

Geochemical and isotopic evolution of high-pH groundwater in a carbonate-bearing glacial aquifer, SW Finland

Nina M. Kortelainen and Juha A. Karhu

ABSTRACT

The glacial Virttaankangas aquifer in SW Finland is characterized by groundwaters with high pH values of up to 9.5. High pH values exceeding 9 are uncommon for shallow groundwaters from unconsolidated glacial formations on crystalline bedrock. To evaluate the geochemical evolution of groundwater, water samples were collected from 17 sites. The samples were analysed for the isotopic composition of oxygen, hydrogen, dissolved inorganic carbon (DIC) and strontium, the activities of radiocarbon and tritium, and for the basic chemical composition. Groundwaters in the Virttaankangas aquifer system show a considerable range in water pH from 6.4 to 9.5. The isotopic and chemical characteristics of the groundwater in the aquifer units were observed to vary depending on the aquifer mineralogy, groundwater residence time and the openness of the system to CO₂ exchange. The pH values were noted to increase in parallel with the contents of Ca and DIC and $\delta^{13}\text{C}_{\text{DIC}}$. In higher pH values, the groundwaters had attained saturation with respect to calcite. These chemical changes were interpreted to result from dissolution of calcite, present in trace amounts in the Virttaankangas sediments. Specifically, the highest pH values were attributed to calcite dissolution under closed system conditions at a low partial pressure of CO₂.

Key words | DIC, Finland, high pH, hydrochemistry, shallow groundwater, stable isotopes

Nina M. Kortelainen (corresponding author)
Geological Survey of Finland,
P.O. BOX 96,
FI-02151 Espoo,
Finland
E-mail: nina.kortelainen@gtk.fi

Juha A. Karhu
Department of Geology,
University of Helsinki,
P.O. BOX 64,
FI-00014 Helsinki,
Finland

NOMENCLATURE

EC	electrical conductivity
P_{CO_2}	partial pressure of soil CO ₂
R_{sample}	the $^{18}\text{O}/^{16}\text{O}$, D/H or $^{13}\text{C}/^{12}\text{C}$ ratio of the sample
R_{standard}	the $^{18}\text{O}/^{16}\text{O}$, D/H or $^{13}\text{C}/^{12}\text{C}$ ratio of the standard
T	temperature
δ	isotopic ratio expressed as a per mil difference relative to the international standard

INTRODUCTION

The variables affecting the geochemical evolution of rainwater to groundwater include the existence and type of

organic topsoil, the mineralogy of the aquifer, the partial pressure of soil CO₂ (P_{CO_2}) and the extent to which CO₂ contributes to the unsaturated and saturated zone of the aquifer. Rainwater in equilibrium with atmospheric CO₂ records a low P_{CO_2} of $10^{-3.4}$ and a pH of 5.6 (Stumm & Morgan 1996; Appelo & Postma 1999). In soil, additional CO₂ is derived from the decomposition of organic matter. Carbonate minerals, if present, are generally the first to dissolve and consume soil CO₂. As a result, pH is raised and Ca²⁺, Mg²⁺ and dissolved inorganic carbon are added to the water. The geochemical evolution of groundwater is notably dependent on the supply of soil CO₂. Under open system conditions, a constant supply of soil CO₂ is available to be used for weathering reactions, whereas in a closed system the flow of CO₂ into or out of the system is

doi: 10.2166/nh.2009.032

constrained and the extent of reaction is limited by the initial amount of CO₂ (e.g. Clark & Fritz 1997; Drever 1997; Appelo & Postma 1999). The dissolved inorganic carbon (DIC) contents, the $\delta^{13}\text{C}$ value of DIC and the activities of ¹⁴C in DIC can be used to evaluate whether open or closed system conditions have prevailed in the groundwater system and also to determine the degree of openness in the system (e.g. Deines *et al.* 1974; Deines 1980; Clark & Fritz 1997).

High pH values of up to 9.5 encountered in the Virttaankangas aquifer, southwest Finland, are not previously reported from groundwaters in unconsolidated glacial formations composed predominantly of silicate minerals, such as potassium and sodium feldspars, quartz and micas. The high values are in strong contrast to the pH values normally recorded in shallow groundwaters of the Fennoscandian shield, averaging 6.4 (Lahermo *et al.* 1990; Tarvainen *et al.* 2001). Two nationwide groundwater surveys were carried out in Finland in the 1990s, neither of which recorded pH values exceeding 9.0 (Lahermo *et al.* 1990; Tarvainen *et al.* 2001). Subsurface waters with pH varying from 9 to 12 are known to occur in connection with alkaline and ultramafic rocks and in the deep saline groundwaters of the crystalline shield areas (e.g. Nurmi *et al.* 1988; Drever 1997; Cipolli *et al.* 2004). However, the hydrogeochemical setting of the Virttaankangas aquifer differs from these examples. The Virttaankangas aquifer will, in the future, be the site for long-term enhanced groundwater recharge activities (Artimo *et al.* 2003a); understanding of the natural efficiency of sediment to buffer the pH in infiltrated water is therefore of high priority.

The high pH values of the Virttaankangas groundwater are suggested to be related to reactions of groundwater with trace amounts of dispersed calcite in the sedimentary matrix. Chemical and isotopic compositional parameters were therefore determined in order to evaluate the interaction of the groundwater with the sediments. Specifically, the isotopic composition of carbon in DIC was applied to study the interaction of the groundwater system with solid carbonates and soil CO₂.

