

Confronting vicinity of the surface water and sea shore in a shallow glaciogenic aquifer in southern Finland

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1 Abstract

2 The groundwater in a shallow, unconfined, low-lying coastal aquifer in Santala, southern
3 Finland, was chemically characterized by integrating multivariate statistical approaches,
4 principal component analysis (PCA) and hierarchical cluster analysis (HCA), based on the
5 stable isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$, hydrogeochemistry and field monitoring data. PCA and HCA
6 yielded similar results and classified groundwater samples into 6 distinct groups that revealed
7 the factors controlling temporal and spatial variations in the groundwater geochemistry, such as
8 the geology, anthropogenic sources from human activities, climate and surface water. High
9 temporal variation in groundwater chemistry directly corresponded to precipitation. With an
10 increase in precipitation, KMnO_4 consumption, EC, alkalinity and Ca concentrations also
11 increased in most wells, while Fe, Al, Mn and SO_4 were occasionally increased during spring
12 after the snowmelt in specific geological conditions. The continued increase in NO_3 and metal
13 concentrations in groundwater indicates the potential contamination risk to the aquifer. Stable
14 isotopes of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ indicate groundwater recharge directly from meteoric water, with an
15 insignificant contribution from lake water, and no seawater intrusion into the aquifer.
16 Groundwater geochemistry suggests that local seawater intrusion is temporarily able to take
17 place in the sulphate reduction zone along the fresh and seawater mixed zone in the low-lying
18 coastal area, but the contribution of seawater was found to be very low. The influence of lake
19 water could be observed from higher levels of KMnO_4 consumption in wells near the lake. The
20 integration of PCA and HCA with conventional classification of groundwater types, as well as,
21 with the hydrogeochemical data provided useful tools to identify the vulnerable groundwater
22 areas represent the impacts of both natural and human activities on water quality and the
23 understanding of complex groundwater flow system for the aquifer vulnerability assessment and
24 groundwater management in the future.

1 **1 Introduction**

2 Shallow permeable aquifers located next to the seashore may face greater risks and challenges
3 in water consumption and management compared with inland water intakes. Aquifers along the
4 coastline are especially vulnerable to seawater intrusion, either due to sea level rise or storm
5 surges (e.g. Oude Essink, 1999, 2001; Barlow, 2003; Pulido-Leboeuf, 2004; Oude Essink et al.,
6 2010; Rasmussen et al., 2013; Luoma et al., 2013; Luoma and Okkonen, 2014), which will
7 presumably be accelerated by the changing climate (IPCC, 2000, 2007; Nicholls et al., 2007).
8 Besides these, increasing water demand for the population and industries as well as changing
9 land use practises as a result of human activities, e.g. exceeding the water intake, gravel
10 excavation pits, car parking, and groundwater contamination risk areas, can expose shallow
11 aquifers to contamination. Ferguson and Gleeson (2012) reported that due to the groundwater
12 abstraction and low hydraulic gradient the saltwater intrusion into the coastal aquifer will be
13 more widespread and significant than assumed by the impact of sea level rise.

14 Under the changing climate, a potential increase in precipitation in the winter, spring and
15 autumn and increased evapotranspiration in summer owing to rising temperatures is expected
16 (Scibek and Allen, 2006; Scibek et al., 2007; Jyrkama and Sykes, 2007; Okkonen and Kløve,
17 2011; Okkonen, 2011; Luoma and Okkonen, 2014). Climate change would potentially affect not
18 only the groundwater, but also the surface water. For sustainable groundwater resources
19 management and land use planning, it is important to understand the hydrogeological processes
20 and the interactions between groundwater and surface water, and factors affecting groundwater
21 quality.

22 Approximately 300 out of the total of 6000 classified shallow groundwater areas in Finland
23 (excluding Åland) are located 100 m or less from the shore of the Baltic Sea (Hertta database,
24 SYKE, 2013). The Baltic Sea is one of the largest brackish water areas in the world (EEA,
25 1999). Although the low salinity, which varies from 3.0–7.0 ‰ in the Gulf of Finland (Alenius
26 et al., 1998; UNEP, 2005; Fagerlund, 2008), does not pose a high risk from seawater intrusion
27 compared to other parts of the world (e.g. Oude Essink, 1999, 2001; Barlow, 2003; Pablo
28 Pulido-Leboeuf, 2004; Oude Essink et al., 2010; Rasmussen et al., 2013), the salinity is at a
29 higher level than the drinking water standard, and in the long term it can damage the
30 infrastructure, such as the pipeline network.

31 Seasonal variations in groundwater quality have been reported in many unconfined shallow
32 aquifers in Finland. For example, a lower dissolved concentration of elements in groundwater

1 during the snowmelt period indicates effects of the snowmelt (Backman et al. 1999; Korkka-
2 Niemi, 2001; Okkonen, 2012). However, there is still no clear understanding of the interactions
3 between surface water and groundwater or the impacts of brackish water intrusion on shallow,
4 low-lying coastal aquifers. Major ion chemistry, as well as the stable isotopic composition of
5 oxygen-18 ($\delta^{18}\text{O}$) and hydrogen ($\delta^2\text{H}$ or deuterium), could be used to assess these interactions,
6 as earlier reported by Allen (2004), Harbison (2007), Kortelainen (2007) and Mongelli (2013),
7 among others.

8 A shallow glaciogenic aquifer in the Hanko area in southern of Finland, our case study area, is
9 confronting these issues in an attempt to maintain water quality within the drinking water
10 standards in the long term. As reported by Luoma and Okkonen (2014), a rise in the sea level
11 due to the global climate change would cause some parts of the Hanko aquifer to be under the
12 sea level, compromising groundwater quality due to seawater intrusion. This, together with the
13 predicted increase in precipitation, would increase groundwater recharge and raise the
14 groundwater levels, consequently contributing to the potential deterioration of groundwater
15 quality or potential flooding in the low-lying aquifer.

16 The objective of this study was to address the following questions: 1) What are the factors
17 controlling groundwater quality, the main water type and the chemical evolution of groundwater
18 in the low-lying coastline aquifer in cold, snow-dominated southern Finland? 2) Is there any
19 influence of seawater on groundwater quality? 3) What are the interactions between the Baltic
20 Sea and lake and groundwater, and the temporal and spatial variations in groundwater and
21 surface water geochemistry in different recharge periods? 4) How the hydrogeochemical data
22 can be used in order to indicate vulnerable areas of the coastal aquifer?

23 The data comprised field investigation and hydrogeochemical data obtained during 2010 and
24 2012. The stable isotope ratios of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were used to determine the origin of
25 groundwater. The geochemistry of water samples was analysed and classified with multivariate
26 statistical methods, i.e. hierarchical cluster analysis (HCA) and principal component analysis
27 (PCA) (Cloutier et al, 2008), in conjunction with conventional groundwater classification using
28 Piper diagrams.

29 **2 The study area**

30 The study area is located in Santala on the northern coast of the Hanko peninsula, southern
31 Finland, at approximately 59°53'N 23°10'E (Fig. 1), and covers approximately 17 km² of the

1 main aquifer. This aquifer is an important source of drinking water and the water supply for
2 Hanko town (with a population of 9 282 in 2013) and local industries. The aquifer consists of
3 porous gravels and sands of an ice-marginal end deposit, and is located in a low-lying coastal
4 area bounded by the Baltic Sea, with a lake in the middle of the aquifer. The topographic
5 landform varies between 10–14 m a.s.l. along the northern ridge of the First Salpausselkä
6 Quaternary ice-marginal formation (Fig. 1) and its elevation decreases to less than two metres
7 along the northern coastline, while in the south and southeast the elevation gradually decreases
8 to 5–7 m a.s.l. The southern part is partly covered by wetlands and peatlands. In the east, the
9 area is covered by sand dune terrain from the Aeolian deposit. The lake and wetlands in the
10 middle of the aquifer are located in a depression that forms part of the First Salpausselkä
11 formation and the sand dune terrain. The lake has a surface area of about 1.8 km², and it is
12 shallow with an average depth of approximately 1–2 m. In many parts of the aquifer, the
13 groundwater level is close to the ground surface, and water intake areas are located along the
14 coastline, where the groundwater level may often fall below the sea level. The groundwater
15 level has previously been observed to rapidly respond to a rise in the sea level, as well to
16 recharge from the spring snowmelt and rainfall (Backman et al., 2007; Luoma et al., 2013).
17 Additionally, human activities in the area, such as gravel excavation pits, local industries or the
18 highway (Fig. 1), could pose a contamination risk to the groundwater quality.

19 The Hanko area belongs to the temperate coniferous-mixed forest climate zone with cold, wet
20 winters. During the study period, the mean annual temperature remained at approximately +6
21 °C, which is consistent with the long-term mean annual temperature in the reference period of
22 1981–2010 (FMI 2013). Meteorological parameters (maximum, minimum and mean
23 temperatures, precipitation and snow) both in 2012 and during the period of 1981–2010
24 measured at the Tvärminne weather station, approx. 5 to 8 km southeast of the study area, are
25 illustrated in Figure 2. The lowest daily temperatures are generally recorded in January and
26 February, and the highest during July and August (Fig. 2). The year 2012 was exceptionally
27 rainy, as the cumulative amount of annual precipitation was 893 mm. This is 41% higher than
28 the long-term mean value of 634 mm (1981–2010).

29 **2.1 Geology and hydrogeology of the study area**

30 The stratigraphy in Hanko area is underlain by the basement of the Precambrian crystalline
31 igneous and metamorphic rock and covered by the Quaternary deposits. The Precambrian
32 bedrock, which mainly consists of granite, quartz diorite and granodiorites, forms a sharp
33 contact with the Quaternary deposits, with some outcrops in the area (Kielosto et al. 1996). The

1 aquifer in the study area is situated in the First Salpausselkä ice-marginal formation deposited
2 during the Weichselian and Holocene deglaciation of the Scandinavian Ice Sheet (Punkari,
3 1980; Fyle, 1991; Saarnisto and Saarinen, 2001). The First Salpausselkä ice-marginal formation
4 consists of glacial till, gravel, sand and clay, together with postglacial littoral gravel, sand and
5 clay (Fig. 1).

6 The primary ice-marginal formation in Hanko was formed in deep water with a low narrow
7 ridge (Fyle, 1991). When the ice sheet withdrew from the area, this formation was covered by
8 fine-grained sediments, silt and clay layers of the Ancylus Lake and Littorina Sea. The sea level
9 has been regressive since the glacial period due to isostatic land uplift. The primary deposit of
10 the First Salpausselkä formation was exposed to sea waves and also to wind (Kielosto et al.,
11 1996). The well-sorted gravels indicate the reworking of materials resulting from the high
12 energy of wave and storm activities over a large area in Santala, the study area, while fine sand
13 from Aeolian deposits covers a large area to the east and southeast of the lake (Fig. 1) (Fyle,
14 1991; Kielosto et al., 1996).

15 The shallow aquifer in Hanko is unconfined, with the thickness of the Quaternary deposits
16 varying from less than one metre to 75 m, and the average thickness being about 25 m. The
17 sediments are generally thick on the western side, in a NE–SW direction conforming to the First
18 Salpausselkä formation, and decrease eastward to less than one meter in the eastern coast area.
19 The groundwater table in Santala is between 2–7 m below the ground surface in the inland area,
20 and less than 2 m below the ground surface in the coastal area, where groundwater discharges
21 into the Baltic Sea. The results of well testing and soil sample analysis have revealed that the
22 hydraulic conductivity of the aquifer varies from 0.3–4.8 m d⁻¹ in silty sand and fine sand, and
23 up to 100 m d⁻¹ in sand and gravel (Luoma and Pullinen, 2011). Groundwater recharge mainly
24 occurs twice a year during spring (late March to early April) and late autumn (November to
25 early December) from the infiltration of snowmelt and rainfall (Luoma et al., 2013).
26 Groundwater mainly flows northwards into the coastal area and also towards the south–
27 southeast into the wetlands and peatlands, as well as towards the Baltic Sea in the east.

28 **3 Materials and Methods**

29 **3.1 Sampling, field investigation and well monitoring**

30 The field investigation and water sampling were carried out four times, during the winter,
31 spring, summer and autumn of 2012. Water samples were collected from 15 sites in the Santala
32 area, including water samples from 12 groundwater observation wells (Table 1), the lake, the

1 Baltic Sea, and a water intake well (Fig. 1). In total, 26 samples were taken for chemical
2 analysis and 59 samples for the analysis of stable isotope compositions of oxygen and hydrogen.
3 In addition, water chemical analysis results for 6 water samples taken during spring 2010, as
4 well as groundwater monitoring data (depth (D), and temperature (T), electrical conductivity
5 (EC) and field measurement data, including D, T, EC, pH, dissolved oxygen (O₂), redox
6 potential (Eh) and dissolved carbon dioxide (CO₂) for 12 wells in the Hanko area performed
7 during 2009–2010 were used to support the interpretation.

8 The field investigation consisted of the down-hole profile logging and field measurement of
9 water samples during water sampling. The profile logging was performed in order to investigate
10 the vertical distribution of physical and chemical parameters of groundwater at the screen
11 intervals of the observation wells, and the water sampling depths were selected based on the
12 results of these logs. The measurement was performed by using either a WTW P4 instrument
13 (during the winter) or a YSI Professional Plus (IP-67), a multi-parameter recording device, for
14 the measurement of EC, pH, T, O₂ and Eh. Dissolved carbon dioxide (CO₂) was measured in the
15 field by using a colorimetric titration method (Csuros, 1994) with 0.02N NaOH. While
16 alkalinity was measured by using automatic potentiometric titration immediately upon arrival of
17 the samples at the laboratory. The pumping rate, time, and amount of water pumped before
18 sampling were recorded. In addition, the groundwater tables were measured before and after
19 pumping.

