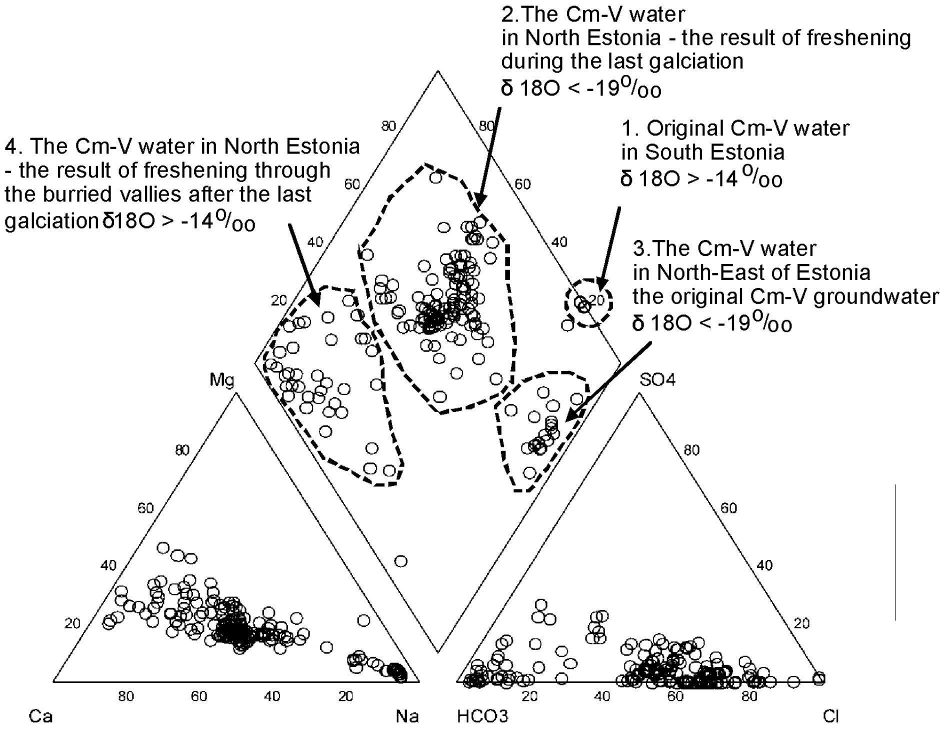

Figure 4. The Piper diagram reflecting major chemical types of Cambrian-Vendian groundwater.

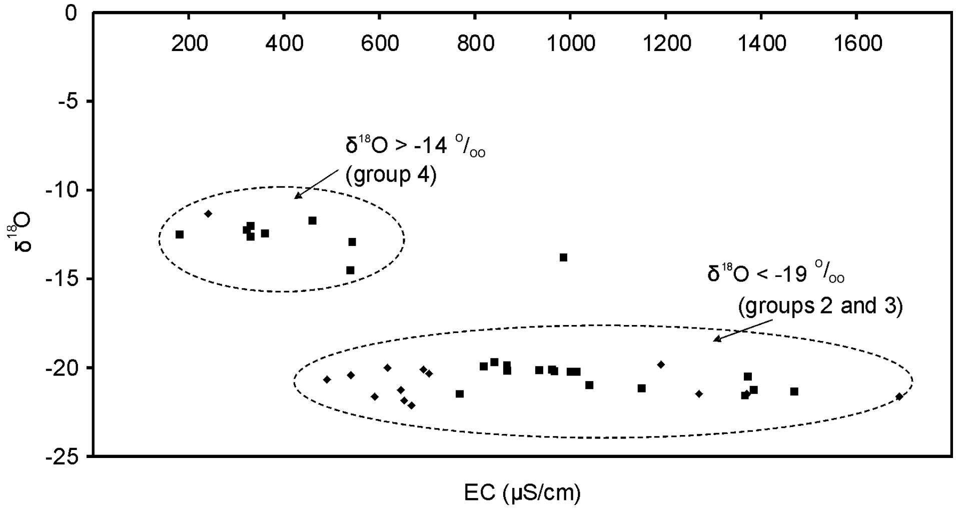

Figure 5. $\delta^{18}O$ versus EC values in the Cambrian-Vendian groundwater.