GEOLOGY OF THE STUDY AREA

The Virttaankangas complex belongs to the Säkylänharju–Virttaankangas glaciofluvial complex, which is part of a

large esker system in southwest Finland (Figure 1(a)). The Säkylänharju–Virttaankangas complex represents an interlobate esker system formed during the Late Weichselian and Early Holocene deglaciation of the Scandinavian Ice Sheet (Punkari 1980). The formation of the complex began ~11,150 years BP (Mäkinen 2003) and it can be divided into three major depositional phases (Artimo *et al.* 2003a; Mäkinen 2003). (1) The lowermost part of the esker formed as a result of repeated deposition of subaqueous fans in a subglacial tunnel containing glaciofluvial sand and gravel. (2) During the second phase, an interlobate ridge containing glaciofluvial sand and silt and related glaciolacustrine silt and clay deposits were formed. (3) After deglaciation, regression of the former Baltic Sea activated intense littoral erosion of the glaciofluvial deposits forming the spit-platform and shore-zone sand deposits of the Virttaankangas plain (Mäkinen & Räsänen 2003). The total thickness of unconsolidated sediments generally varies from 20 to 50 m, but reaches 90 m locally in a bedrock fault zone.

Based on the sedimentological, structural and hydrogeological reconstructions by Mäkinen (2003), Mäkinen & Räsänen (2003) and Artimo *et al.* (2003a,b), three distinct aquifer units are recognized in the Virttaankangas formation (Figure 1(b)). Unit 1 is an unconfined esker core aquifer, composed of glaciofluvial medium sand and gravel. Unit 2 is a semi-confined aquifer in the east and northeast parts of the formation, containing fine sand and silt of glaciofluvial/glaciolacustrine origin. The confining interlayers are discontinuous and are composed of silt and clay. Locally, these confining beds hold perched water tables of Unit 3, i.e. Unit 2 underlies Unit 3 (Figure 1(b)). Unit 3 is an unconfined perched aquifer, composed of highly permeable, sorted littoral sand and gravel. Instead of being a continuous structure, the perched aquifer is composed of three separate basins (Figure 1(b)). One of the basins is connected to Lake Kankaanjärvi (Figure 1(b)), a kettle pond formed in front of the retreating ice sheet. The confining beds around Lake Kankaanjärvi are tilted and littoral sands of up to about 30 m in thickness were deposited in the kettle hole.

The majority of groundwater flow in the Virttaankangas aquifer takes place in Unit 1, flowing southeast parallel to the Säkylänharju–Virttaankangas complex (Figure 1). At the southern end of the Virttaankangas plain the flow turns south-southeast, following a NNW–SSE fault zone in the