20 Well monitoring was carried out for 8 groundwater observation wells during March to
21 November 2012 and in Lake Sandösträsket during September to November 2012. Measurement
22 was performed by installing a Schlumberger Mini-Diver data logger and pressure transducer at
23 the same sampling depths. Three wells located near the northern coastline area were monitored
24 for T, D and EC. Lake water and 5 inland wells, which were situated far from the coastline and
25 the water intake well, were monitored for T and D. All data were recorded hourly. Time series
26 of climate data (air temperature and precipitation as rainfall or snow thickness) and sea level
27 recordings in the Hanko area from the same period were obtained from the Finish
28 Meteorological Institute (FMI, 2013) and used for comparison.

29 The groundwater from the observation wells was pumped for a minimum of 20 minutes until all
30 parameters readings (e.g. T, EC) were constant before sampling. Groundwater from the water
31 intake well was taken from the tap by allowing water to flow out until all parameters (e.g. T,
32 EC) were constant. The surface water samples (seawater and lake water) were taken with a
33 Limnos water sampler from 1 m below the water surface. The number and sampling depth of

1 groundwater samples from each well was selected according to the profile-logged results. If
2 there were no variations in the profile, a sample was taken from the middle of the screen
3 interval, at least 2 m below the top screen. If there were variations in the profile, the partition
4 samples were taken by placing an inflatable packer at the discrete depth of the selected zones,
5 and a single groundwater sample was collected at a time, beginning with the top section and
6 continuing downwards to the bottom section.

7 **3.2 Analytical methods and quality control**

8 For cation analysis, water samples were filtered through 0.45- μm membrane filters and
9 collected into 100-ml high-density polyethylene (HDPE) bottles. The samples were acidified
10 and analysed in the accredited laboratory of Labtium Ltd in Espoo. Filtered and acidified water
11 samples were analysed for major and minor elements (Ag, Al, As, B, Ba, Be, Bi, Cd, Co, Cr,
12 Cu, I, K, Li, Mn, Mo, Ni, P, Pb, Rb, Sb, Se, Sr, Th, Tl, U, V, Ca, Fe, Mg, Na, Si and S) by using
13 inductively coupled plasma atomic emission and mass spectrometry (ICP-AES and ICP-MS).
14 Alkalinity (as HCO_3), EC, pH and KMnO_4 consumption were measured from unfiltered and
15 unpreserved samples immediately upon arrival of the samples at the laboratory. They were also
16 analysed for anions (Br, Cl, F, NO_3 , PO_4 and SO_4) using ion chromatography (IC). To ensure
17 the quality of the equipment and chemical analysis, a zero sample was prepared from distilled
18 water and four duplicate pairs of groundwater samples were also analysed. The zero and
19 duplicated sample analysis results indicated no field contamination. The charge balance error
20 (BE) (Drever, 1997) was calculated for all water samples. For 26 of the 34 water samples, $\text{BE} <$
21 $\pm 5\%$, while 8 samples had BE values between $\pm 6\%$ and $\pm 10\%$. The chemical analysis and
22 quality control results from Labtium Ltd indicated high proportions of anions in some water
23 samples, and the BE cutoff of $\pm 10\%$ was acceptable. Many previous studies, such as Appelo and
24 Postma (2005) and Allen (2004), have recommended a BE cutoff of less than $\pm 5\%$ for good
25 water analysis, while Drever (1997) and Harbison (2007) used a BE cutoff of $\pm 10\%$ due to the
26 presence of high organic acid concentrations in fresh groundwater samples from a shallow
27 coastal aquifer.

28 **3.3 Stable isotopes oxygen and hydrogen analysis**

29 The stable isotopes $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are commonly used in studies on groundwater flow and the
30 interaction of groundwater and surface water. These traditional water isotopes are effective
31 tracers that can be used to identify the origin of water as well as the mixing processes of
32 isotopically distinct water masses and evaporation in surface water reservoirs (Gonfiantini,

1 1986; Richter and Kreitler 1991; Taylor and Howard 1996; Clark and Fritz, 1997; Kendall and
2 McDonnell, 1998; Allen 2004; Faure and Mensing, 2005). The recent regional isotopic
3 composition of both atmospheric precipitation and groundwater are well known in southern
4 Finland (Kortelainen, 2007; Kortelainen and Karhu 2004). Based on monthly isotopic values of
5 oxygen and hydrogen in Finnish precipitation, the national scale meteoric water line ($\delta^2\text{H} = 7.67$
6 $\delta^{18}\text{O} + 5.79\text{‰}$) was established by Kortelainen in 2007. The line agrees well with local lines
7 derived for the southern coast of Finland (Kortelainen, 2007, 2009) and could consequently be
8 applied in this study. In temperate climates such as in Finland, the isotopic composition of the
9 local groundwater closely follows that of local precipitation. (Kortelainen 2007; Kortelainen and
10 Karhu 2004). The stable isotope method has been widely applied in Finland, especially to
11 evaluate natural groundwater–surface water interaction (Rautio and Korkka-Niemi, 2011) and
12 artificially enhanced surface water infiltration into aquifers (Kortelainen and Karhu, 2006;
13 Hendriksson, 2012).

14 For analysis of the stable isotopes $\delta^{18}\text{O}$ and $\delta^2\text{H}$, filtered water samples ($<45\ \mu\text{m}$) of about 60 ml
15 were collected in HDPE bottles and were kept in a dark cooler box and out of direct sunlight
16 during transport to the Research Laboratory of Geological Survey of Finland in Espoo. The
17 isotopic composition of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ was analysed by laser-based cavity ring-down
18 spectroscopy (CRDS), using a Picarro isotopic water analyser. In the CRDS method, the
19 absolute abundances of water molecules with different combinations of the stable isotopes of
20 $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are measured from a vaporized sample in an optic chamber. The isotopic
21 composition of water is reported using the δ -notation per mill (‰) relative to the VSMOW
22 (Vienna Standard Mean Ocean Water) standard. The δ -value is defined as $\delta = ((R_{\text{SA}} -$
23 $R_{\text{VSMOW}})/R_{\text{VSMOW}}) \times 1000$, where SA is the sample and VSMOW is the standard, $\delta = \delta^{18}\text{O}$ and R
24 $= {}^{18}\text{O}/{}^{16}\text{O}$ for oxygen, and $\delta = \delta^2\text{H}$ and $R = {}^2\text{H}/\text{H}$ for hydrogen. The repeatability of analyses
25 was $<0.1\text{‰}$ for $\delta^{18}\text{O}$ and $<0.5\text{‰}$ for $\delta^2\text{H}$.

26 **3.4 Statistical analysis**

27 Data correlations and statistical analyses were performed using the IBM SPSS statistical
28 package (IBM SPSS Statistics, 2013) to determine the variables that represent the controlling
29 factors behind the geochemistry of all the water samples taken during April and August 2012.
30 The correlations between variables were carried out for all raw data by using the Pearson
31 correlation coefficient to identify the relationships between variables among the water sampling
32 sites.

1 Two multivariate statistical approaches, principal component analysis (PCA) and hierarchical
2 cluster analysis (HCA), were used to group the water samples or variables analysed. PCA is a
3 factor analysis method that is used to extract components representing the information contained
4 in the data that explain the pattern of correlations and differences within a group of variables
5 (Korkka-Niemi, 2001; IBM SPSS Statistics, 2013). The number of factors or components was
6 extracted by PCA with Varimax rotation based on Kaiser normalization.

7 HCA is a classification method that reveals natural groupings or clusters within a data set by
8 reorganizing the data into homogeneous groups and linking the two most similar clusters until
9 all of the variables are joined in a complete classification tree (Korkka-Niemi, 2001; IBM SPSS
10 Statistics, 2013). The results of HCA are presented in a dendrogram, which is constructed using
11 the Ward's method (Ward, 1963) with the Euclidean distance as a measure of similarity between
12 the samples. Ward's method is one of the most widespread hierarchical clustering methods for
13 the classification of hydrogeochemical data by using the minimum variance to evaluate the
14 distances between the clusters (Güler et al., 2002; Cloutier et al., 2008; Templ et al., 2008).

15 The data used for PCA and HCA comprised the stable isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$, chemical
16 parameters, pH and EC. The dataset include variables having normal or close to normal
17 distributions from the chemical parameters (alkalinity, B, Ba, Ca, I, Li, Mg, Na, Rb, S, Si, Sr),
18 and $\delta^2\text{H}$, $\delta^{18}\text{O}$, pH and EC. The variables having a non-normal distribution (Al, Cl, Cu, Mn, K,
19 KMnO_4 , Mo, Ni, NO_3 , SO_4 , U and Zn) were log-transformed prior to statistical analysis. The
20 variables below or close to the detection limit (Ag, Be, Bi, Br, Cd, Co, Cr, F, Fe, P, PO_4 , Se, Th
21 and Tl) were excluded from the analysis. The data were standardized by subtracting the sample
22 mean from each variable and dividing the resulting value by the standard deviation (Z score
23 standardization) prior to multivariate analysis to ensure that each variable was weighted equally
24 (Güler et al., 2002; Cloutier et al., 2008; Templ et al., 2008).

25 **3.5 Data processing**

26 Data analysis was performed in Microsoft Excel for data storage, cross-plots and basic
27 calculation. GWChart (USGS, 2012) was used to produce piper diagrams, which are plots of the
28 relative concentration of major dissolved species of anions and cations, in order to identify the
29 water types (Piper, 1944; Appelo and Postma, 2005). ArcGIS/ArcMap was used for
30 visualization of the geochemical data points and the groundwater level was mapped by kriging.
31 For comparison with the chemical analysis results from the water samples, median values of
32 groundwater compositions of Finnish shallow aquifers (Lahermo et al., 2002) and the

1 precipitation (rainfall and snowmelt) collected from the Tvärminne weather station (Vuorenmaa
2 et al., 1999; Järvinen and Vänni, 1996, 1997), as well as recommended values for drinking
3 water for Finnish household wells from the Ministry of Social Affairs and Health (STM, 2001)
4 were used as references.

5 **4 Results**

6 **4.1 Water levels**

7 The results of lake level monitoring during September to November 2012, groundwater levels
8 from monitoring wells during March to November 2012 and daily precipitation and temperature
9 data from the Tvärminne weather station in the Hanko area (FMI, 2013) are presented in Figure
10 3. The variation in groundwater levels indicated that the main recharge takes place twice a year:
11 during spring (early April) immediately after the snowmelt period (Fig. 3B), when groundwater
12 reaches its highest level, and during late autumn (October to December). Groundwater levels
13 reached the lowest levels during the winter and late summer due to the snow cover and
14 evapotranspiration, respectively. The mean groundwater levels ranged from 8.4 m a.s.l. at Obs8
15 to 12.3 m a.s.l. at Obs1 for the inland wells, and from 0.4 m a.s.l. at Obs11 to 0.5 m a.s.l. at
16 Obs10 for the wells in the coastal area. The time series of lake level data during September to
17 November 2012 varied from 11.83–11.98 m a.s.l. (Fig. 3B). The previous measurements of lake
18 levels during this study were 11.75 m a.s.l. in November 2009 and 12.08 m a.s.l. in January
19 2012. The variation in lake levels during the year was less than 0.5 m. Sampling point Obs2 is
20 located approximately 170 m west of the lake shoreline. The groundwater level at Obs2 during
21 March to November 2012 varied between 11.13 and 11.79 m a.s.l., which is lower than the lake
22 level. The fluctuation in the groundwater level at Obs2 was positively correlated with the lake
23 level, with a Pearson correlation coefficient of 0.94 ($\rho < 0.01$).

24 **4.2 Geochemistry of water**

25 Summary statistics for the groundwater and surface water geochemistry are presented in Table
26 2. The EC profile logging at Obs8 and Obs6 revealed higher values in the top section than in the
27 bottom section of the observation well. The partition samples were taken from Obs8 and Obs6
28 during the summer for chemical and stable isotopic analysis, and during autumn for stable
29 isotopic analysis. Figure 4 presents the profile log results from Obs6 and the sampling depths.
30 The bottom samples could not be taken from a deeper depth because the packer became stuck in
31 the observation well at certain depths.

1 4.3 Stable isotopes of oxygen and hydrogen

2 The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of groundwater varied spatially and temporally within the range of -
3 86.90‰ to -76.50‰ VSMOW and -12.30‰ to -10.62‰ VSMOW, with mean values of -80.39
4 ± 2.52 (1σ) ‰ and -11.37 ± 0.36 (1σ) ‰ VSMOW, respectively. The mean $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values
5 for the lake water were -55.57 ± 9.65 ‰ and -6.85 ± 2.08 ‰, respectively, and the respective
6 values for the seawater were -57.65 ± 2.35 ‰ and -7.55 ± 0.38 ‰. The variations of the $\delta^2\text{H}$ and
7 $\delta^{18}\text{O}$ data from 59 water samples collected in Santala are presented in Figure 5.

8 5 Discussions

9 5.1 Origin of groundwater

10 The stable isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$ were used to differentiate the meteoric origin of groundwater
11 from a surface water origin. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values in groundwater from this study were
12 consistent with the results of Kortelainen and Karhu (2004) and Kortelainen (2007), who
13 reported mean $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of groundwater from southern Finland ($n = 37$) of $-82.0 \pm$
14 0.9 ‰ and -11.55 ± 0.14 ‰ VSMOW, respectively. The stable isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of
15 groundwater in Santala are also consistent with the mean $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the
16 precipitation from southern Finland ($n = 60$), which are -82.0 ± 23.6 ‰ and -11.54 ± 3.1 ‰
17 VSMOW, respectively. These values are distinct from those of surface water, as the mean $\delta^2\text{H}$
18 and $\delta^{18}\text{O}$ values of lake water are -55.57 ± 9.6 ‰ and -6.85 ± 2.1 ‰, respectively, and the
19 respective means of seawater are -57.65 ± 2.4 ‰ and -7.55 ± 0.4 ‰.