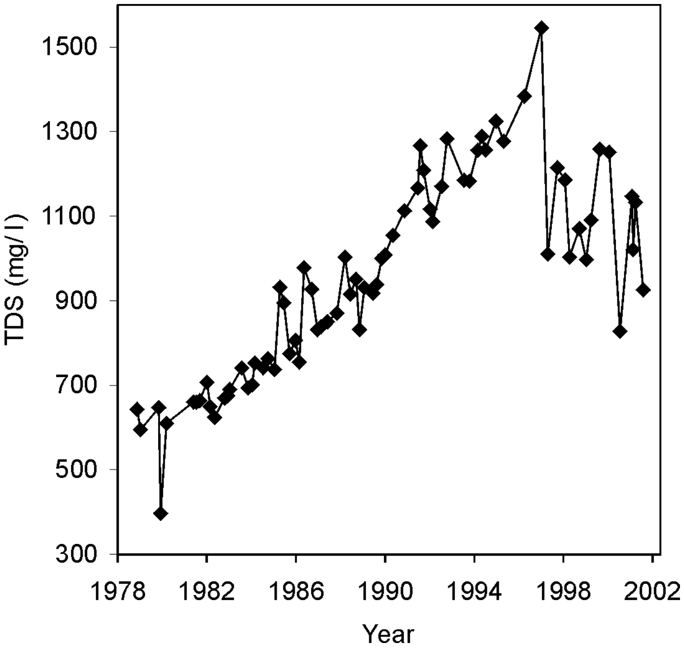

Figure 6. Temporal changes of TDS in groundwater in the Cambrian-Vendian aquifer on Kopli peninsula, Tallinn (abstraction well no 613).

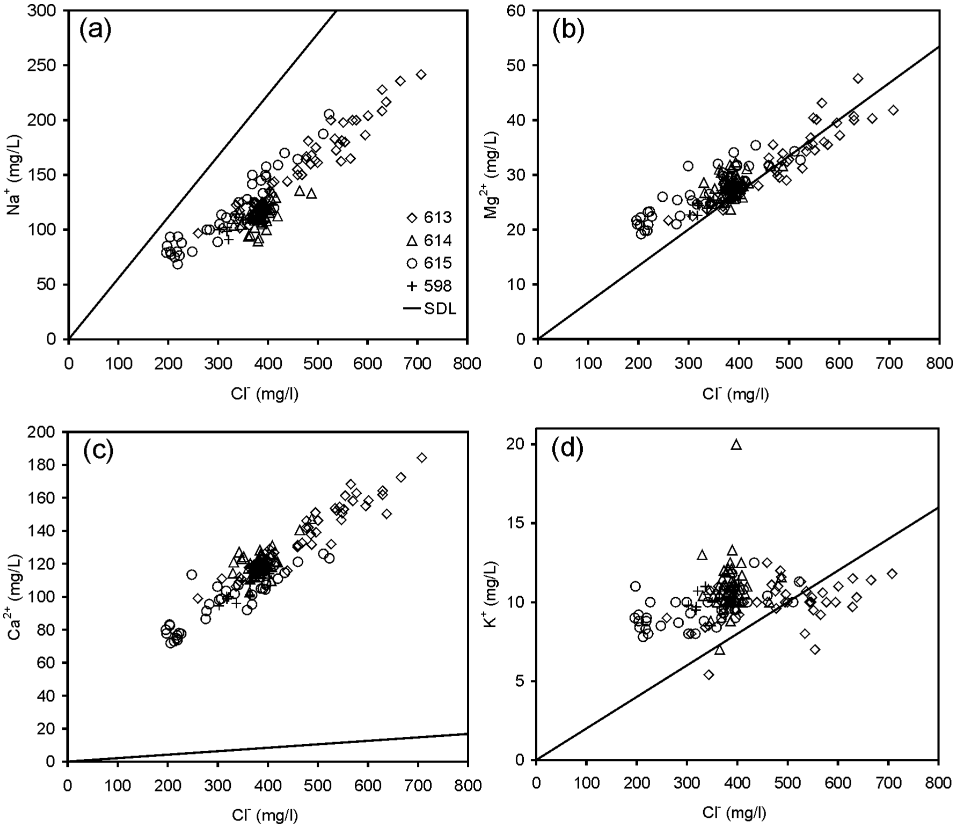

Figure 7. The concentrations of various ions plotted against chloride concentration; SDL – seawater dilution line (Karro et al. 2004).