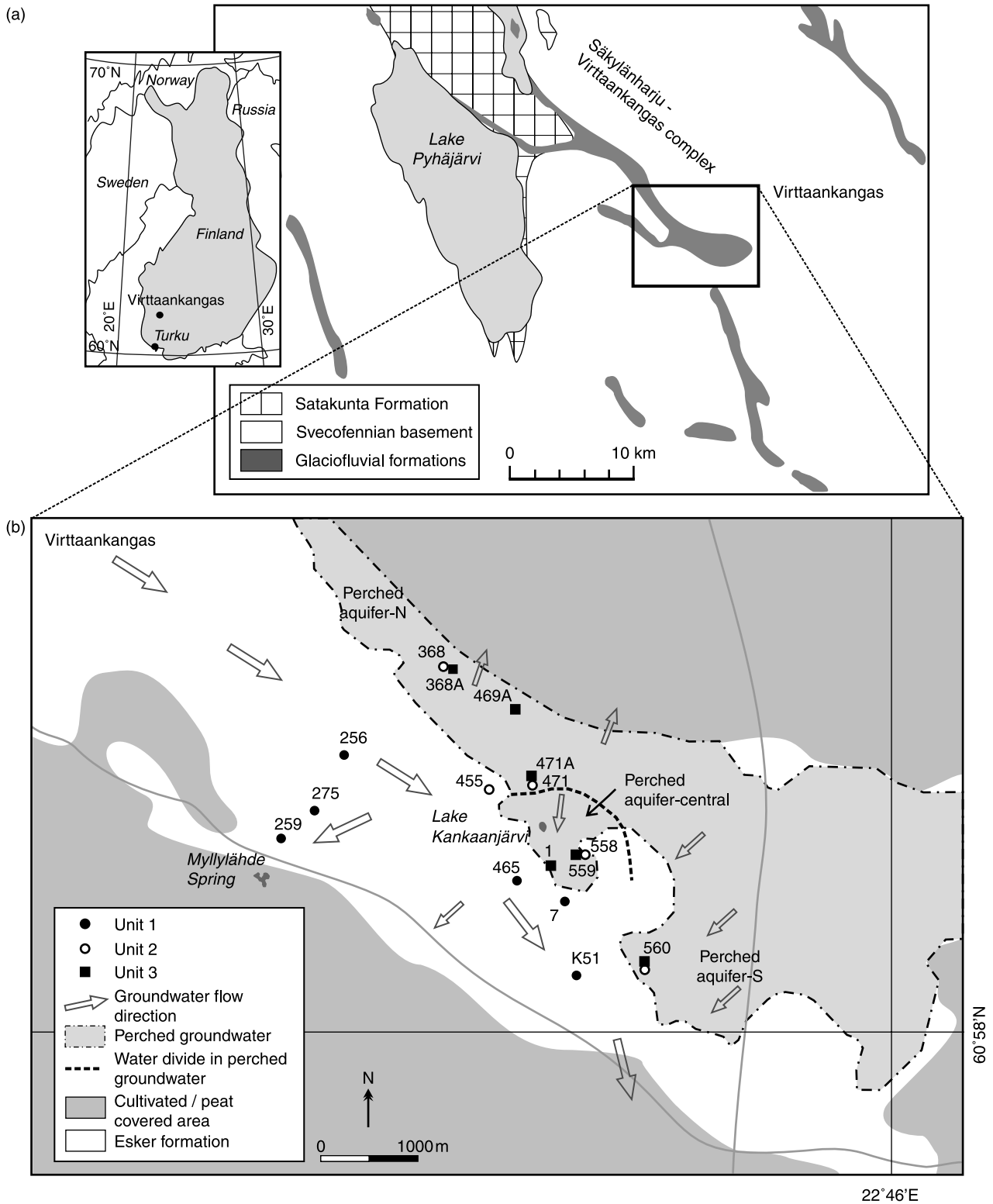


Figure 1 | (a) Location of the Virttaankangas area; (b) groundwater sampling sites and the corresponding aquifer units. The semi-confined aquifer of Unit 2 underlies the perched aquifer of Unit 3. The outlined study area covers about 80 km².

bedrock. In the west, the groundwater from Unit 1 flows through a tributary esker branch and discharges at Myllylähde Spring (Figure 1(b)). The main groundwater flow directions are illustrated in Figure 1(b). Groundwater flow in Unit 2 occurs mainly towards the esker core of Unit 1. Discharge from Unit 2 takes place by artesian springs in the east and northeast. Perched waters of Unit 3 flow into underlying Unit 2 predominantly by overflow but also very slowly by percolating through the confining beds. Compared to the units 1 and 2, the volume of Unit 3 is minor and it may also drain during dryer years. Lake Kankaanjärvi is connected to the perched aquifer of Unit 3, and the lake's water table follows the perched water table. The kettle pond lacks inlet or outlet ditches. Due to evaporative losses, the water flow is predominantly towards the lake. Leaks from the lake to the groundwater system are possible although uncommon, as no evidence for evaporated waters have been observed in the oxygen and hydrogen isotope ratios of groundwaters.

The complex has been deposited on the Paleoproterozoic (1,900–1,800 Ma) crystalline basement consisting mostly of plutonic quartz-diorite and tonalite (Salli 1953). The southeast contact of the Mesoproterozoic Satakunta sandstone is met approximately 10–15 km west and north-west from the Virttaankangas study area (Hämäläinen 1994; Figure 1(a)). The Satakunta Formation has provided large amounts of easily eroded sandstone material to the Säkyänharju–Virttaankangas complex and, as a consequence, the Virttaankangas sediments are characterized by reddish sands and abundant sandstone clasts (Kaitanen & Ström 1978). The dispersed calcite in the Virttaankangas deposits has been derived from the Satakunta sandstone (Kortelainen *et al.* 2007).

MATERIALS AND METHODS

Sampling

Water samples were collected at 17 sites representing all three aquifer units (Figure 1(b)). The hydrogeologic background of sampled wells is presented in Table 1. Prior to sampling, the observation wells and the production wells were pumped for 20 minutes or more in order to replace the water volume in the well several times. For observation

wells, a frequency-controlled electric submersible pump was used for sample collection. Eleven sites were sampled once or twice for the determination of the isotopic composition of DIC and for the investigation of basic hydrochemical parameters. Of those, nine sites were also sampled once for the analysis of radiocarbon (^{14}C) and tritium (^3H) activities. Additionally, eight sites were sampled for the determination of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of dissolved strontium. Tables 2 and 3 summarize the sampling sites, dates and the conducted analyses. The isotopic ratios of oxygen and hydrogen were continuously monitored at eight sites for five years, four to six times a year (Table 4). Three sites were also sampled four to six times for the isotopic analysis of carbon in DIC.

Analytical procedures

Geochemical methods

Filtered and acidified water samples ($<0.45\ \mu\text{m}$) were analysed for cations using ICP-MS and ICP-AES. Anions were analysed from unfiltered samples using an IC method. Both cations and anions were analysed at the Geolaboratory of the Geological Survey of Finland (GTK). Charge balance errors for all analyses remained below 5%. Temperature, pH, electrical conductivity (EC), alkalinity and dissolved O_2 in unfiltered water were determined in the field. T, pH, EC and O_2 were measured with a WTW P4 instrument. Field measurements were conducted immediately after the water samples were uplifted from the well, in order to avoid degassing or dissolution of atmospheric gases. Alkalinity titrations were performed with a Hach digital titrator on a 100 ml sample using 0.16 N sulphuric acid. As waters in the study area have low alkalinity values, the titration end point at a pH value of 5.1 was used (e.g. Clark & Fritz 1997). The results were expressed in mmol/L HCO_3^- . The speciation of the dissolved carbonate components and the total content of DIC were calculated using the PHREEQC computer program for low-temperature aqueous geochemical calculations (Parkhurst & Appelo 1999).