20 Most of the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of groundwater from Santala fall closely on the Finnish local
21 meteoric water line (Fig. 5, LMWL), indicating direct recharge from precipitation (snowmelt
22 and rainfall) with no indication of evaporation or a contribution from the surface water. Due to
23 evaporation, the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of lake and seawater deviate to the right from the LMWL.
24 The higher the evaporation effect is, the further to the right the values deviate from the local
25 groundwater and the LMWL (Gonfiantini, 1986). In surface waters, high seasonal variations are
26 also recorded (Fig. 5). The variations are larger in lake water than in seawater. Both lake and sea
27 water show the highest evaporation effect in the summer samples.

28 The only sign of possible mixing of groundwater and surface water was observed from a sample
29 taken in spring (11 April 2013) at Obs2, approx. 170 m west of the lake shoreline, where
30 slightly higher $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values were recorded than in the autumn and a small deviation
31 from the LMWL. Water monitoring data implied that the water flow direction was from the lake

1 into Obs2. The KMnO_4 consumption of samples from Obs2 in April 2012 and August 2012
2 were high relative to the surrounding wells, and close to the concentration from lake water,
3 which indicates the influence of lake water on this well.

4 The majority of the groundwater samples, including the top and bottom samples from Obs6
5 (except from Obs8, Obs7 and Obs2), showed narrow temporal and spatial variation with low
6 standard deviations of 1.6‰ and 0.23‰ for $\delta^2\text{H}$ and $\delta^{18}\text{O}$, respectively (Fig. 5, insert figure). At
7 Obs6, where the multilevel samples were taken, small variations were observed in $\delta^2\text{H}$ and $\delta^{18}\text{O}$
8 between top and bottom samples; furthermore, the samples at each interval (top or bottom)
9 displayed very small seasonal variations between summer and autumn. The narrow variations of
10 most of the data may indicate the same source of groundwater recharge with a short percolation
11 time. The fluctuation in groundwater levels in many observation wells (Fig. 3) indicates a rapid
12 response of the groundwater level to precipitation during the snowmelt period and heavy rainfall
13 events, which reflect the short percolation time. This is consistent with many wells that contain
14 quite a thin vadose zone (Table 1) and/or the high hydraulic conductivity of aquifer materials.
15 However, the observation wells next to a gravel excavation pit (Obs8, Obs7) and the lake
16 shoreline (Obs2) showed high seasonal variation with high standard deviations of 3.21‰ and
17 0.49‰ for the $\delta^2\text{H}$ and $\delta^{18}\text{O}$, respectively. High temporal and spatial variation in $\delta^2\text{H}$ and $\delta^{18}\text{O}$
18 was more clearly observed in the top and bottom samples from Obs8. This high variation may
19 indicate a short percolation time and the influence of surface water from the gravel excavation
20 pit and lake water.

21 The median concentrations of major ions in the groundwater were low and close to the median
22 concentrations of precipitation (Vuorimaa et al., 1999; Järvinen and Vänni, 1996, 1997), being
23 lower than the median values of shallow groundwater in Finland (Lahermo et al. 2002). The
24 concentrations of minor ions and trace elements (F, Fe, Ag, Be, Bi, Br, Cd, Co, Cr, P, PO_4 , Se,
25 Th and Tl) in many wells were below or close to the detection limit. However, the median
26 values of metals and trace elements such as Fe, As, Cd, Cr, Ni, Pb, Sb, Se, I, Li and PO_4 from
27 groundwater samples were higher than those reported by Lahermo et al. (2002) (Table 2).

28 The piper diagram in Figure 6 illustrates that the composition of groundwater in Santala is
29 mainly of the Ca-HCO_3 type, with no cation exchange taking place, and only the top and mixed
30 samples from Obs6 fall closer to the Na-Cl type. The Ca-HCO_3 type of groundwater, with low
31 dissolved ion concentrations, low pH, alkalinity, Ca and Mg, is a common groundwater type for
32 glaciated areas in Finland (e.g. Backman et al., 1999; Soveri et al., 2001; Korkka-Niemi, 2001;

1 Lahermo et al., 2002; Backman, 2004). Allen (2004) reported that this type of groundwater
2 indicates young groundwater derived from direct percolation or having a short resident time, or
3 that no substrate, e.g. clay minerals, is present for cation exchange. This is consistent with the
4 finding of low dissolved concentrations of elements in many groundwater samples.

5 The chloride concentrations of all groundwater samples varied between 1.5 and 28.3 mg l⁻¹, and
6 differed considerably from the seawater sample, which had a Cl concentration of 2 690 mg l⁻¹.
7 Elevated Na and Cl concentrations found in top sample from Obs6 were much higher than those
8 in the bottom sample from the same observation well in and nearby wells, and they had no
9 correlations with the other variables. Obs6 is situated about 50 m in a downstream direction
10 from the highway running through the middle of the aquifer. Elevated concentrations of Na and
11 Cl in this well indicate the influence of de-icing chemicals (NaCl) on the top section of Obs6,
12 while the bottom section contained low dissolved concentrations overall, which were the same
13 as in the nearby wells. The use of salt for de-icing purposes in Finland increased in 1987, with a
14 peak in 1990, when 157 000 tons of salt was applied along the highways in Southern Finland.
15 Many of these run on top of the First Salpausselkä formation, including the Hanko area. There
16 have been attempts to reduce the use of de-icing road salt since 1993 (Gustafsson and Nystén,
17 2000). The aquifer materials in the area of Obs6 consist of the interbedded layers of sand and
18 fine-grained sediments (Luoma et al., 2013). The fine-grained layers could prevent the
19 distribution of Na and Cl from groundwater to the top section of the well.

20 No intrusion of seawater was observed in Obs10 or Obs11, which are located close the coastline
21 and the water intake well. The chloride concentration of seawater in this study was 2 690 mg l⁻¹,
22 which is consistent with other studies, e.g. Alenius et al. (1998) and Fagerlund (2008). The Cl
23 contribution to the groundwater in Obs10 and Obs11, calculated from the Cl concentrations of
24 water samples, seawater and fresh water (Appelo and Postma, 2005), was less than 0.5%, which
25 was very small and could have had another origin than direct seawater intrusion, e.g.
26 atmospheric fallout. However, according to the piper diagram, sulphate reduction may possibly
27 be observed in Obs11, approx. 60 m from the coastline. Obs11 is located in a low-lying area
28 with a well head elevation of 0.5 m a.s.l. Water from this well had the highest SO₄ concentration
29 of 38.3 mg l⁻¹, with CO₂ and O₂ concentrations of 29.0 and 4.1 mg l⁻¹, respectively. Based on the
30 geochemistry of three water samples from this well, SO₄ showed a strong negative correlation
31 with HCO₃ (r = 0.98). Seawater has a high SO₄ concentration, and when it intrudes into an
32 aquifer, especially into an anoxic low-lying coastal aquifer, it may result in sulphate reduction
33 (Andersen, 2001; Appelo and Postma, 2005) and have a negative correlation with HCO₃.

1 However, the reduction of sulphate combined with the enrichment of bicarbonate in the mixing
2 zone suggests bacterial reactions (Magaritz and Luzier, 1985). The monitoring data indicate that
3 the groundwater level is occasionally lower than the seawater level, either due to overpumping
4 or sea level rise, which could temporarily cause seawater intrusion into the aquifer.

5 **5.2 Spatial distribution of groundwater geochemistry**

6 **5.2.1 Principal Component Analysis (PCA)**

7 Statistically significant correlations were detected between certain variables and therefore,
8 principal component analysis (PCA) was conducted (Table 3) in order to group the variables.
9 After Varimax rotation with Kaiser normalization, four principal components having
10 eigenvalues higher than one were chosen, because they explained over 80% of the total variance
11 observed (Cloutier et al, 2008; IBM SPSS Statistics, 2013). The factor score of each principal
12 component was calculated for each of the samples as showed in Table 4.

13 PC1 is characterized by highly positive loading in SO₄, K, Ba, Cu, Mo, Mg, I, Mn, Li, and Si,
14 explaining 43.8% of the total variance. The highest scores were found in Obs10, Obs9 and
15 Obs11, and moderate to low positive scores were also observed in Obs1 and Obs2_0412
16 samples. PC1 mainly indicates the natural groundwater quality, and comprises wells that
17 penetrate the primary deposit of the First Salpausselkä formation (Luoma et al. 2013), together
18 with Obs10 and Obs11 located further in the discharge area. The primary deposit of the First
19 Salpausselkä formation consists of glacial till, gravel, sand and clay of the glaciogenic
20 sediments resulting from the erosion of the pre-existing Precambrian bedrock, e.g. granite,
21 quartz diorite and granodiorites. PC1 reveals the influence of a natural origin on groundwater
22 quality from the dissolution of minerals bearing the aquifer material, such as sulphide, K-
23 feldspar or clay minerals (Lahermo et. al., 2002; Shand and Edmunds, 2008). Shotyk et al.
24 (2009) reported high concentrations of S, Si, Ba, Mg, Mn, Li and Rb in groundwater resulting
25 from weathering of the dominant silicate minerals in sediments of a discharge area in two
26 natural artesian flows in Ontario, Canada.

27 PC2 has the highest loadings for Ca, alkalinity, pH, EC, NO₃ and Sr, explaining 18.0% of the
28 total variance. It has a highly positive loading in Obs8 and Obs10. A low positive loading was
29 also observed in Obs6_0812top sample. The variables in PC2 have a strong to very strong
30 positive correlation among each other, especially Ca, alkalinity, Sr and EC, which have Pearson
31 correlation coefficients among each other of between 0.99 and 0.92 ($\rho < 0.01$). PC2 is related to
32 the solution of carbonate in the groundwater. Obs8 and Obs10 contain the highest

1 concentrations of Ca, Sr and EC, and are distinct from the other wells in the study area. Obs8 is
2 located next to a gravel pit and a concrete factory, and Obs10 is located in a downstream
3 direction from Obs8. The excess Sr associates with Ca and HCO_3 (alkalinity) compared with the
4 surrounding wells, indicating the potential contamination of the groundwater from human
5 activity, similarly to NO_3 , which has the highest concentrations in Obs8 and Obs10. Although
6 NO_3 could be derived from the dissolution of organic matter under reducing conditions, the
7 increases in NO_3 , EC and other dissolved ion concentrations in Obs10 since 2010 during the
8 sampling period may indicate an anthropogenic effect from human activity taking place in this
9 area.

10 PC3 explains 11.6% of the total variance and has a high positive loading in KMnO_4
11 consumption and the stable isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$. The highest scores were found in lake water
12 and Obs2_0412 samples, and moderate scores in Obs2_0812 and Obs10. PC3 reveals the
13 influences of surface water on the groundwater. The KMnO_4 consumption values in
14 groundwater indicate an influence of surface water or dissolved organic matter (Korkka-Niemi,
15 2001; Lahermo et. al., 2002). In many wells, the concentrations of major ions and some other
16 dissolved ions in groundwater were higher in spring samples than in summer samples, while
17 KMnO_4 consumption was higher in summer than in spring. Based only on KMnO_4
18 consumption, the influence of surface water should be more clearly observed in summer.
19 However, the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values reveal the possible influence of surface water from the lake
20 in Obs2_0412, but no influence of surface water in Obs2_0812 and Obs10. Obs11 is located
21 closer to the seashore than Obs10. Based on its location, Obs11 should display a greater
22 influence from seawater than Obs10. However, PC3 extracted the information existing in
23 Obs10, which has a higher KMnO_4 consumption than Obs11 and contributed a higher factor
24 score loading than Obs11. PC3 indicates the influences of surface water or surface water-
25 induced dissolved organic matter on groundwater quality at Obs10.

26 PC4 has highly positive loadings in Na and Cl, and explains 7.1% of the total variance. The
27 highest scores were found in mixed and top samples from Obs6, while the Obs6 bottom sample
28 showed a negative score. Moderate to low positive scores were also found in Obs9, Obs10 and
29 Obs11. PC4 indicates the impact of human activities on groundwater quality, such as the
30 influences of road de-icing salt in the top section of Obs6, which is located about 50 m in a
31 downstream direction from the highway. The median concentrations of Na and Cl in Obs9,
32 Obs10 and Obs11 (7.3 and 7.9 mg l^{-1} , respectively) were higher than the background values
33 reported by Lahermo et al. (2002; 4.18 and 4.40 mg l^{-1} , respectively). Sodium and Cl of those 3

1 wells showed a positive correlation with Ca, alkalinity, Sr and EC, the main factor components
2 found in PC2. PC1 reveals the natural impact on the groundwater quality in Obs9, Obs10 and
3 Obs11, while PC4 may indicate some influences of human activity on these wells.

4 Overall, PCA is a useful tool to extract the main components that represent the impacts of both
5 natural and human activities on water quality, either at regional or site-specific scales, and
6 Obs10 has been identified as the most vulnerable well, which has been impacted by both natural
7 and human activities.

8 **5.2.2 Hierarchical cluster analysis (HCA)**

9 The results of HCA are presented based on the sample locations in the dendrogram in Figure 7.
10 The clusters were classified based on the linkage distance in the dendrogram, indicating the
11 level of similarity of variables between clusters. The shorter the linkage distance, the higher the
12 similarity of variables between clusters. Based on the linkage distance at 9, the water samples
13 were classified into 6 clusters (C1–C6). C1 consists of Obs3, Obs4, Obs5, Obs6_bottom and
14 Obs7, C2 consists of Obs6_top and Obs6_mixed samples, and C3 consists of Obs1, Obs2 and
15 lake water. C4 consists of all samples from Obs8, C5 of samples from Obs10, and C6 consists
16 of Obs9 and Obs11. The median values of the main variables in each cluster (excluding lake
17 water) are summarized in Table 5.