CURRICULUM VITAE

I General Data

1. **Name:** Andres Marandi
2. **Date and place of birth:** 16.05.1973, Viljandi, Estonia
3. **Nationality:** Estonian
4. **Marital status:** married
   Wife: Triin Marandi
   Son: Mark Marandi (07.03.1993)
   Daughter: Mona Marandi (04.04.1999)
5. **Address:** Nooruse 60, 50411 Tartu, Estonia, **GSM:** ++37 250 58116, **e-mail:** andres.marandi@ut.ee
6. **Present employment:** researcher at Instiute of Geology in Tartu University and researcher at Institute of Geology at Tallinn Technical University
7. **Education:**
   19.06.1995 – BSc of Tartu University on geology,
   18.01.1999 – MSc of Tartu University on Applied Geology (Formation of chemical composition of phreatic groundwater under conditions of military pollution in the Pakri Peninsula)
8. **Language competencies:** Estonian, English, Russian and German
9. **Professional career:**
   From 1995 to 1999 engineer at Institute of Geology at Tallinn Technical University
   From 1998 to 1999 engineer at Institute of Geology at Tartu University
   From 1999 PhD student at Tartu University
   From 1999 to 2003 lector on hydrogeology at Institute of Geology at Tartu University
   From 2000 to 2003 researcher at Institute of Geology at Tallinn Technical University
   From 2003 o 2004 Program specialist on projects fund raising at Tartu University Institute of Technology
   From 2004 to 2007 head of fundraising department at Tartu University Institute of Technology

II Academic activity

1. Main fields of research:
Hydrogeology
Hydrogeochemistry
Environmental geochemistry

2. The number of publications: 27

3. Major publications:

- **Marandi, A.; Karro, E.** 2007. Natural background levels and threshold values of monitored parameters in the Cambrian-Vendian groundwater body, Estonia. Environmental Geology. Online First.
- **Karro, E.; Indermitte, E.; Saava, A.; Haamer, K.; Marandi, A.** 2006. Fluoride occurrence in publicly supplied drinking water in Estonia. Environmental Geology, 50(3), 389–396.
- **Karro, E., Marandi, A., Vaikmäe, R. (2004).** The origin of increased salinity in the Cambrian-Vendian aquifer system on the Kopli Peninsula, northern Estonia. Hydrogeology Journal 12:424–435
- **Marandi, A., Karro, E., Puura, E. (2004).** Barium anomaly in the Cambrian-Vendian aquifer system in North Estonia. Environmental Geology 47:132–139.
- **Karro, E., Marandi, A. (2003).** Mapping of potentially hazardous elements in Cambrian-Vendian aquifer system, northern Estonia. Bulletin of the Geological Society of Finland **75** (2), 17–27.
- **Meriste, M.; Motus, L.; Kelder, T.; Helekivi, J.; Marandi, A.** (2005). On Geospatial Agents. In: Proceedings: 1st International Conference on Web Information Systems and Technologies (WEBIST2005); Miami, USA; 26.–28.05.2005. INSTICC Press, 2005, 210–213.
- **Meriste, M.; Helekivi, R.; Kelder, T.; Marandi, A.; Motus, L.; Preden, J.** 2005. Location Awareness of Information Agents. In: Advances in Databases and Information Syatems, Proceedings: 9th East European Conference on Advances in Databases and Information Systems, ADBIS2005; Tallinn; 12–15 September, 2005. (Toim.) Eder, J; Haav, H.M.; Kalja, A.; Penjam, J. Springer, 2005, (Lecture notes in computer science; 3631), 199–208.