Isotopic methods

For the analysis of $\delta^{13}\text{C}$ in DIC, a phosphoric acid reaction technique was applied, modified from that published by

Table 1 | Hydrogeologic background data on the Virttaankangas sampling sites

Sampling site	Mean gw table*, m a.s.l.	Ground level, m a.s.l.	Depth of well pipe, m	Vadose zone, m	Adjacent well in Unit 3
Unit 1					
7	85.5	104.2	36.3	18.7	–
256	88.2	112.5	55.8	24.2	–
259	86.9	91.7	11.0	4.9	–
275	87.4	98.3	50.3	11.0	–
465	85.6	102.4	36.8	16.8	–
K51 [†]	84.2 [‡]	–	37.0	–	–
Unit 2					
368	88.0	97.2	52.0	9.1	368A
455	87.5	116.8	42.7	29.3	Unconfined
471	87.1	114.6	65.0	27.5	471A
558	86.3	110.2	28.0	23.9	559
561	86.1	101.9	28.0	15.8	560
Unit 3					
1	95.5	112.3	38.0	16.8	–
368A	93.1	97.0	9.0	3.9	–
469A	95.5	98.1	9.0	2.6	–
471A	100.0	114.6	25.0	14.7	–
560	99.6	102.0	6.0	2.4	–
559	99.6	110.1	17.0	10.5	–

*Mean value of groundwater level in 2000–2005; m a.s.l. = metres above sea level.

[†]K51 is a production well.

[‡]Measured from the observation well 25, 100 m north from K51, right outside of depression cone.

Atekwana & Krishnamurthy (1998). In the field, the water samples were filtered (<0.45 or <0.20 µm) into pre-evacuated glass septum tubes (20 or 60 ml), loaded with 85% phosphoric acid and a magnetic stir bar. The evolved CO₂ gas was extracted in a vacuum line, with the sample vessel stirred in a water bath at 50°C for 10 minutes. CO₂ gas was purified cryogenically and the yield was measured. For the analysis of δ¹⁸O in water, the water samples were equilibrated with CO₂ gas and the isotopic composition of CO₂ was analysed. The isotopic composition of hydrogen in water was analysed after reduction of water to H₂ using zinc metal (Coleman *et al.* 1982). The zinc reagent was prepared from pure metal by adding Na as an impurity (Karhu 1997). Isotopic ratios of CO₂ and H₂ were measured by a Finnigan MAT 251 gas source mass spectrometer at GTK. Isotopic ratios are reported using the δ-notation as a per mil (‰) difference relative to the international Vienna Standard Mean Ocean Water (VSMOW) for oxygen and hydrogen

and the Vienna Pee Dee Belemnite (VPDB) standard for carbon. The δ-value is defined as

$$\delta = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000$$

where R is the ¹⁸O/¹⁶O, D/H or ¹³C/¹²C ratio of the sample or standard and δ is δ¹⁸O, δD or δ¹³C. The δ¹⁸O and δD values are normalized to values of –55.5‰ and –428‰, respectively, for Standard Light Antarctic Precipitation (SLAP) relative to VSMOW (Coplen 1994). The repeatability of analyses was ≤0.1‰ for oxygen and ≤1.0‰ for hydrogen in water and ≤0.2‰ for carbon in DIC.

Filtrated groundwater samples (<0.45 µm) were taken for strontium analyses. ⁸⁷Sr/⁸⁶Sr ratios were determined in a dynamic mode on a VG SECTOR 54 mass-spectrometer at GTK. The isotopic ratios were normalized to a ⁸⁶Sr/⁸⁸Sr value of 0.1194. The 2σ uncertainty of the measurements varied within ±0.00002 – 0.00009. The average value

Table 2 | Geochemical and isotopic data for groundwater samples from the Virttaankangas area

