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## The recharge of glacial meltwater and its influence on the geochemical evolution of groundwater in the Ordovician-Cambrian aquifer system, northern part of the Baltic Artesian Basin



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#### A R T I C L E I N F O

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#### ABSTRACT

The geochemical evolution of groundwater in the Ordovician-Cambrian aquifer system in the northern part of the Baltic Artesian Basin (BAB) illustrates how continental glaciations have influenced groundwater systems in proglacial areas. The aquifer system contains water that has originated from various end-members: recent meteoric water, glacial meltwater and relict Na-Cl brine. The saline formation water that occupied the aquifer system prior to the glacial meltwater intrusion has been diluted by meltwaters of advancing-retreating ice sheets. The diversity in the origin of groundwater in the aquifer system is illustrated by a wide variety in  $\delta^{18}$ O values that range from -11% to -22.5%. These values are mostly depleted with respect to values found in modern precipitation in the area. The chemical and isotopic composition of groundwater has been influenced by mixing between waters originating from different end-members. In addition, the freshening of a previously saline water aquifer due to glacial meltwater intrusion has initiated various types of water-rock interaction (e.g. ion exchange, carbonate mineral dissolution).

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### 1. Introduction

Aquifers in sedimentary basins once covered by continental glaciers had sufficient transmissivity to discharge subglacial meltwater (Boulton et al., 1995; Piotrowski, 1997; Person et al., 2007; Lemieux et al., 2008; McIntosh et al., 2011). The recharge of glacial meltwater was able to modify groundwater flow patterns in these basins with water penetrating much deeper and faster under high hydraulic gradient induced by continental ice sheets compared to modern topographically driven recharge. The reorganisation of groundwater flow patterns also influenced the iso-topic and chemical composition of the basinal fluids. Many studies have shown a direct influence of Quaternary glaciations on the formation of groundwater in proglacial sedimentary basins in North America and in Europe (e.g. Clayton et al., 1966; Siegel and

\* Corresponding author. E-mail address: joonas.parn@ttu.ee (J. Pärn). Mandle, 1984; Siegel, 1989, 1991; Stueber and Walter, 1991, 1994; Vaikmäe et al., 2001; Grasby et al., 2000; McIntosh et al., 2002; McIntosh and Walter, 2005, 2006; Ferguson et al., 2007; Raidla et al., 2009, 2012). Fluid pressure anomalies associated with the ice sheets have in most cases dissipated (except few cases such as described in Alberta Basin, Western Canada; e.g. Bekele et al., 2003) leaving the chemical and isotopic composition of groundwater as the main tool for studying the ice sheet-aquifer interactions during Pleistocene.

The influence of glacial meltwater recharge from the Scandinavian Ice Sheet on the proglacial sedimentary aquifers in the Baltic Artesian Basin (BAB) has been documented in Ediacaran and Cambrian sandstones (i.e. Cambrian-Vendian aquifer system) in its shallow northern part (e.g. Yezhova et al., 1996; Mokrik, 1997, 2003; Vaikmäe et al., 2001, 2008; Karro et al., 2004; Marandi, 2007; Raidla et al., 2009, 2012, 2014). Groundwater in the northern part of the Cambrian-Vendian aquifer system has the lightest isotopic composition recorded in Europe ( $\delta^{18}$ O values ranging from -18.5%to -23%) (Vaikmäe et al., 2001) that is depleted with respect to isotopic composition of the modern precipitation in the area (the annual weighted mean  $\delta^{18}$ O value of -10.4%; Punning et al., 1987).

In this paper we study the geochemical evolution of groundwater in the Ordovician-Cambrian (O-Cm) aquifer system. This aquifer system overlies the Cambrian-Vendian aquifer system in the northern part of the BAB. Specific aims are (1) to reconstruct the origin of groundwater in the aquifer system; (2) to reveal the sources of salinity in the studied waters and the main geochemical processes that control the groundwater chemistry; and (3) to assess the influence of glacial meltwater recharge on the geochemical evolution of groundwater in the aquifer system.

Understanding the processes influencing recharge, mixing and geochemical evolution of groundwater in O-Cm aquifer system is crucial for predicting the effects of groundwater abstraction on its composition and availability. The O-Cm aquifer system is an important source of public water supply in northern Estonia. In addition, the rocks associated with the aquifer strata contain several mineral resources that could have potential economic significance in the future. These include the shell detritus of phosphatic brachiopods in Lower Ordovician sandstones which form the biggest phosphorite deposit in Europe (Raudsep, 1997). It was mined for phosphatic fertilizer production from 1920s up to late 1980s. Furthermore, the Lower Ordovician organic-rich black shale known as graptolite argillite overlying the aquifer system contains high concentrations of trace metals and REE elements (e.g. U, Mo, V, Ni, Cd, Au, Sb, As, Pt) (Voolma et al., 2013; Hade and Soesoo, 2014). Any future plans for mining these mineral resources need to take into account the origin and renewability of groundwater in the O-Cm aquifer system.