4. Teaching (lecture courses):

Hydrogeology of Estonia
Hydrogeological Methods of Exploration
The exploitation and protection of groundwater

I have been supervisor of 3 graduate students (BSc) and one master student (MSc)

5. Other administrative and professional activities:

Head of Estonian Water Association
Secretary of Estonian Groundwater Comision
Member of Estonian Geological Society,
Member of IAH (International Association of Hydrogeologists)

6. Projects that I have been connected with:

From 2001 to 2007 Monitoring of microcompounds in groundwater. Contract research for Estonian Ministry of Environment

2004 – R&D project “New technology for anaerobic digestion of organic wastes”

2004 – R&D project “Constructed wetland for sewage treatment”
2000. EIA of Toomemägi general plan. Tartu City.
1999–2000. EIA of Kuressare town general plan.
1999–2000. Spatial planning of miming area at Ida-Viru County
1999. EIA of Supilinna general plan. Tartu City.
1999. EIA of Karula orphanage’s sewage treatment facility.
1998–1999. EIA of regular tunnel/bridge connection between mainland and Saaremaa island.
1997. Environmental Impact Assessment (EIA) of activities of Tallinn-Tartu-Luhamaa highway construction
1995–1998. Water monitoring at Pakri Peninsula.
1995–1998. Water monitoring at Kunda-Aru limestone open pit.

III Professional development

Two weeks in June & July 2003 IBM Business Consulting Services training – *“Basic knowledge of the process of Technology transfer and innovative project management”*. Certificate of training of Technology Transfer 2003

17.10.2000 – 20.10.2000 EPYS training *“Water modeling as a tool in river basin management within the water framework directive”*. 1st European Platform for Doctoral Students and Young Scientists, EPYS. October 17–20, 2000, Madrid, Spain.

Three months (04.05.1998–01.08.1998) fellowship in Slovakia financed by International Atomic Energy Agency. The subject of the fellowship was the *process of site selection of final shallow ground disposal of low-level radioactive wastes.*

On the 18th of September 1998 graduated one-week course of *Environmental Restoration Project Management* organised by U.S. Department of Energy.

CURRICULUM VITAE

I. Üldandmed

1. **Nimi:** Andres Marandi.
2. **Sünniaeg ja koht:** 16.05.1973 a. Viljandi.
3. **Kodakondsus:** Eesti.
4. **Perekonnaseis:** abielus
   Abikaasa: Triin Marandi
   Poeg: Mark Marandi
   Tütar: Mona Marandi.
5. **Elukoht:** Nooruse 60 Tartu, tel: 7381122.
6. **Töökoht:** TÜ GI erakorraline teadur, TTÜ GI erakorraline teadur
7. **Haridus:**
   19.06.1995 Tartu Ülikool *baccalaureus scientarumi* kraad geoloogia erialal – „Pakri poolsaare hüdrogeoökoloogiline seisund“
   18.01.1999 Tartu Ülikooli *magister scientarumi* kraad rakendusgeoloogia erialal – “Maapinnalähedase põhjavee keemilise koostise kujunemine militaarreostuse tingimustes Pakri poolsaare näitel”.
8. **Keelteoskus:** eesti keel, inglise keel, vene keel.
9. **Teenistuskäik:**
   2004–2007 a. TÜ TI finantsvahendite osakonna juhataja
   2003–2004 a. TÜ TI projektivõimaluste analüütik
   2000–2003 a. TTÜ Geoloogia Instituudis teadur,
   2000–2003 a. TÜ geoloogia instituudis lektor,
   1999–2001 a. Hendrikson & Ko projektijuht
   1998–1999 a. TÜ geoloogia instituudis v. insener,
   1995–1999 a. TTÜ Geoloogia Instituudis insener,

II. Teaduslik tegevus

1. **Peamised uurimisvaldkonnad:**
   hüdrogeoloogia;
   hüdrogeokeemia;
   keskkonnageoloogia.
2. **Teaduslike publikatsioonide üldarv:** 27
3. **Olulisemad publikatsioonid:**
   - **Marandi, A.; Karro, E.** 2007. Natural background levels and threshold values of monitored parameters in the Cambrian-Vendian groundwater body, Estonia. Environmental Geology. Online First.
   - **Karro, E.; Indermitte, E.; Saava, A.; Haamer, K.; Marandi, A.** 2006. Fluoride occurrence in publicly supplied drinking water in Estonia. Environmental Geology, 50(3), 389–396.