Site name	Sampling date	T°C	O ₂ mg/L	EC mS/cm	pH	Alk.* mmol/L	K mg/L	Ca mg/L	Mg mg/L	Na mg/L	Si mg/L	Cl mg/L	No ₃ mg/L	SO ₄ mg/L	DIC	mCO ₃ ²⁻ mmol/L, calculated	mHCO ₃ ⁻ mmol/L, calculated	mCO _{2(aq)}	logSI _{cal}	δ ¹³ C ‰, VPDB	¹⁴ C pmC†	³ H TU
Unit 1																						
7	7-Mar-01	5.0	11.7	72	9.0	0.51	0.64	9.36	0.74	2.03	4.72	0.99	<0.2	5.08	0.48	1.50E-02	0.46	1.35E-03	-0.19	-16.04	-	-
7	3-May-01	7.3	10.8	70	9.0	0.48	0.68	9.84	0.76	1.97	4.73	0.93	<0.2	5.11	0.45	1.41E-02	0.43	1.28E-03	-0.19	-15.09	81.9 ± 0.4	15.7 ± 0.2
259	1-Jul-03	7.3	10.4	86	8.7	0.65	0.73	12.10	0.96	2.39	4.45	1.00	0.40	5.40	0.63	1.03E-02	0.61	3.65E-03	-0.24	-15.69	-	-
259	8-Mar-05	5.5	10.6	87	8.7	0.68	0.68	12.70	1.10	2.28	4.83	1.18	0.40	5.40	0.66	1.12E-02	0.64	3.65E-03	-0.20	-15.30	-	-
275	1-Jul-03	7.1	10.1	89	8.9	0.69	0.81	12.80	0.97	2.41	4.58	1.00	0.50	5.30	0.66	1.68E-02	0.63	2.38E-03	-0.02	-15.32	-	-
275	8-Mar-05	5.6	10.6	91	9.0	0.70	0.69	13.50	1.16	2.33	4.86	1.09	0.50	5.40	0.67	1.98E-02	0.64	2.02E-03	0.07	-15.00	-	-
465	7-Mar-01	4.0	11.7	72	9.2	0.49	0.56	9.17	0.95	1.80	4.69	1.87	<0.2	6.21	0.45	1.80E-02	0.43	9.82E-04	-0.12	-16.18	-	-
465	3-May-01	7.4	10.9	72	9.0	0.43	0.61	9.80	0.98	1.71	4.75	1.89	<0.2	6.20	0.40	1.27E-02	0.38	1.14E-03	-0.24	-15.98	88.3 ± 0.9	11.6 ± 0.2
K51	7-Mar-01	5.7	11.0	85	8.6	0.62	0.72	11.20	1.16	2.14	4.76	1.23	0.70	6.35	0.61	6.73E-03	0.59	5.21E-03	-0.47	-15.65	-	-
K51	3-May-01	5.8	14.3	85	8.8	0.57	0.80	12.00	1.16	2.02	4.71	1.21	0.72	6.26	0.55	1.07E-02	0.53	2.60E-03	-0.24	-15.29	79.7 ± 0.4	13.6 ± 0.2
	Mean‡	6.1	11.2	81	8.9	0.58	0.69	11.25	0.99	2.11	4.71	1.24	0.40	5.67	0.56	1.35E-02	0.53	2.42E-03	-0.18	-15.55	83.3	13.6
	<i>Stdev‡</i>	<i>1.2</i>	<i>1.2</i>	<i>8</i>	<i>0.2</i>	<i>0.10</i>	<i>0.08</i>	<i>1.59</i>	<i>0.16</i>	<i>0.24</i>	<i>0.12</i>	<i>0.35</i>	<i>0.20</i>	<i>0.52</i>	<i>0.10</i>	<i>3.99E-03</i>	<i>0.10</i>	<i>1.38E-03</i>	<i>0.15</i>	<i>0.41</i>	<i>4.5</i>	<i>2.1</i>
Unit 2																						
455	7-Mar-01	3.8	13.0	59	9.5	0.41	0.60	8.04	0.22	1.52	4.09	1.05	<0.2	4.72	0.34	2.91E-02	0.31	3.11E-04	0.03	-12.70	-	-
455	3-May-01	7.3	12.5	58	9.4	0.37	0.65	8.50	0.25	1.46	4.19	1.01	<0.2	4.82	0.31	2.31E-02	0.28	3.35E-04	-0.03	-13.13	81.5 ± 0.4	18.2 ± 0.2
558	2-May-01	7.1	10.5	65	9.3	0.40	0.59	9.70	0.60	2.07	4.32	1.19	0.66	5.81	0.35	2.10E-02	0.32	4.82E-04	-0.02	-16.15	73.4 ± 0.4	21.7 ± 0.2
561	7-Mar-01	4.7	10.1	70	9.2	0.37	0.67	8.32	0.71	1.76	4.05	0.95	5.89	6.09	0.33	1.57E-02	0.31	5.92E-04	-0.23	-17.20	-	-
561	2-May-01	7.5	8.9	75	9.3	0.36	0.67	10.20	0.70	1.71	4.37	0.94	8.27	5.61	0.31	1.90E-02	0.28	4.19E-04	-0.06	-17.14	70.2 ± 0.4	20.6 ± 0.2
	Mean	6.1	11.0	65	9.3	0.38	0.64	8.95	0.50	1.70	4.20	1.03	3.04	5.41	0.33	2.16E-02	0.30	4.28E-04	-0.06	-15.26	75.0	20.2
	<i>Stdev</i>	<i>1.7</i>	<i>1.7</i>	<i>7</i>	<i>0.1</i>	<i>0.02</i>	<i>0.04</i>	<i>0.94</i>	<i>0.24</i>	<i>0.24</i>	<i>0.14</i>	<i>0.10</i>	<i>3.78</i>	<i>0.61</i>	<i>0.02</i>	<i>5.02E-03</i>	<i>0.02</i>	<i>1.14E-04</i>	<i>0.10</i>	<i>2.19</i>	<i>5.8</i>	<i>1.8</i>
Unit 3																						
1	7-Mar-01	4.3	16.0	50	7.2	0.34	0.49	5.67	1.03	1.81	4.79	0.90	0.2	4.87	0.40	1.75E-04	0.34	0.06	-2.32	-18.24	-	-
1	2-May-01	6.8	12.1	51	7.3	0.33	0.51	6.14	1.06	1.74	4.73	0.95	0.2	4.98	0.38	2.11E-04	0.33	0.05	-2.20	-16.98	107 ± 0.5	11.4 ± 0.2
559	2-May-01	7.7	12.0	28	6.4	0.09	0.37	2.72	0.47	1.40	3.47	1.17	0.2	4.96	0.18	6.85E-06	0.08	0.10	-4.01	-17.53	111 ± 0.6	10.3 ± 0.2
560	2-May-01	6.0	10.8	40	6.6	0.12	0.42	4.23	0.56	1.40	3.47	0.68	0.31	8.30	0.21	1.48E-05	0.12	0.09	-3.50	-22.26	111 ± 0.5	11.4 ± 0.2
	Mean	6.2	12.7	42	6.9	0.22	0.45	4.69	0.78	1.59	4.12	0.92	0.23	5.78	0.29	1.02E-04	0.22	0.08	-3.01	-18.75	110	11.0
	<i>Stdev</i>	<i>1.4</i>	<i>2.3</i>	<i>11</i>	<i>0.4</i>	<i>0.13</i>	<i>0.06</i>	<i>1.54</i>	<i>0.31</i>	<i>0.22</i>	<i>0.75</i>	<i>0.20</i>	<i>0.06</i>	<i>1.68</i>	<i>0.11</i>	<i>1.06E-04</i>	<i>0.14</i>	<i>0.02</i>	<i>0.89</i>	<i>2.39</i>	<i>2</i>	<i>0.6</i>

*Alkalinity is expressed in HCO₃ mmol/L.†¹⁴C is corrected for fractionation to -25‰.