#### 2. Geology and hydrogeological setting

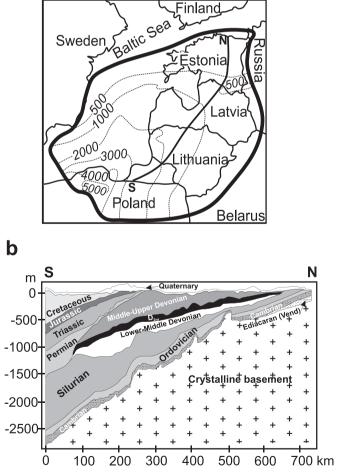
The O-Cm aquifer system is a confined water body in the northern part of the BAB. BAB is a Phanerozoic sedimentary basin that covers the territories of Estonia, Latvia, Lithuania and parts of Russia, Poland and Belarus (Fig. 1a) (Mokrik, 1997, 2003; Virbulis et al., 2013). Approximately half of the BAB is covered by the Baltic Sea. The thickness of the sedimentary cover reaches 5000 m in the south-western part of the basin, while the crystalline basement reaches to the surface at its northern and south-eastern parts. In the northern part of the BAB (Estonia and Latvia) the sedimentary cover contains rocks of Ediacaran to Devonian age which overlie the Paleoproterozoic crystalline basement (Fig. 1b). In the southern part of the basin in Lithuania and Poland the sedimentary succession is continued with sedimentary rocks of Mesozoic and Cenozoic age. General flow direction of deep groundwater in the BAB is directed from the south-western parts of the basin towards the periphery monoclines.

The O-Cm aquifer system is hosted by sand- and siltstones of Cambrian and Early Ordovician age which are located between the underlying Lower Cambrian claystones (i.e. Lükati-Lontova regional aquitard) and the overlying Lower Ordovician argillites, sandstones and carbonate rocks (Fig. 2). The sandstones in Cambrian and Lower Ordovician are mainly quartz arenites or subarkoses, with quartz content up to 90% (Raidla et al., 2006). The rocks forming the O-Cm aquifer system are distributed in most of the Estonian territory, except in the coastal region of northern Estonia and Mõniste-Lokno uplift area in southern Estonia (Fig. 2). The thickness of the aquifer system increases from 20 to 60 m in northern Estonia to ~120 m in Latvia (Juodkazis, 1980; Savitskaja et al., 1995; Perens and Vallner, 1997). The depth of the aquifer strata is 10-20 m from the ground surface in northern Estonia and increases to over 1000 m in Latvia. The lateral hydraulic conductivity of Cambrian and Lower Ordovician sandstones ranges from 1 to 3 m d<sup>-1</sup> (Perens and Vallner, 1997). Transmissivity ranges from 25 to 50 m<sup>2</sup> d<sup>-1</sup> in northern Estonia and from 80 to 130  $\text{m}^2 \text{d}^{-1}$  in southern Estonia due to the increased thickness of the water-bearing rocks (Perens and Vallner, 1997).

The O-Cm aquifer system is confined by the overlying Silurian-Ordovician regional aquitard. The northern part of the aquitard consists of Lower Ordovician limestones, marls, siltstones, clays and argillites, extending ~100 km southward from the Estonia's northern coast (Fig. 2). The whole Silurian-Ordovician sedimentary sequence can be viewed as a regional aquitard at increasing depths as the number of fissures and cavities which are the main water conducting zones in carbonate rocks decreases with depth (Perens and Vallner, 1997). The transversal hydraulic conductivity of the Silurian-Ordovician regional aquitard ranges from  $10^{-7}$  to  $10^{-5}$  m d<sup>-1</sup> (Perens and Vallner, 1997).

The O-Cm aquifer system is separated from the underlying Cambrian-Vendian aquifer system by the Lükati-Lontova regional aquitard which consists of siltstones and clays of the Lower Cambrian Lükati and Lontova Formations that have a transversal hydraulic conductivity of  $10^{-7}$  m d<sup>-1</sup> (Perens and Vallner, 1997). In western Estonia the Lontova Formation is laterally replaced by siltstones and sandstones of the Voosi Formation (Fig. 2). The aquitard becomes sandier and thinner with its transversal hydraulic conductivity increasing to  $\geq 10^{-5}$  m d<sup>-1</sup> (Perens and Vallner, 1997). In western Estonia and south-western Estonia, the Ediacaran





**Fig. 1.** (a) The location and boundaries of the Baltic Artesian Basin (BAB) together with contour lines marking the depth of the crystalline basement in meters b.s.l., (b) the geologic cross-section of the BAB along the line N-S on Fig. 1a.  $D_{2nr}$  – Narva regional aquitard, Q – Quaternary (modified from: Juodkazis, 1980; Virbulis et al., 2013).

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