- **Karro, E., Marandi, A., Vaikmäe, R. (2004).** The origin of increased salinity in the Cambrian-Vendian aquifer system on the Kopli Peninsula, northern Estonia. Hydrogeology Journal 12:424–435
- **Marandi, A., Karro, E., Puura, E. (2004).** Barium anomaly in the Cambrian-Vendian aquifer system in North Estonia. Environmental Geology 47:132-139.
- **Karro, E., Marandi, A. (2003).** Mapping of potentially hazardous elements in Cambrian-Vendian aquifer system, northern Estonia. Bulletin of the Geological Society of Finland **75** (2), 17–27.

4. **Saadud uurimistoetused ja lepingud.**

Euroopa 5. raamprojekti raames finantseeritava rahvusvahelise "BASELINE" projekti põhitäitja.

Euroopa 6. raamprogrammi raames finantseeritava projekti BRIDGE Eesti poolne koordinaator.

5. **Muu teaduslik organisatsiooniline ja erialane tegevus:**

Eesti Veeühingu juhataja
Eesti Põhjaveekomisjoni sekretär
IAH (Rahvusvaheline Hüdrogeoloogide Assotsiatsioon) liige;
EGS liige;

III. Õppetöö

Loengukursused:

Täismahus loetavad ained:
"Eesti hüdrogeoloogia" (1,5 AP)
"Hüdrogeoloogilised uurimismeetodid" (1,5 AP)
"Põhjavee Tarbimine ja kaitse" (2 AP)

Juhendamine: juhendanud 3 referaati ja 2 keskastmetööd ning 2 ülemastmetööd, 2 lõputööd, 1 magistritöö.

IV. Administratiivtöö ja muud kohustused

Eesti Põhjaveekomisjoni sekretär

Keskkonnaministri 20. märtsi 1998. a. käskkirja nr 92 põhjal *radioaktiivsete jäätmete lõpphoidla eeluuringute läbiviimiseks ja vastavate ettepanekute tegemiseks moodustatud komisjoni liige.*

Alates 1998.a. Peipsi järve projektis *Peipsi järve valgla haldamisprogrammi põhjavee alamprogrammi koordinaator.*

V. Erialane enesetäiendus

2003. a. juunis ja juulis 2 nädalane IBM Business consulting Services poolt korraldatud kursus *„Basic knowledge of the process of Technology transfer and innovative project management".*

21.05.2003 – 23.05.2003 OÜ Keskkonnauuringute keskuse poolt korraldatud veeproovivõtja 20-tunniline koolituskursus.

17.10.2000 – 20.10.2000 EPYS koolitus *"Water modeling as a tool in river basin management within the water framework directive"*. 1st European Platform for Doctoral Students and Young Scientists, EPYS. October 17-20, 2000, Madrid, Spain.

05.05.1999 – 18.05.1999 **TEMPUS projekti õppejõudude vahetusprogrammi raames korraldatud *enesetäiendus külastus Turu Ülikoolis.***

14.09.1998 – 18.09.1998 USA Energeetikaministeeriumi (U.S. Department of Energy) poolt Tallinnas korraldatud kursused *"Environmental Restoration Project Management"*.

04.05.1998 – 01.08.1998 Rahvusvahelise Aatomienergia Agentuuri (IAEA) korraldatud kolme kuuline *radioaktiivsete jäätmete lõpphoidla asukoha valiku protsessi alane täienduskoolitus* Slovakkias Trnavas radioaktiivsete jäätmete käitlusega tegelevas ettevõttes Decom Slovakia.

1996. a. ja 1997. a. **kokku 4 nädalat Helsinki Tehnikaülikoolis *hüdrogeoloogilise modelleerimise alast täienduskoolitust.***

VI. Muu

1995 – Geoloogia insituudis läbi viidud uuringute ajal olin vastutav Pakri poolsaare hüdrogeoloogilise kaardi, pinnakattekaardi ja põhjavee reostustkaitstuse kaardi koostamise eest.

1997 – juhtisin Pakri saarte hüdrogeoloogilist-, pinnakatte- ja põhjavee reostuskaitstuse kaardistamist.