‡Mean compositions of each unit are given with standard deviations.

Table 3 | Strontium data for groundwater samples from the Virttaankangas area

Site name	Sampling date	$^{87}\text{Sr}/^{86}\text{Sr} \pm 2\sigma$	Sr $\mu\text{g/L}$
Unit 1			
259	8-Mar-05	0.73964 ± 0.00003	15.3
259	17-Aug-05	0.73965 ± 0.00003	16.0
275	8-Mar-05	0.73917 ± 0.00002	15.8
K51	31-Aug-05	0.73621 ± 0.00003	15.0
Unit 2			
471	29-Jul-05	0.74713 ± 0.00003	22.0
368	17-Aug-05	0.75189 ± 0.00008	22.0
Unit 3			
368A	17-Aug-05	0.71836 ± 0.00003	12.0
471A	29-Jul-05	0.71946 ± 0.00009	10.0

for SRM987 standard over the analysis period was 0.710261 ± 0.000011 (2σ , $n = 12$) for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio.

^3H and ^{14}C in water samples were analysed at the University of Groningen, the Netherlands (CIO). ^3H was determined from samples enriched by electrolysis using liquid scintillation counting (LSD). ^3H concentrations are expressed as tritium units (TU), with an analytical error of ± 0.2 TU. ^{14}C in water samples was measured by accelerator mass spectrometry (AMS). ^{14}C activities are normalized to a common $\delta^{13}\text{C}$ value of -25‰ and are expressed in percent modern carbon (pmC). The analytical errors varied within $\pm 0.4 - 0.9$ pmC.

Table 4 | Mean δD , $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ at the groundwater monitoring sites in Virttaankangas

Site name	δD ‰, VSMOW			$\delta^{18}\text{O}$ ‰, VSMOW			$\delta^{13}\text{C}$ ‰, VPDB		
	Average	Stdev*	n†	Average	Stdev	n	Average	Stdev	n
Unit 1									
256	-88.7	0.8	14	-12.41	0.10	14	-	-	-
K51	-88.3	1.1	27	-12.40	0.14	27	-15.72	0.97	6
Unit 2									
455	-88.5	1.0	13	-12.46	0.08	13	-13.11	0.30	4
471	-88.9	1.2	11	-12.50	0.11	10	-	-	-
Unit 3									
560	-90.5	1.4	18	-12.71	0.31	18	-21.62	0.85	4
368A	-86.8	1.3	17	-12.17	0.15	17	-	-	-
469A	-86.7	0.8	15	-12.25	0.12	15	-	-	-
471A	-88.9	1.1	22	-12.47	0.11	22	-	-	-

*Stdev = standard deviation.

†n = number of sampling occasions during 2000–2005.

RESULTS AND DISCUSSION

Chemical analyses, the $\delta^{13}\text{C}_{\text{DIC}}$ values, the activities of $^{14}\text{C}_{\text{DIC}}$ and the ^3H contents of Virttaankangas groundwaters are presented in Table 2. The calculated speciation of DIC and the solubility indexes ($\log \text{SI}_{\text{Cal}}$) of calcite are also given. Table 2 summarizes the mean compositional parameters and standard deviations for each aquifer unit. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and the Sr concentrations determined in groundwater samples are presented in Table 3. The mean $\delta^{18}\text{O}$, δD and $\delta^{13}\text{C}$ values and their standard deviations (1SD), based on a monitoring period of five years, are summarized in Table 4.

Isotopic and hydrogeochemical characteristics

The hydrogeochemical units of the Virttaankangas aquifer are characterized by considerable variations in water pH ranging from 6.4 to 9.5. The large range in pH values and especially the high values exceeding 9 are unusual in glacial aquifers on Precambrian crystalline bedrock (Lahermo *et al.* 1990; Tarvainen *et al.* 2001). Trace amounts of fine-grained clastic calcite was observed to occur in the glaciofluvial and glaciolacustrine depositional units of the Virttaankangas formation, whereas the topmost littoral sands are practically devoid of calcite (Kortelainen *et al.* 2007). Calcite was observed to be commonly present in the

<0.2 mm fraction, and occasionally also in the 2.0 to 0.2 mm fraction. According to x-ray diffraction (XRD) analyses, the highest content of calcite in the fine fraction was 3.7 to 5 wt-%, which corresponds to 0.5 to 1.4 wt-% of calcite in the total sediment. The carbonate grains are about 0.1 mm in diameter with an angular morphology. Based on microprobe analyses, chemically the sediment carbonate is practically stoichiometric calcite (CaCO_3) (Kortelainen *et al.* 2007).