18 C1, C2 and C3 comprise lower median values of variables compared with C4, C5 and C6. The
19 main differences between C1, C2 and C3 are that C2 contains the highest Na and Cl
20 concentrations compared to the others, and C3 contains the highest concentrations of Al and
21 KMnO_4 consumption. These clusters consist of wells that are located in the groundwater recharge
22 area in the middle of the aquifer, and could be grouped into the same cluster. However, with the
23 classification based on the linkage distance at 9, C2 could emphasize the influences of de-icing
24 with road salt in the top section of Obs6, and C3 the influence of lake water on groundwater in
25 Obs2 and Obs1. C2 and C3 are in agreement with PC4 and PC3, respectively, except that PC3
26 shows no principal component loading for Obs1.

27 C4, C5 and C6 consist of wells located closer to the groundwater discharge and areas of human
28 activity. Some dissolved ions in groundwater found in C4 were quite low and close to C1, C2
29 and C3, but elevated concentrations of Ca, HCO_3 , Sr, EC, pH and NO_3 linked it to C5, which
30 indicates the impact of human activities from the gravel excavation pit and the concrete factory.
31 C5 and C6 contain higher dissolved solute concentrations than the other clusters and are linked

1 together due to sharing the same or a similar natural origin and probably also some influences
2 from human activities. C4 and C5 are consistent with PC2, and PC5 and PC6 are consistent with
3 PC1.

4 Well-proven PCA and HCA approaches have been used before in order to determine natural
5 components affecting groundwater quality (e.g. Cloutier et al., 2008; Güler et al., 2002). In this
6 study, the integration of PCA and HCA with conventional classification of groundwater types,
7 and the hydrogeochemical data provided useful tools to classify groundwater samples based on
8 the main (natural or anthropogenic) variable components that may influence the geochemistry of
9 groundwater in Finland as performed also by Korkka-Niemi (2001). Moreover, this integration
10 seem to be suitable to identify the vulnerable groundwater areas impacted by both natural and
11 human activities on water quality, and the results could contribute to the groundwater
12 vulnerability assessments of the coastal aquifers (Ferguson and Gleeson, 2012).

13 **5.3 Temporal variability in groundwater geochemistry**

14 Temporal variations in dissolved solute concentrations in groundwater were examined for all
15 groundwater samples between different seasons: spring (April) 2010, spring (April) 2012 and
16 summer (August) 2012. Only data from 4 observation wells (Obs1, Obs8, Obs10 and Obs11)
17 were available for all 3 seasons. The annual precipitation of 2012 was exceptionally high, being
18 about 41% higher than the mean annual precipitation of 1981–2010, and it was the highest
19 recorded precipitation since 1963 (FMI, 2013). The annual precipitation from April 2011 to
20 April 2012 (876 mm) was 322 mm higher than the period April 2009 to April 2010 (554 mm).
21 In 2012, groundwater reached the highest level in April 2012, immediately after snowmelt.
22 However, the amount of precipitation continued to increase during June to the end of the year
23 due to the increase in heavy rain events during that period (Fig. 2). The percentage changes
24 between seasons in the concentrations of selected dissolved elements in different observation
25 well locations are presented in Table 6. A positive number indicates an increase in dissolved
26 concentrations. Table 6 indicates the variations in the amount of precipitation or timing of
27 recharge in different seasons, which has an effect on groundwater quality. However, the aquifer
28 area has mostly received the same amount of precipitation at a time, and the dissolved
29 concentrations of elements in groundwater have varied spatially in different well locations.
30 Overall, the concentrations of Ca, HCO₃, EC, and KMnO₄ consumption increased in most wells
31 with an increase in precipitation. Obs6 and Obs4 showed very high variations in KMnO₄
32 consumption relative to the other wells. An increase in KMnO₄ consumption implies the

1 influences of surface water or dissolved organic matter (Korkka-Niemi, 2001; Lahermo et al.,
2 2002).

3 Obs10 had higher EC and dissolved ion concentrations than the other wells, and EC, Ca, HCO₃,
4 and KMnO₄ consumption have increased since April 2010, while the Cl concentration has
5 decreased. Obs10 contained the highest NO₃ concentration, although an increasing
6 concentration of NO₃ since April 2010 was observed in Obs11, downstream from Obs10. In
7 addition, Obs10 showed an increase in metals concentrations in groundwater following the
8 increase in precipitations since April 2010. Okkonen and Kløve (2011) and Korkka-Niemi
9 (2001) reported a decrease in the concentration of NO₃ in groundwater during the spring, when
10 recharge from snowmelt occurs. In contrast, high NO₃ concentrations in spring and autumn
11 were found due to increased nitrogen leaching associated with the increase in runoff from forest
12 (Lepistö, 1996) and drained peatlands (Kløve, 2001).

13 The concentrations of Fe, Al, Mn, and SO₄ were occasionally high during spring, immediately
14 after the snowmelt (both in April 2010 and April 2012). However, their concentrations were
15 highly variable and often associated with low pH values observed in Obs1, Obs2, Obs4 and
16 Obs11. Iron, Mn and SO₄ are redox-sensitive elements in groundwater and are soluble under
17 reducing conditions (Hem, 1985; Shand and Edmunds, 2008). High concentrations of Al can be
18 associated with clay minerals or organic matter, and Al had a high positive correlation with
19 KMnO₄ consumption, with a Pearson correlation coefficient of 0.79 ($\rho < 0.01$).

20 Based on the future climate scenarios A1B and B1, by the end of 2100, precipitation in the
21 Hanko area is expected to increase by 12–26% compared with the current situation and the sea
22 level will rise by up to 0.51 m above the current mean sea level (Luoma and Okkonen, 2014).
23 The potential increase in precipitation during the autumn and winter in the future could cause
24 more freshwater to enter the aquifer and possibly a greater influence of seawater intrusion due
25 to the sea level rise and storm surges. Based on the observed seasonal variation, an increase in
26 the concentrations of some dissolved elements, as mentioned earlier, and changes in the
27 groundwater geochemistry of wells along the coastline can be expected.

28 **6 Conclusions**

29 This study clearly demonstrated that the geochemistry of groundwater in the shallow,
30 unconfined, low-lying coastal aquifer in Santala has spatial and temporal variability depending
31 on the geological, anthropogenic, seawater and climate factors. The groundwater is mainly of

1 the Ca-HCO₃ type, with low dissolved element concentrations, low pH, alkalinity, Ca and Mg
2 concentrations due to rapid percolation or a short residence time. An important finding was that
3 the groundwater geochemistry of the coastal aquifer in Santala was generally very similar to that
4 of inland shallow aquifers in Finland. The stable isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$ clearly suggest that the
5 Santala aquifer recharges directly from meteoric water (snowmelt and rainfall), with minor or
6 insignificant contributions from the Baltic Sea and the lake above the aquifer. However, the
7 high temporal and spatial variability of the stable isotopes from wells near the gravel excavation
8 pit and the lake indicate the direct influence of surface water, indicating local mixing between
9 groundwater and surface water within the aquifer. This was observed from the increases in
10 KMnO₄ consumption in wells near the lake. While both $\delta^2\text{H}$ and $\delta^{18}\text{O}$ provided no evidence of
11 seawater intrusion in the aquifer, the geochemistry of groundwater suggests sulphate reduction
12 in the mixed zone between fresh and seawater, indicating local seawater intrusion may
13 temporarily take place. Although the salinity of the Baltic Sea is low, the groundwater pumping
14 wells need to be carefully positioned and the pumping rates well managed to avoid such a
15 mixing zone. The findings also showed that the use of stable isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$ alone to
16 identify seawater–aquifer interaction is not sufficient to determine the rate of water exchange.

17 The geochemistry of groundwater in Santala aquifer varies spatially and temporally according to
18 changes in the hydrological conditions, such as precipitation events and snowmelt. The
19 concentrations of Ca and HCO₃, EC, and KMnO₄ consumption increased in most monitored
20 wells with an increase in precipitation, while the concentrations of Fe, Al, Mn, and SO₄ were
21 occasionally higher soon after snowmelt. The multivariate statistical approaches PCA and HCA
22 yielded similar results. Those are useful tools to extract the main components that are able to
23 identify the vulnerable areas of the coarse grained glaciogenic aquifer impacted by natural or
24 human activities, either at regional or site-specific scales. In coastal aquifers with low hydraulic
25 gradient, the hydrogeochemistry should be used to confirm the intrusion of seawater.

26 Based on the future climate scenarios, precipitation in the Hanko area is expected to increase, as
27 well as the Baltic Sea level. This could cause increased recharge of the aquifer from surface
28 water, but also some seawater intrusion due to the sea level rise and storm surges as well as
29 increased groundwater abstraction. An increase in the concentrations of some dissolved
30 elements and changes in groundwater geochemistry along the coastline can be expected in the
31 future. The integration of PCA and HCA with conventional classification of groundwater types,
32 as well as, with the hydrogeochemical data provided an understanding of complex groundwater
33 flow system for the aquifer vulnerability assessment and groundwater management in the future.

1 The approach used in this study could be applied in the other low-lying coastline aquifers
2 worldwide, including the Baltic Sea Region such as in Finland, where approximately 300 of the
3 total classified 6000 Finnish shallow groundwater aquifers locate less than 100 m from the
4 Baltic Sea shoreline.

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13 **References**

- 14 Alenius, P., Myrberg, K., and Nekrasov, A.: The physical oceanography of the Gulf of Finland:
15 a review, *Boreal Environment Research*, 3, 97-125, 1998.
- 16 Allen, D. M.: Sources of groundwater salinity on islands using ^{18}O , ^2H , and ^{34}S , *Ground Water*,
17 42, 17-31, 2004.
- 18 Andersen, M. S.: Geochemical processes at a seawater-freshwater interface, Ph.D. Thesis,
19 Technical University of Denmark, Kgs. Lyngby, 2001.
- 20 Appelo, C. A., and Postma, D.: *Geochemistry, groundwater and pollution*, A.A. Balkema
21 Publishers, Leiden, the Netherlands, 2005.
- 22 Backman, B., Lahermo, P., Väisänen, U., Paukola, T., Juntunen, R., Karhu, J., Pullinen, A.,
23 Rainio, H., and Tanskanen, H.: *Geologian ja ihmisen toiminnan vaikutus pohjaveteen,*
24 *Seurantatutkimuksen tulokset vuosilta 1969–1996, Summary: The effect of geological*
25 *environment and human activities on groundwater in Finland, Results of monitoring in 1969–*
26 *1996, Report of Investigations 147, Geological Survey of Finland, Espoo, 1999.*
- 27 Backman, B.: Groundwater quality, acidification, and recovery trends between 1969 and 2002
28 in South Finland, *Bulletin 401, Geological Survey of Finland, Espoo, 2004.*

- 1 Backman, B., Luoma, S., Schmidt-Thomé, P., and Laitinen, J.: Potential risks for shallow
2 groundwater aquifers in coastal areas of the Baltic Sea, a case study in Hanko area in south
3 Finland, CIVPRO Working Paper 2007: 2, Geological Survey of Finland, Espoo, 2007.
- 4 Barlow, P. M.: Ground water in fresh water-salt water environments of the Atlantic Coast, U.S.
5 Geological Survey circular 1262, 2003.
- 6 Clark, I. D., and Fritz, P.: Environmental Isotopes in Hydrology, CRC Press, Lewis Publishers,
7 Boca Raton, Florida, 1997.
- 8 Cloutier, V., Lefebvre, R., Therrien, R., and Savard, M. M.: Multivariate statistical analysis of
9 geochemical data as indicative of the hydrogeochemical evolution of groundwater in a
10 sedimentary rock aquifer system, *Journal of Hydrogeology*, 353, 294-313, 2008.
- 11 Csuros, M.: Environmental sampling and analysis for technicians, Lewis Publishers/CRC Press
12 Boca Raton, Florida. USA. 1994.
- 13 Drever, J. I.: The geochemistry of natural waters, *Surface and Groundwater Environments*, 3rd
14 Editions, Prentice – Hall, 1997.
- 15 EEA: Groundwater quality and quantity in Europe, Nixon, S. (Ed.), European Environment
16 Agency, Copenhagen, 1999.
- 17 Fagerlund, G.: Chloride transport and reinforcement corrosion in concrete exposed to sea water
18 pressure, Division of Building Materials, Lund University, 2008.
- 19 Faure, G., and Mensing, T. M.: *Isotopes: Principles and Applications*, Wiley, John and Sons,
20 Incorporated, 2005.
- 21 Ferguson, G., and Gleeson, T.: Vulnerability of coastal aquifers to groundwater use and climate
22 change, *Nature Climate Change*, 2, 342-345, 2012. doi:10.1038/nclimate1413.
- 23 FMI: Finnish Meteorological Institute (FMI), <http://www.fmi.fi> , last access 20 March 2013.
- 24 Fyfe, G. J.: The morphology and sedimentology of the Salpausselkä I Moraine in southwest
25 Finland, Cambridge University: Fitzwilliam College, 1991.
- 26 Gonfiantini, R.: Environmental isotopes in lake studies, In: Fritz, P., and Fontes, J., C. (Eds.),
27 *Handbook of Environmental Isotope Geochemistry*, The Terrestrial Environment B, 2, Elsevier,
28 Amsterdam, 113–168, 1986.
- 29 Güler, C., Thyne, G. D., McCray, J. E., and Turner, A. K.: Evaluation of graphical and
30 multivariate statistical methods for classification of water chemistry data, *Journal of*
31 *Hydrogeology* 10, 455-474, 2002.