1999–2001 aastatel Hendrikson & Ko OÜ-s projektijuhina töötades osalesin ning juhtisin mitmeid projekte:

1999. Supilinna detailplaneeringu KMH. Tartu linn.
1999. Karula lastekodu reoveepuhasti KMH.
1999–2000. Kuressaare linna detailplaneeringu KMH.
2000. Toomemäe detailplaneeringu KMH. Tartu linn.
1999–2001. Ida-Viru kaevandusalade maakasutuse planeering.

Lisaks sellele olen osalenud erinevates Keskkonnaalaste projektides või juhtinud neid:

1995–1998. Pakri poolsaare veekeskkonna seire.
1995–1998. Kunda-Aru karjääri veeseire.
1997. Tallinn-Tartu-Luhamaa Mäo piirkonna maantee rekonstrueerimistööde KMH.
1998–1999. Saaremaa püsiühenduse trassivariantide KMH
2001–2002 Baariumi seire Põhja-Eesti Kambriumi – Vendi põhjavees.

DISSERTATIONES GEOLOGICAE UNIVERSITATIS TARTUENSIS

1. **Пээп Мянник.** Конодонты в верхнеордовикских и нижнесилурийских отложениях Эстонии. Тарту, 1992, 355 с.
2. **Elvi Tavast.** Fennoskandia kilbi lõunanõlva ja sellega piirnevate alade aluspõhja reljeef. Tartu, 1992, 357 lk.
3. **Kaarel Orviku.** Characterisation and evolution of Estonian seashores. Tartu, 1992, 19 p.
4. **Анатолий Молодьков.** ЭПР-анализ скелетного вещества моллюсков в хроностратиграфических исследованиях позднего кайнозоя. Тарту, 1992, 33 с.
5. **Jaan Lutt.** Late- and postglacial deposits on the Estonian shelf. Tartu, 1993, 31 p.
6. **Reet Karukäpp.** Gotiglatsiaalne morfogenees Skandinaavia mandriliustiku kagusektoris. Tartu, 1997, 181 p.
7. **Argo Jõeleht.** Geothermal studies of the Precambrian basement and Phanerozoic sedimentary cover in Estonia and Finland. Tartu, 1998, 125 p.
8. **Jüri Nemliher.** Mineralogy of Phanerozoic skeletal and sedimentary apatites: an XRD study. Tartu, 1999, 134 p.
9. **Kalle Kirsimäe.** Clay mineral diagenesis on the Lower Cambrian "Blue Clay" in the northern part of the Baltic Paleobasin. Tartu, 1999, 113 p.
10. **Jüri Plado.** Gravity and magnetic signatures of meteorite impact structures. Tartu, 2000, 87 p.
11. **Olev Vinn.** Morphogenesis and phylogenetic relationships of Clitambonitidines, Ordovician Brachiopods. Tartu, 2001, 127 p.
12. **Leho Ainsaar.** The middle Caradoc facies and faunal turnover in the late Ordovician Baltoscandian palaeobasin: sedimentological and carbon isotope aspects. Tartu, 2001, 109 p.
13. **Oive Tinn.** Early Ostracode evolution and Palaeoenvironmental application in the Ordovician of Baltoscandia. Tartu, 2002, 145 p.
14. **Maris Rattas.** Subglacial environments in the formation of drumlins — The case of the Saadjärve Drumlin Field, Estonia. Tartu, 2004, 117 p.
15. **Ene Kadastik.** Upper-Pleistocene stratigraphy and deglaciation history in northwestern Estonia. Tartu, 2004, 129 p.
16. **Helje Pärnaste.** Early Ordovician trilobites of suborder Cheirurina in Estonia and NW Russia: systematics, evolution and distribution. Tartu, 2004, 138 p.
17. **Mari-Ann Mõtus.** Silurian (Llandovery-Wenlock) tabulate corals of Baltoscandia: taxonomy, palaeoecology, distribution. Tartu, 2005, 167 p.
18. **Alar Rosentau**. Development of proglacial lakes in Estonia. Tartu, 2006, 114 p.

19. **Evelin Verž.** Development of impact-induced hydrothermal system at Kärdla impact structure. Tartu, 2006. 96 p.
20. **Sigitas Radzevičius.** The genus *Pristiograptus* in wenlock of East Baltic and the Holy Cross Mountains. Tartu, 2007. 133 p.