Geochemically, Unit 1 represents a Ca-HCO_3 type groundwater whereas Units 2 and 3 contain significant quantities of SO_4 in addition to Ca and HCO_3 . The groundwaters of Unit 3 are highly undersaturated with respect to calcite ($\log \text{SI}_{\text{Cal}} \ll 0$; Table 2). Natural waters having $\log \text{SI}_{\text{Cal}}$ values within ± 0.1 units of zero are considered saturated with calcite (Langmuir 1971). Chemically, they represent typical shallow groundwaters of the calcite-lacking Precambrian shield areas with a low pH value of < 7 , low electrical conductivity (EC) (Lahermo *et al.* 1990; Tarvainen *et al.* 2001) and generally low $\delta^{13}\text{C}_{\text{DIC}}$ of $< -20\text{‰}$ (Aravena *et al.* 1992; Kortelainen and Karhu 2006). Somewhat higher $\delta^{13}\text{C}$ values of up to -17‰ were encountered in perched groundwater taken from Wells 1 and 559 (Table 3), representing one of the perched sub-aquifers in the Lake Kankaanjärvi area (Figure 1(b)). Groundwater in Unit 2 is saturated with calcite ($\log \text{SI}_{\text{Cal}} \approx 0$; Table 2) and pH values are high, from 9.2 to 9.5, exceeding values observed elsewhere in the Virttaankangas formation. In the unconfined esker core aquifer of Unit 1, the groundwater has a pH of 8.6 to 9.2 and is slightly

undersaturated or saturated with calcite ($\log \text{SI}_{\text{Cal}} \leq 0$; Table 2). The high pH values in Units 1 and 2 appear to be related to the dissolution of calcite into groundwater. The rise in pH is paralleled by increases in the contents of Ca and DIC and in the values of $\delta^{13}\text{C}_{\text{DIC}}$ from the shallow aquifer of Unit 3 to the deep aquifers of Units 1 and 2 (Figure 2).

The activities of ^3H and ^{14}C in groundwater were used as a qualitative tool for tracing the relative residence times of water in the aquifers. An average ^3H content of 21 TU was determined for the groundwater in the confined aquifer of Unit 2 (Figure 3(a)). The elevated value is a strong indication of the presence of thermonuclear 'bomb' ^3H in water (Suess 1969; Gat 1980; Meijer *et al.* 1995). In the perched aquifer of Unit 3 the average ^3H content of 11 TU reflects that in recent precipitation (Meijer *et al.* 1995; Pitkänen *et al.* 1996, 1999; Gat *et al.* 2001). A relatively short residence time of water in Unit 3 is supported also by the distinct seasonal variations recorded in the $\delta^{18}\text{O}$ and the δD values of water (Figure 4). In the esker core of Unit 1, the variation in the ^3H concentration from 11.6 to 15.7 TU is dependent on the proportions of recharged recent precipitation and older water from Unit 2 and/or that stored in Unit 1 itself. The $\delta^{18}\text{O}$ and δD values of waters in all units are typical for groundwater formed under the present climatic conditions (Kortelainen & Karhu 2004; Figure 4). No signs of evaporated waters have been recorded in the long-term monitoring of the isotopic composition of oxygen and hydrogen in the Virttaankangas groundwater.

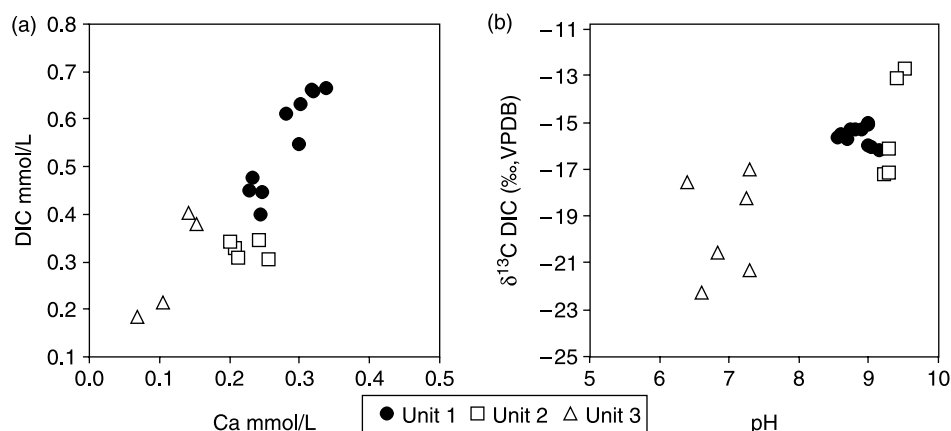


Figure 2 | (a) The Ca versus DIC concentrations and (b) pH versus $\delta^{13}\text{C}_{\text{DIC}}$ for the three aquifer units.

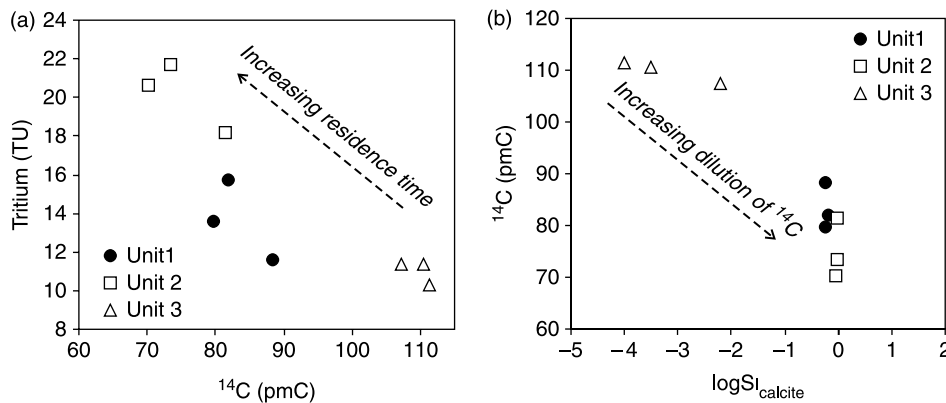


Figure 3 | Age constraints for the groundwaters in the Virttaankangas aquifer. (a) ^{14}C activity versus ^3H concentration in groundwaters. The arrow illustrates the direction of an increasing proportion of groundwater labelled with 'bomb' tritium, i.e. the increasing residence time of groundwater in the system. (b) ^{14}C activity versus $\log \text{Si}_{\text{calcite}}$ of water samples. The arrow illustrates the increasing amount of dissolved ^{14}C -free calcite in groundwater.