- 1 Gustafsson, J., and Nystén, T.: Trends of chloride concentration in groundwater and results of
2 risk assessment of road salting in Finland. In: Bjerg, P., Engesgaard, P., and Krom, T. (Eds.),
3 Ground Water 2000: Proceedings of the International Conference on Ground Water Research,
4 Copenhagen, Denmark, A.A. Balkema, Rotterdam, Netherlands, 249-251, 2000.
- 5 Harbison, J. E.: Groundwater chemistry and hydrological processes within a Quaternary coastal
6 plain: Pimpama, Southeast Queensland, PhD Thesis, Queensland University of Technology,
7 2007.
- 8 Hem, J. D.: Study and Interpretation of the Chemical Characteristics of Natural Water, 3rd
9 Editions, Alexandria, VA: Department of the Interior, U.S. Geological Survey Water Supply
10 Paper 2254, 1985.
- 11 Hendriksson, N., Saraperä, S., and Artimo, A.: Stable isotopes in monitoring artificial recharge
12 and validating 3D groundwater flow model results - congress program and abstracts, The 39th
13 International Association of Hydrogeologists Congress, September 16-21, 2012, Niagara Falls,
14 Canada, 402-403, 2012.
- 15 Hertta Database-SYKE: HERTTA - Environmental information data systems from Finnish
16 Environment Institute (SYKE), <http://www.ymparisto.fi/>, last access: 27 November 2013.
- 17 IBM SPSS Statistics: Data and Statistical Analysis Software System Version 21, 2013.
- 18 IPCC: Emissions Scenarios: Summary for Policymakers – A Special Report of IPCC Working
19 Group III, 2000.
- 20 IPCC: Summary for Policymakers. In: Parry, M. L., Canziani, O. F., Palutikof, J. P., Van der
21 Linden, P. J., and Hanson, C. E., (Eds.), Climate Change 2007: Impacts, Adaptation and
22 Vulnerability, Contribution of Working Group II to the Fourth Assessment Report of the
23 Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, UK, 7-
24 22, 2007.
- 25 Järvinen, O., and Vänni, T.: Sadeveden pitoisuus- ja laskeuma-arvot Suomessa vuonna 1995
26 (Concentrations of rainwater and deposition values in Finland during 1995, in Finnish), Finnish
27 Environment Institute (SYKE), 1997.

- 1 Järvinen, O., and Vänni, T.: Sadeveden pitoisuus- ja laskeuma-arvot Suomessa vuonna 1994
2 (Concentrations of rainwater and deposition values in Finland during 1994, in Finnish), Finnish
3 Environment Institute (SYKE), 1996.
- 4 Jyrkama, I. M., and Sykes, J. F.: The impact of climate change on spatially varying groundwater
5 recharge in the grand river watershed (Ontario), *Journal of Hydrology*, 338, 237-250, 2007.
- 6 Kendall, C., and McDonnell, J. J. (Eds.): *Isotope tracers in catchment hydrology*, Elsevier, The
7 Netherlands, 1998.
- 8 Kielosto, S., Kukkonen, M., Sten C. G., and Backman, B.: Hangon ja Perniön kartta-alueiden
9 maaperä, English summary: Quaternary deposits in the Hanko and Perniö map-sheet areas,
10 Geological map of Finland 1: 100 000, Explanation to the maps of Quaternary deposits, sheets
11 2011 and 2012, Geological Survey of Finland, Espoo, 1996.
- 12 Kløve, B.: Characteristics of nitrogen and phosphorus loads in peat mining wastewater, *Water
13 Research*, 35 (10), 2353-2362, 2001.
- 14 Korkka-Niemi, K.: Cumulative geological, regional and site-specific factors affecting
15 groundwater quality in domestic wells in Finland, *Monographs of the Boreal Environment
16 Research*, 20, 2001.
- 17 Kortelainen, N. M., and Karhu, J. A.: Regional and seasonal trends in the oxygen and hydrogen
18 isotope ratios of Finnish groundwaters: a key for mean annual precipitation, *Journal of
19 Hydrology* 285, 143–157, 2004.
- 20 Kortelainen, N., and Karhu, J. A.: Tracing the decomposition of dissolved organic carbon in
21 artificial groundwater recharge using carbon isotope ratios. *Applied Geochemistry*, 21 (4), 547-
22 562, 2006.
- 23 Kortelainen, N.: Isotopic fingerprints in surficial waters: stable isotope methods applied in
24 hydrogeological studies, Geological Survey of Finland, Ph.D. Thesis, Department of Geology,
25 Faculty of Science, Helsinki University, Finland, 2007.
- 26 Kortelainen, N.: Isotopic composition of atmospheric precipitation and shallow groundwater in
27 Olkiluoto: O-18, H-2 and H-3, Working Report 2009-06, Olkiluoto, Posiva, 2009.
- 28 Lahermo, P., Tarvainen, T., Hatakka, T., Backman, B., Juntunen, R., Kortelainen, N., Lakomaa,
29 T., Nikkarinen, M., Vesterbacka, P., Väisänen, U., and Suomela, P.: Tuhat kaivoa- Suomen
30 kaivovesien fysikaalis-kemiallinen laatu vuonna 1999 (Summary: One thousand wells-the

- 1 physical-chemical quality of Finnish well waters in 1999), Report of Investigation 155,
2 Geological Survey of Finland, Espoo, 2002.
- 3 Lepistö, A.: Hydrological processes contributing to nitrogen leaching from forested catchments
4 in Nordic conditions, Monographs of the Boreal Environment Research 1, 1-71, 1996.
- 5 Luoma, S., and Pullinen, A.: Field Investigation and Estimates of Hydraulic Conductivity from
6 Slug Tests in the First Salpausselkä formation in the Santala area, Hanko, south Finland,
7 Archived report, Geological Survey of Finland, Espoo, 2011.
- 8 Luoma, S., Klein, J., and Backman, B.: Climate change and groundwater: Impacts and
9 Adaptation in shallow coastal aquifer in Hanko, south Finland, In: Schmidt-Thomé, P., and
10 Klein, J. (Eds.), Climate Change Adaptation in Practice – From Strategy Development to
11 Implementation, Wiley-Blackwell, ISBN: 978-0470977002 137-155, 2013.
- 12 Luoma, S., and Okkonen, J.: Impacts of Future Climate Change and Baltic Sea Level Rise on
13 Groundwater Recharge, Groundwater Levels, and Surface Leakage in the Hanko Aquifer in
14 Southern Finland, *Water*, 6, 3671-3700, 2014. doi:10.3390/w6123671. 2014.
15 <http://www.mdpi.com/2073-4441/6/12/3671> , last access: 28 November 2014.
- 16 Magaritz, M., and Luzier, J. E.: Water-rock interactions and seawater-freshwater mixing effects
17 in the coastal dunes aquifer, Coos Bay, Oregon, *Geochimica et Cosmochimica Acta*, 49, 2515-
18 2525, 1985.
- 19 Mongelli, G., Monni, S., Oggiano, G., Paternoster, M., and Sinisi, R.: Tracing groundwater
20 salinization processes in coastal aquifers: a hydrogeochemical and isotopic approach in the Na-
21 Cl brackish waters of northwestern Sardinia, Italy, *Hydrology and Earth System Sciences*, 17,
22 2917-2918, Doi: 10.5194/hess-17-2917-2013, 2013.
- 23 Nicholls, R. J., Wong, P. P., Burkett, V. R., Codignotto, J. O., Hay, J. E., McLean, R. F.,
24 Ragoonaden, S., and Woodroffe, C. D.: Coastal systems and low-lying areas, *Climate Change*
25 2007: Impacts, Adaptation and Vulnerability, Contribution of Working Group II to the Fourth
26 Assessment Report of the Intergovernmental Panel on Climate Change, Parry, M. L., Canziani,
27 O. F., Palutikof, J. P., Van der Linden, P. J., and Hanson, C.E. (Eds.), Cambridge University
28 Press, Cambridge, UK, 315-356, 2007.
- 29 Okkonen, J., and Kløve, B.: Assessment of temporal and spatial variation in chemical
30 composition of groundwater in an unconfined esker aquifer in the cold temperature climate of
31 Northern Finland, *Cold Regions Science and Technology*, 118-128, 2011.

- 1 Okkonen, J.: Groundwater and its response to climate variability and change in cold snow
2 dominated regions in Finland: Methods and Estimations, Ph.D. Thesis, University of Oulu,
3 Finland, 2011.
- 4 Oude Essink, G. H. P.: Impact of sea-level rise in the Netherlands, In: Bear, J., Cheng, A. H. D.,
5 Sore, S., Quasar, D., and Herrera, I. (Eds.), *Seawater Intrusion in Coastal Aquifers: Concepts,*
6 *Methods and Practices, Theory and Applications of transport in Porous Media,* Kluwer
7 Academy, Norwell, Massachusetts, 507-530, 1999.
- 8 Oude Essink, G. H. P.: Improving fresh groundwater supply-problems and solutions, *Ocean and*
9 *Coastal Management*, 44, 429-449, 2001.
- 10 Oude Essink, G. H. P., Van Baaren, E. S., and De Louw, P. G. B.: Effects of climate change on
11 coastal groundwater systems: A modeling study in the Netherlands, *Water Resources Research*,
12 46 (1), W00F04, doi: 10.1029/2009WR008719, 2010.
- 13 Pulido-Leboeuf, P.: Seawater intrusion and associated processes in a small coastal complex
14 aquifer (Castell de Ferro, Spain), *Applied Geochemistry*, 19, 1517-1527, 2004.
- 15 Piper, A. M.: A graphic procedure in the geochemical interpretation of water analyses:
16 *American Geophysical Union Transactions*, 25, 914–923, 1944.
- 17 Rasmussen, P., Sonnenborg, T. O., Goncear, G., and Hinsby, K.: Assessing impacts of climate
18 change, sea level rise, and drainage canals on saltwater intrusion to coastal aquifer, *Hydrology*
19 *and Earth System Sciences*, 17, 421-443, 2013.
- 20 Rautio, A., and Korkka-Niemi, K.: Characterization of groundwater-lake water interactions at
21 Pyhäjärvi, a lake in SW Finland, *Boreal Environment Reserarch*, 16, 363-380, 2011.
- 22 Richter, B. C., and Kreitler, C. W.: *Geochemical Techniques for Identifying Sources of Ground*
23 *water Salinization*, CRC Press, Inc. Boca Raton, Florida, 1993.
- 24 Saarnisto, M., and Saarinen, T.: Deglaciation chronology of the Scandinavian Ice Sheet from the
25 Lake Onega basin to the Salpausselkä end moraines, In: Thiede, J. et al. (Eds.) *The Late*
26 *Quaternary stratigraphy and environments of northern Eurasia and the adjacent Arctic seas –*
27 *new contributions from QUEEN: selected papers from the annual QUEEN workshop held in*
28 *Øystese, Norway, April 1999, and in Lund, Sweden, April 2000, Global and Planetary Changes,*
29 31 (1-4), 387-405, 2001.

- 1 Scibek, J., and Allen, D. M.: Modeled Impacts of Predicted Climate Change on Recharge and
2 Groundwater Levels, *Water Resources Research*, 42, W11405, doi:10.1029/2005WR004742,
3 2006.
- 4 Scibek, J., Allen, D. M., Cannon, A., and Whitfield, P.: Groundwater-surface water interaction
5 under scenarios of climate change using a high-resolution transient groundwater model, *Journal*
6 *of Hydrology*, 333, 165-181, 2007.
- 7 Shand, P., and Edmunds, W. M.: The Baseline Inorganic Chemistry of European Groundwaters,
8 In: Edmunds, W. M., and Shand, P. (Eds.), *Natural Groundwater Quality*, Blackwell Publishing
9 Ltd., 22-58, 2008.
- 10 Shotyk, W., Krachler, M., Aeschbach-Hertig, W., Hillier, S., and Zheng, J.: Trace elements in
11 recent groundwater of an artesian flow system and comparison with snow: enrichments,
12 depletions, and chemical evolution of the water, *Journal of Environmental Monitoring*, 12, 208–
13 217, 2010.
- 14 Soveri, J., Mäkinen, R., and Peltonen, K.: *Changes in Groundwater Levels and Quality in*
15 *Finland 1975-1999*. Tummavuoren kirjapaino Oy, Helsinki, Finland, 2001.
- 16 STM: Decree of the Ministry of Social Affairs and Health (STM) relating to the quality and
17 monitoring of water intended for human consumption No. 461/ 2000, available at:
18 <http://www.finlex.fi/fi/laki/kaannokset/2000/en20000461.pdf> , 2001.
- 19 Taylor, R. G., and Howard, K. W. F.: Groundwater recharge in the Victoria Nile basin of east
20 Africa: support for the soil moisture balance approach using stable isotope tracers and flow
21 modeling, *Journal of Hydrology*, 180, 31–53, 1996.
- 22 Templ, M., Filzmoser, P., and Reimann, C.: Cluster analysis applied to regional geochemical
23 data: Problems and possibilities, *Applied Geochemistry*, 23, 2198-2213, 2008.
- 24 UNEP - Lääne, A., Kraav, E., and Titova, G.: *Baltic Sea - GIWA Regional assessment 17*,
25 University of Kalmar, Kalmar, Sweden, 2005.
- 26 USGS: GW_Chart (Version 1.26), U.S. Geological Survey, available at:
27 http://water.usgs.gov/nrp/gwsoftware/GW_Chart/GW_Chart.html , 2012.
- 28 Ward, J. H.: Hierarchical grouping to optimise an objective function, *Journal of the American*
29 *Statistical Association*, 58, 236-244, doi:10.2307/2282967, 1963.

- 1 Vuorenmaa, J., Järvinen, O., and Vänni, T.: Sadeveden pitoisuus- ja laskeuma-arvot Suomessa
- 2 vuonna 1997 (Concentrations of rainwater and deposition values in Finland during 1997, in
- 3 Finnish), Finnish Environment Institute (SYKE), 1999.

Table 1. Observation well information of the sampling depth, screen depth, and vadose zone thickness during the sampling periods. The negative vadose zone thickness means that well was flooded during the measurement.

Well	Sampling depth from ground surface (m)	Depth of diver from ground surface (m)	Screen interval from ground surface (m)	Screen length (m)	Well depth (m)	Vadose zone thickness in winter (m)	Sediments between ground surface and screen bottom (%)		
							Silt & fine sand	Sand	Gravel
Obs1	8	7	5.8-17.8	12	17.8	1.80	35	48	17
Obs2	10	8	3.5-18.5	15	28.5	1.62	63	38	
Obs3	10	no diver	5.4-32.4	27	36.4	3.89	14		86
Obs4	10	no diver	7.2-25.2	18	36.2	4.95	16	25	59
Obs5	8	no diver	4.8-10.8	6	10.8	5.90			100
Obs6	9	8	4.0-49.0	45	49.0	1.39	56	11	33
Obs6	7	partition sample - top							
Obs6	12	partition sample - bottom							
Obs7	7	8	5.7-8.7	3	8.7	2.95	88	4	8
Obs8	9	13	6.9-31.9	25	31.9	6.58	20	22	58
Obs8	7.7	partition sample - top							
Obs8	13.7	partition sample - bottom							
Obs9	10	8	6.0-14	8	17.0	2.79		45	55
Obs10	6	4	1.4-8.4	7	8.4	1.61	11	64	24
Obs11	6	5	1.7-8.7	7	8.7	-0.15	39	32	29
Obs12	4	no diver	1.0-5.0	4	5.0	1.88	31	38	31

Table 2. Characteristics of groundwater in Santala area, Hanko (number of samples, n = 32) compare with data from lake water, seawater, the median values from Lahermo et al. (2002) and precipitation from Vuorenmaa et al.(1999) and Järvinen and Vänni (1997, 1996), and safe drinking water (STM, 2001).

Variable	Unit	Min.	Median	Mean	Max.	Lake water (n=1)	Seawater (n=1)	Lahermo et al. 2002 (n=739)	Precip. (n=36)	Drinking water
Temperature	°C	5.70	7.00	7.39	10.40	8.50	7.80	6.80		
Eh	mV	161	255	258	354	279	230			
O ₂	mg l ⁻¹	0.84	5.19	6.08	11.7	7.70	13.1	60.9		
CO ₂	mg l ⁻¹	1.00	12.0	12.1	36.0	6.33	1.00	34.0		
EC	mS m ⁻¹	3.75	13.4	13.6	30.2	4.51	826		2.82	250
pH		5.50	6.55	6.61	8.00	6.20	8.41		4.50	6.5-9.5
Na	mg l ⁻¹	1.76	3.10	5.11	14.7	3.04	1360	4.18	0.66	
K	mg l ⁻¹	0.31	0.86	1.39	4.84	0.24	59.2	2.78	0.16	
Ca	mg l ⁻¹	2.48	9.94	17.0	47.0	3.38	69.3	11.4	0.40	
Mg	mg l ⁻¹	0.64	1.54	1.85	4.63	1.01	162	2.38	0.12	
Cl	mg l ⁻¹	1.50	3.50	6.50	28.3	3.60	2690	4.46	1.10	100
SO ₄	mg l ⁻¹	5.30	9.50	13.2	38.3	7.40	356	10.4	0.90	250
NO ₃	mg l ⁻¹	<0.2	0.75	1.97	7.00	1.50	<20	3.19	0.53	50.0
Alkalinity	mmol l ⁻¹	0.10	0.45	0.85	2.43	0.07	1.42	0.54		
HCO ₃	mg l ⁻¹	6.10	27.5	52.1	148	4.27	86.6	32.9		
KMnO ₄	mg l ⁻¹	0.32	1.80	2.56	10.0	21.0	26.0	4.50		20.0
Al	µg l ⁻¹	1.02	9.89	37.7	227	12.0	9.98	101		200
Mn	µg l ⁻¹	0.06	2.14	15.1	80.8	3.18	7.07	4.36		100
Fe	mg l ⁻¹	<0.03	0.08	0.15	0.31	0.06	<0.03	<0.03		0.40
As	µg l ⁻¹	<0.05	0.26	0.39	1.12	0.37	0.65	0.14		10.0
B	µg l ⁻¹	4.46	10.4	10.8	24.3	8.40	579	13.8		1000
Cd	µg l ⁻¹	<0.02	0.03	0.04	0.12	0.03	<0.02	<0.02		5.00
Cr	µg l ⁻¹	<0.20	0.39	0.47	1.15	<0.20	<0.20	0.20		50
Cu	µg l ⁻¹	<0.10	0.66	1.23	4.39	0.37	0.85	2.49		2000
Ni	µg l ⁻¹	<0.05	1.28	2.19	10.6	<0.05	0.95	0.84		20.0
Pb	µg l ⁻¹	<0.05	0.09	0.10	0.17	0.38	0.06	0.04		10.0
Sb	µg l ⁻¹	0.02	0.04	0.04	0.13	0.11	0.11	0.03		5.00
Se	µg l ⁻¹	<0.50	1.57	1.61	1.87	<0.50	25.1	<0.5		10.0
F	mg l ⁻¹	<0.10	0.24	0.31	0.73	<0.10	<1.00	<0.1		1.40
Ba	µg l ⁻¹	0.85	3.51	5.04	16.7	2.80	19.6	18.1		
Br	mg l ⁻¹	<0.10	<0.10	<0.10	<0.10	<0.10	19.1	9.92		
I	µg l ⁻¹	<2.00	4.68	6.44	19.8	2.62		2.12		
Li	µg l ⁻¹	<0.10	1.47	1.98	6.94	1.41	25.3	0.77		
PO ₄	mg l ⁻¹	<0.02	0.03	0.04	0.13	<0.02	0.10	<0.02		
Si	mg l ⁻¹	3.64	6.13	6.57	9.85	0.10	0.37			
Sr	µg l ⁻¹	13.0	42.7	62.6	163	11.9	1300	59.9		
Zn	µg l ⁻¹	0.69	4.20	7.20	53.4	12.2	7.75	10.4		

Table 3. Principal component loadings from factor analysis and explained variances of geochemical variables and stable isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of water samples. Factor loadings > 0.7 are marked as bold.

Parameter	Principal component (PC)			
	1	2	3	4
$\delta^2\text{H}$	-0.08	-0.17	0.86	-0.05
$\delta^{18}\text{O}$	-0.13	-0.14	0.86	-0.05
KMnO_4 (mg l^{-1})	0.19	0.12	0.82	0.03
SO_4 (mg l^{-1})	0.86	0.27	0.11	0.23
K (mg l^{-1})	0.83	0.40	-0.11	0.20
Mo ($\mu\text{g l}^{-1}$)	0.78	0.47	-0.15	-0.13
Mg (mg l^{-1})	0.75	0.24	-0.07	0.28
I ($\mu\text{g l}^{-1}$)	0.75	0.25	0.00	0.20
Ba ($\mu\text{g l}^{-1}$)	0.82	0.17	0.23	0.26
Mn ($\mu\text{g l}^{-1}$)	0.75	-0.27	0.40	0.26
Cu ($\mu\text{g l}^{-1}$)	0.81	0.34	0.37	-0.10
Si (mg l^{-1})	0.69	-0.40	-0.43	0.19
Li ($\mu\text{g l}^{-1}$)	0.69	0.59	0.16	0.06
Ca (mg l^{-1})	0.35	0.93	-0.04	-0.03
Alkalinity (mmol l^{-1})	0.38	0.90	-0.07	-0.09
Sr ($\mu\text{g l}^{-1}$)	0.41	0.88	-0.05	-0.01
EC (mS m^{-1} at 25°C)	0.46	0.84	-0.05	0.26
pH	0.04	0.84	-0.27	-0.26
NO_3 (mg l^{-1})	0.20	0.79	0.37	-0.14
Na (mg l^{-1})	0.20	-0.06	-0.05	0.94
Cl (mg l^{-1})	0.12	-0.19	-0.01	0.95
Explained variance	12.3	5.1	3.2	2.0
% of Explained variance	43.8	18.0	11.6	7.1
Cumulative % of variance	43.8	61.8	73.4	80.5

Table 4. Factor score from principal component loading contribute to each case (Observation wells and seasons, where 0412 and 0812 represent samples taken during April2012 and August2012, respectively). Positive factor scores are marked as bold.

Case	Principal component (PC)			
	1	2	3	4
Lake water_0812	-1.33	-0.06	4.06	-0.24
Obs1_0412	0.84	-1.22	-0.03	-0.86
Obs1_0812	0.34	-1.12	-0.15	-0.57
Obs2_0412	0.25	-1.00	1.13	-0.71
Obs2_0812	-0.12	-0.83	0.75	-0.35
Obs3_0412	-0.16	-0.62	-0.66	-0.89
Obs4_0412	-0.44	-0.40	-0.86	-1.13
Obs4_0812	-0.48	-0.47	-0.18	-0.76
Obs5_0412	-0.41	-0.58	-0.80	-0.85
Obs6_0812top	-1.34	0.24	-0.58	1.87
Obs6_0412mixed	-0.79	-0.16	-0.59	2.43
Obs6_0812mixed	-0.93	-0.28	0.15	2.41
Obs6_0812bottom	-0.66	-0.39	-0.36	-0.16
Obs7_0412	-0.97	-0.43	-0.87	-0.33
Obs7_0812	-1.14	-0.33	-0.20	-0.11
Obs8_0412mixed	-0.35	1.60	-0.04	-0.67
Obs8_0812top	-0.53	1.85	-0.59	-0.91
Obs8_0812mixed	-0.32	1.22	-0.16	-0.64
Obs8_0812bottom	-0.46	1.89	-0.74	-0.49
Obs9_0412	1.80	-0.79	-0.54	0.37
Obs9_0812	1.27	-0.76	0.01	0.75
Obs10_0412	2.02	1.52	0.64	0.60
Obs10_0812	1.48	1.74	0.74	0.26
Obs11_0412	1.36	-0.54	-0.13	0.35
Obs11_0812	1.05	-0.10	-0.01	0.62

Table 5. Median values of variables in each cluster from groundwater samples (n = 24) taken during spring (April) and summer (August) 2012.

Cluster	1	2	3	4	5	6
Number of samples	7	3	4	4	2	4
Eh (mV)	292	312	273	201	267	219
O ₂ (mg l ⁻¹)	11.3	8.77	5.89	5.79	1.20	2.68
CO ₂ (mg l ⁻¹)	3.0	13.0	18.0	1.5	16.0	31.0
pH	6.6	6.2	5.7	7.8	7.1	6.6
EC (mS m ⁻¹ at 25°C)	4.74	12.9	4.79	22.7	29.9	15.3
Alkalinity (mmol l ⁻¹)	0.22	0.23	0.16	2.06	2.17	0.84
KMnO ₄ (mg l ⁻¹)	0.6	1.8	4.90	1.5	5.0	1.9
K (mg l ⁻¹)	0.55	0.59	0.66	0.94	4.19	1.88
Ca (mg l ⁻¹)	4.28	8.00	3.33	38.5	45.2	14.1
Mg (mg l ⁻¹)	0.93	1.40	0.85	1.96	2.82	3.56
Na (mg l ⁻¹)	2.46	12.7	2.94	2.41	6.63	7.89
Cl (mg l ⁻¹)	2.78	25.0	3.21	1.95	5.48	8.47
SO ₄ (mg l ⁻¹)	7.18	8.40	8.60	8.22	29.3	17.0
NO ₃ (mg l ⁻¹)	<0.20	0.30	0.90	2.95	5.40	0.39
Si (mg l ⁻¹)	5.37	5.70	7.15	4.73	6.52	8.87
F (mg l ⁻¹)	<0.10	<0.10	0.11	<0.10	0.40	0.53
Sr (µg l ⁻¹)	15.5	29.9	20.9	131.0	144.5	64.6
I (µg l ⁻¹)	3.69	3.27	3.14	5.68	14.5	10.3
Li (µg l ⁻¹)	0.61	0.16	0.14	2.05	6.10	2.61
Mn (µg l ⁻¹)	0.25	1.22	17.3	0.15	48.5	21.6
Cu (µg l ⁻¹)	<0.10	<0.10	0.52	0.44	3.55	0.79
Al (µg l ⁻¹)	8.02	13.8	121.3	3.95	1.68	35.8
As (µg l ⁻¹)	0.10	<0.05	0.10	0.47	0.79	0.18
B (µg l ⁻¹)	11.3	5.69	9.43	5.93	14.0	15.0
Ba (µg l ⁻¹)	1.30	3.14	5.01	1.64	14.7	7.25
Cr (µg l ⁻¹)	<0.20	<0.20	0.25	0.60	0.29	<0.20
Mo (µg l ⁻¹)	0.14	0.09	0.28	0.45	2.08	0.55

Table 6. Changes of selected dissolved concentrations (%) between seasons in different observation well locations. Numbers in the first row (1 to 11) represent observation well numbers (Obs1 to Obs11). Positive numbers are marked as bold, indicates increasing of dissolved concentrations.

Variable	Aril2010 to April2012				Aril2010 to August2012				Aril2012 to August2012								
	1	8	10	11	1	8	10	11	1	8	10	11	2	6	4	9	7
pH	9	4	3	16	5	4	3	17	-3	0	0	1	-2	-2	-1	-3	-2
EC	23	67	4	-9	13	-3	39	7	-8	-17	2	7	-4	-12	5	-3	1
KMnO ₄	-47	23	-26	-57	-73	46	15	33	-49	19	56	54	14	556	200	28	66
Alkalinity	21	102	7	46	36	63	14	61	12	-19	6	10	40	10	27	-7	13
Ca	8	75	1	-12	-2	48	9	1	-9	-15	8	15	-5	-19	4	-12	-4
Mg	10	16	33	-4	-1	6	7	0	-10	-9	-20	4	-10	-17	0	-12	-5
K	-1	2	2	-16	-43	-34	-26	-25	-42	-35	-27	-11	-27	-36	-21	-31	-15
Na	9	-14	2	-4	5	-4	-39	-9	-3	12	-40	-5	-4	-14	0	-5	0
Cl	-6	-31	-25	-3	-11	-8	-35	10	-5	34	-13	13	-22	-12	13	19	3
NO ₃	-24	-29	-42	45	-31	-34	6	100	-9	-8	84	38	2	-32	-73	0	-52
SO ₄	22	-9	19	-42	4	-7	-5	-48	-14	2	-20	-10	3	-8	6	-6	-6
Al	107	-72	-45	-58	-2	-85	-71	-88	-53	-47	-46	-72	-33	-32	100	-53	-62
Mn	-33	-93	283	-60	-66	-53	-23	-80	-49	586	-80	-50	-41	150	800	-59	60
Sr	22	85	-9	-11	-16	26	-13	-8	-31	-32	-5	4	-32	-34	-13	-23	-11
F	200	0	0	22	0	-50	-40	0	-67	-50	-40	-18	-55	-77	0	-35	-58
Fe	29	-67	0	0	-58	-67	0	0	-68	0	0	0	-20	0	0	-67	0
P	0	0	116	0	360	0	180	0	360	0	30	0	0	0	460	0	0
Si	15	-6	17	-11	8	-1	13	-13	-6	5	-4	-3	3	2	1	-6	1
Cd	60	0	100	-42	60	0	50	-58	0	0	-25	-29	25	50	100	-17	0
Co	34	488	367	-48	-8	-37	167	-81	-31	-89	-43	-64	-37	-56	-97	-46	-97
Cr	0	-42	220	100	0	72	150	0	0	195	-22	-50	67	0	0	0	0
Cu	-38	-42	16	-42	-51	-59	54	-28	-22	-31	34	24	-26	0	240	72	0
Ni	36	-37	587	-42	-40	120	158	-78	-56	251	-62	-62	-84	-88	-85	-50	-77
Pb	-58	260	0	0	-58	0	140	340	0	-72	140	340	-63	143	340	260	100

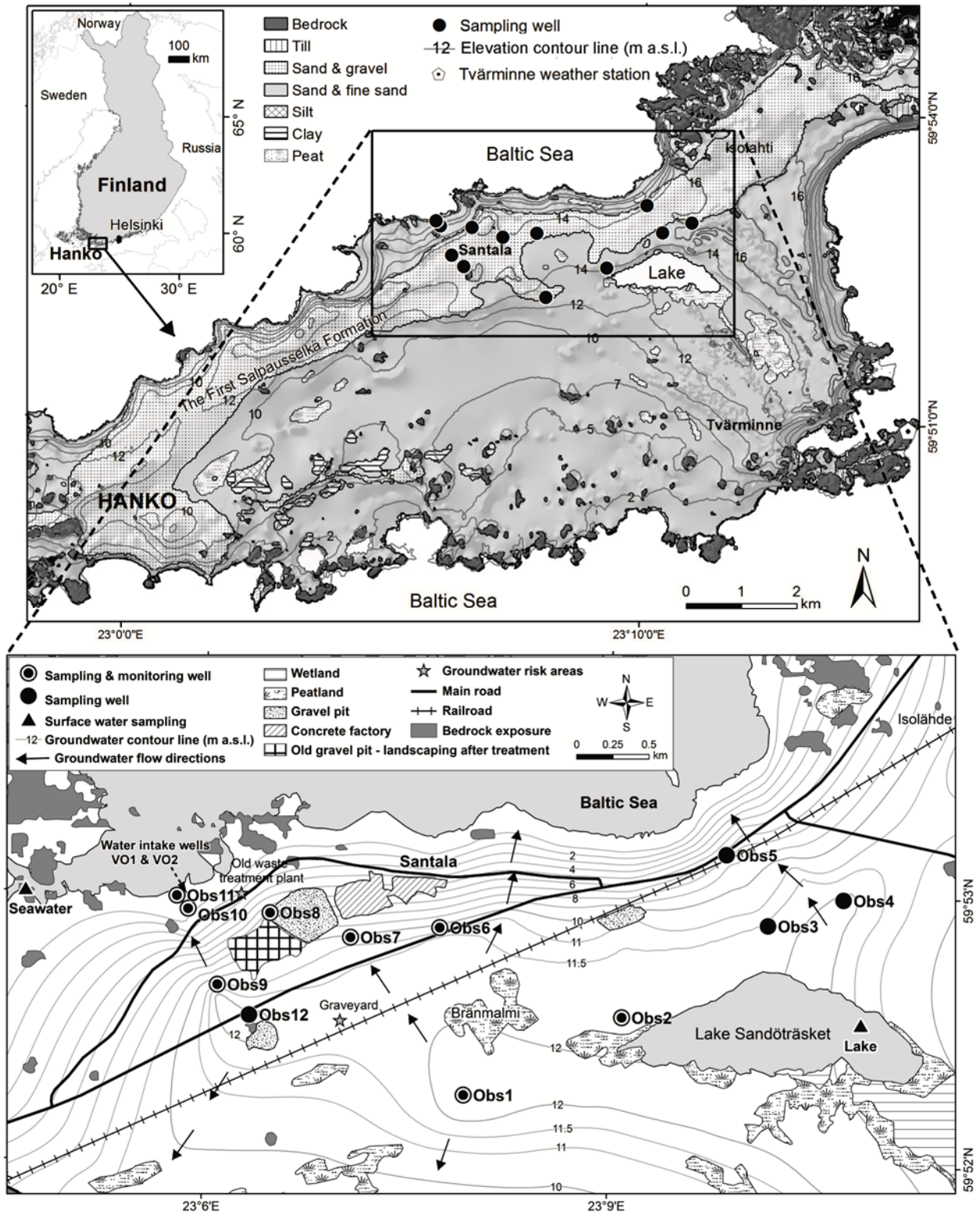


Fig. 1. Location and Quaternary geological deposit map of the study area in the eastern Baltic Sea region.

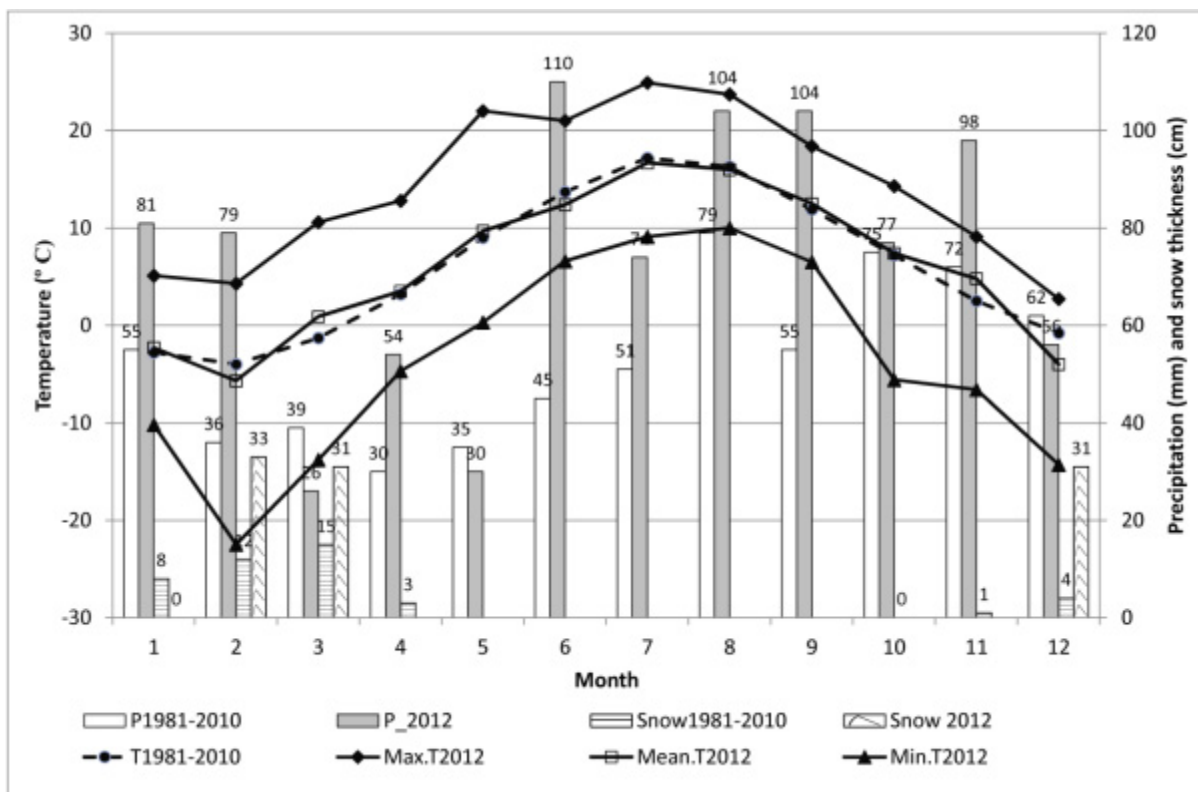


Fig. 2. Monthly maximum, mean, minimum temperatures (solid lines, in °C), monthly precipitation (gray bar, in mm, as rainfall and snow) and snow thickness (wavy bar, in cm) in the Tvärminne weather station in Hanko during January-December 2012. Mean monthly temperature (dash line, in °C), monthly precipitations (white bar, in mm, as rainfall and snow) and snow thickness (straight line bar, in cm) of years 1981-2010, are plotted for comparison. Data are received from FMI (2013).

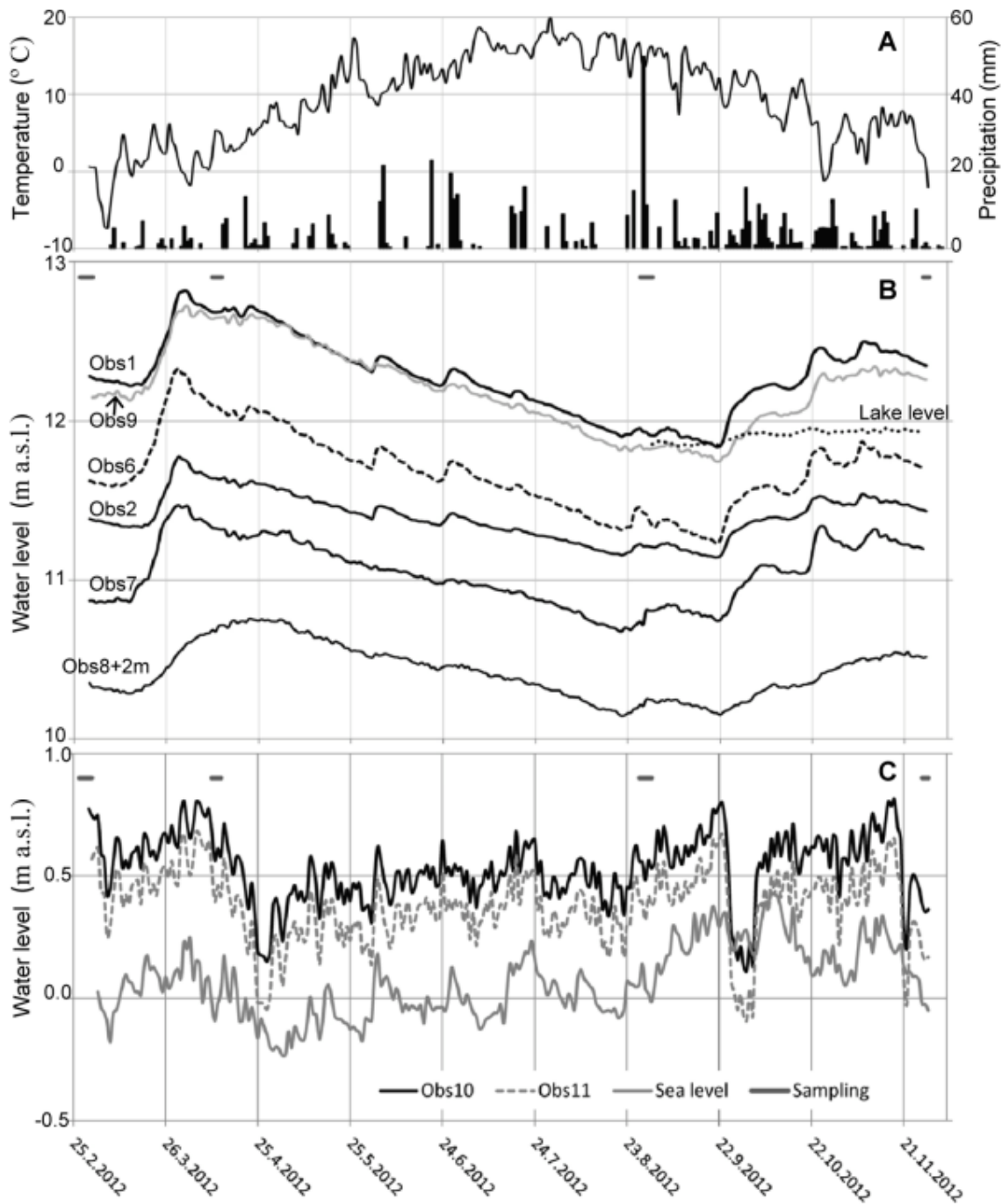


Fig. 3. A: Daily temperature (line) and precipitation (bar) during March – November 2012 from the Tvärminne weather station, Hanko (FMI, 2013). B: Groundwater levels from monitoring wells during the same periods for wells locate in the mainland and lake level during September – November 2012. C: Groundwater levels from wells locate nearby the coastline and sea level data. Groundwater level of Obs8 was shifted up 2 m in order to get the all data fit in one figure. The sample periods present on the top of figures B and C.

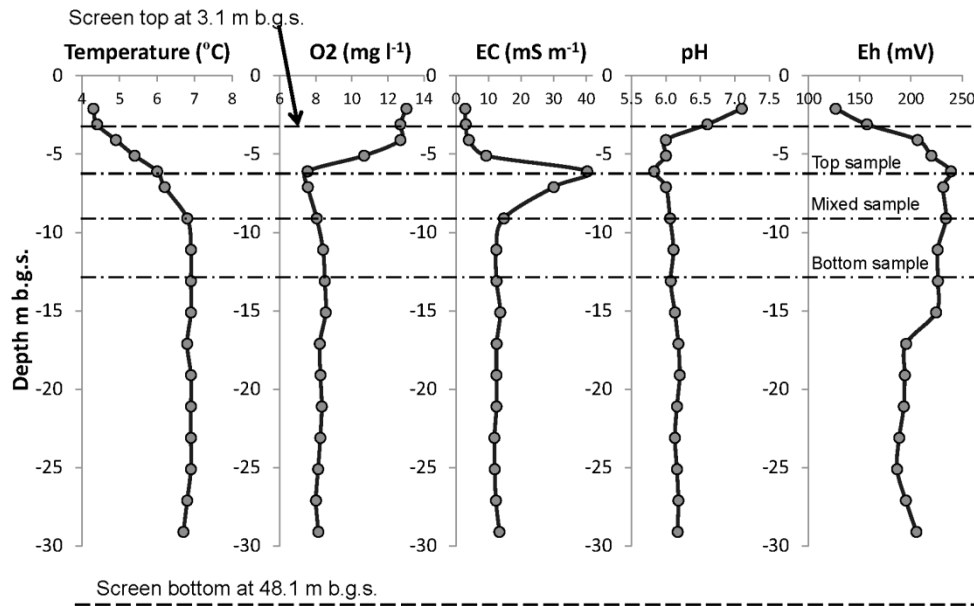


Fig. 4. Depth profile of parameters: Temperature, dissolved oxygen (O₂), electrical conductivity (EC), pH and redox potential (Eh), in the well screen section of Obs6 (50 m from the highway) during spring 2012. m b.g.s = metre below ground surface.

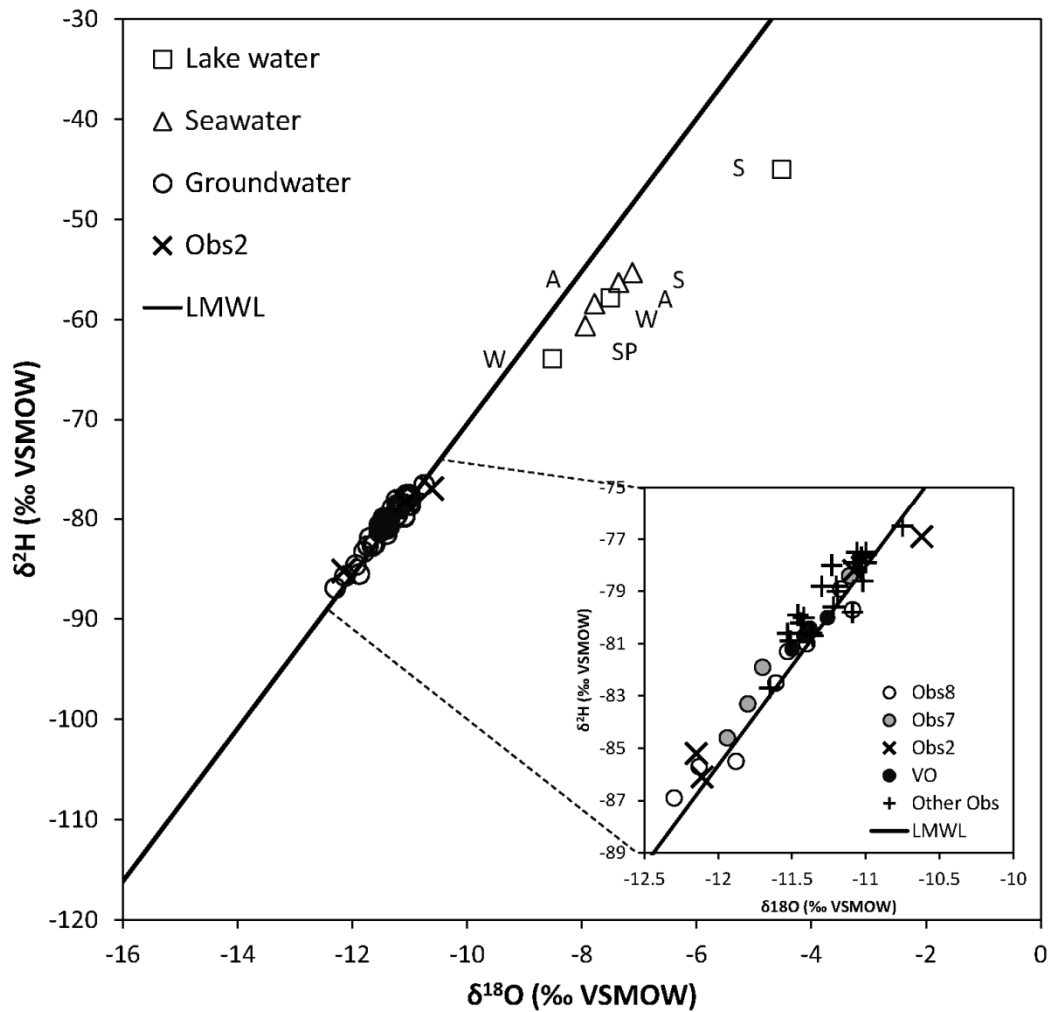


Fig. 5. Plot of the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ data for lake water, seawater, groundwater from the observation wells (Obs), and water intake well (VO) from Santala during 2012 with the Finnish local meteoric water line (LMWL) for comparison. Labels at surface water indicate the sampling period: S = summer, SP = spring, A = autumn and W = winter. Locations of water samplings are showed in Fig.1.

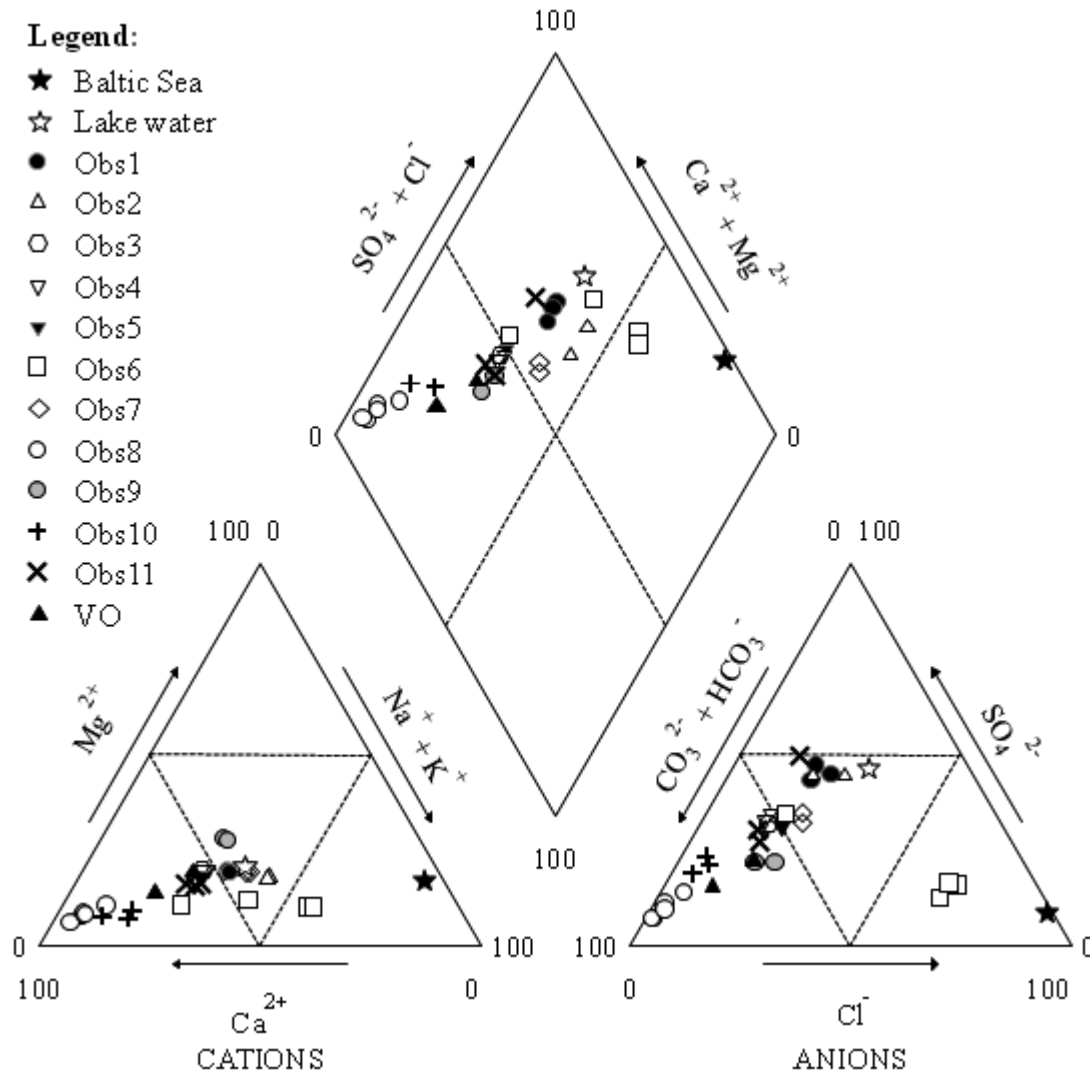


Fig. 6. Piper diagram showing the major ion chemistry of groundwater and surface water samples from the Santala, Hanko.

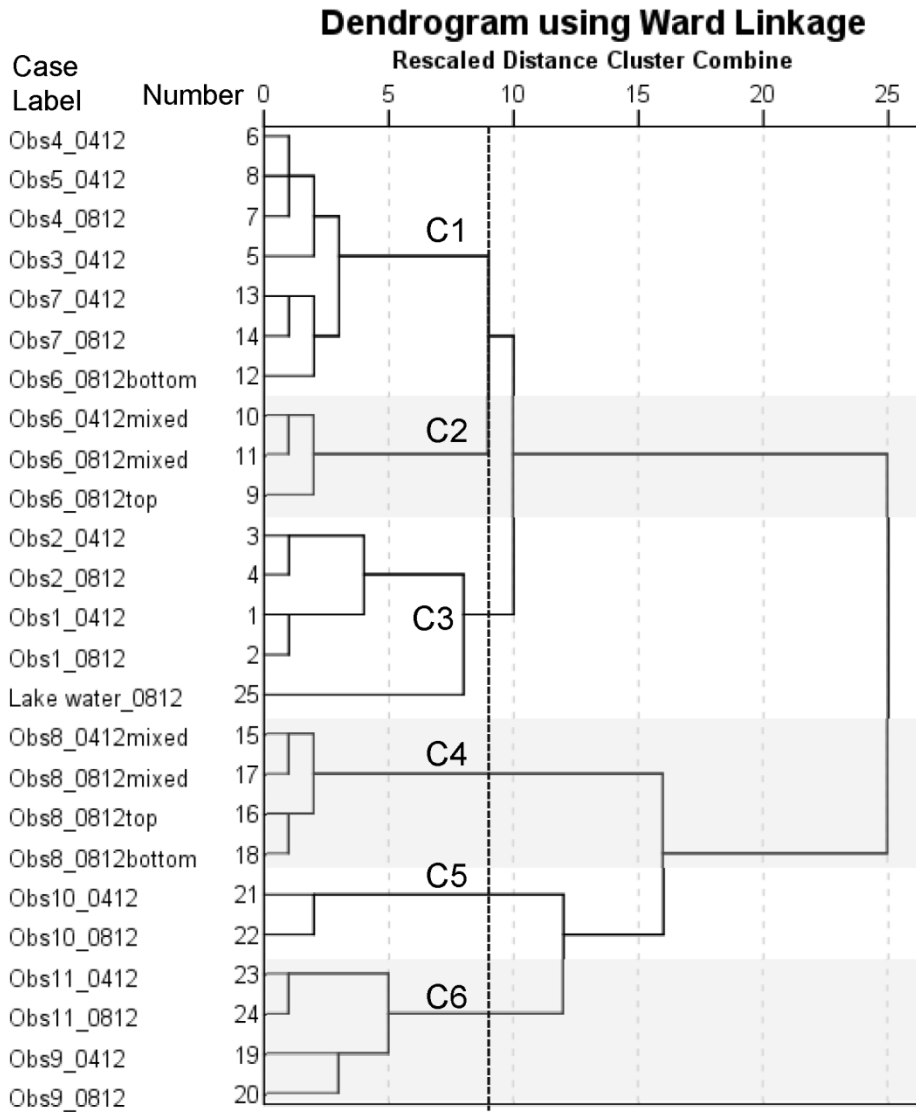


Fig. 7. Hierarchical clustering results (dendrogram) of water samples (n = 25) taken during spring (April) and summer (August) 2012.