The highest $^{14}\text{C}_{\text{DIC}}$ activity of 111 pmC was measured for waters in the perched aquifer of Unit 3. These high values are similar to those reported in recent precipitation (Pitkänen *et al.* 1996, 1999). The lowest $^{14}\text{C}_{\text{DIC}}$ of 71 pmC was attained in the confined aquifer of Unit 2. In the esker core of Unit 1, intermediate values from 79.7 to 88.3 pmC were recorded. Figure 3(b) illustrates the covariation of $^{14}\text{C}_{\text{DIC}}$ activity with the saturation index for calcite. The higher saturation indexes and the lower $^{14}\text{C}_{\text{DIC}}$ activities in Units 1 and 2 are compatible with calcite dissolution. The possible thermonuclear 'bomb' ^{14}C signal (Manning *et al.* 1990; Meijer *et al.* 1995) in waters from Units 1 and 2

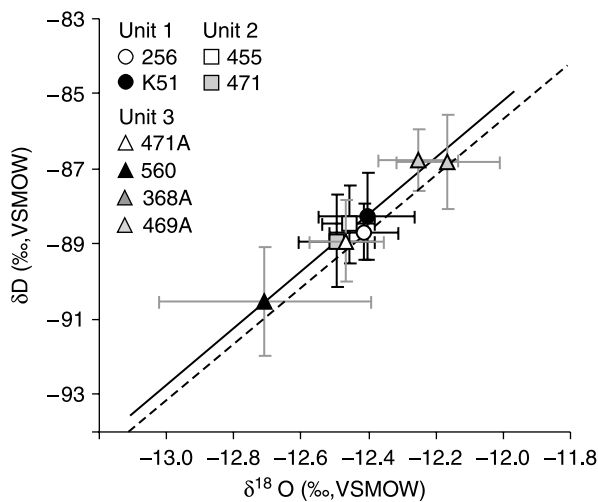


Figure 4 | The $\delta^{18}\text{O}$ and δD values and their variations (1SD) at the monitoring sites (Table 4). The trend line through the data points (solid line) defines an equation of $\delta\text{D} = 7.34 \delta^{18}\text{O} + 2.81$. The broken line is the local meteoric water line determined at Espoo, on the south coast of Finland (Kortelainen 2007).

can therefore be expected to have been erased by the dissolution of old ^{14}C -free carbonate minerals. This leads to an inverse correlation between the ^3H and $^{14}\text{C}_{\text{DIC}}$ in the water units (Figure 3(a)).

Sr concentrations and isotope ratios also showed systematic differences between the aquifer units (Table 3). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr concentrations increased as a function of increasing residence time of waters in the aquifer units, from Unit 3 to Unit 1 and finally to Unit 2 (Figure 5). The most important Sr-carrying minerals in the Virttaankangas sediments are micas, feldspars and calcite. The isotopic composition of Sr was measured in mica and feldspar (plg + kfsp) separates and in a calcite leachate. A $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.92797 was recorded in mica, 0.76050

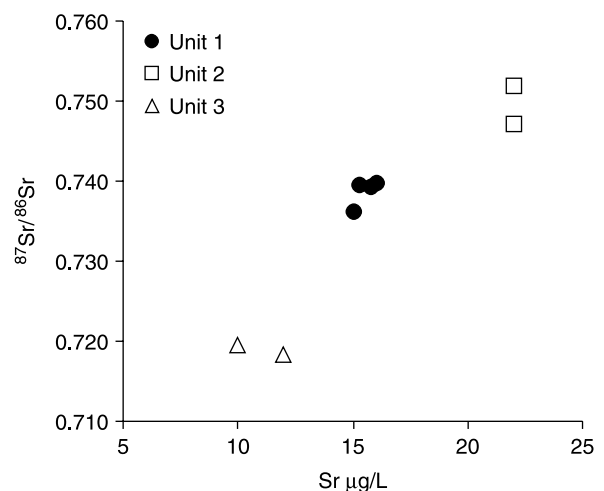


Figure 5 | $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and the concentrations of Sr in groundwater samples.

in feldspar and 0.71434 in calcite. The highly radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of up to 0.75189 suggest a mixed input of radiogenic Sr from micas and feldspars into groundwater by geochemical weathering. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of about 0.719 in Unit 3 suggest that Sr has been derived from atmospheric deposition. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in precipitation over the Fennoscandian Shields have yielded a range of values from 0.710 to 0.720 (Åberg *et al.* 1989; Jacks *et al.* 1989; Negrel *et al.* 2003).

Evolution of groundwater geochemistry

The groundwater of the perched aquifer of Unit 3 at Virttaankangas is clearly undersaturated with respect to calcite. In contrast, the deep groundwater of Units 1 and 2 are in or close to equilibrium with calcite and have unusually high pH values (Table 2). Nevertheless, the DIC contents are relatively low compared to those recorded in carbonate terrains (e.g. Langmuir 1971; Deines *et al.* 1974; Lahermo *et al.* 1990; Appelo & Postma 1999). These characteristics place important constraints on the evolution of groundwater chemistry and the openness of the aquifer units with respect to CO_2 .

The overall reaction describing carbonate dissolution and precipitation may be written:



The availability of CO_2 and the extent to which the CO_2 in water can be replenished have a major effect on the pH of the groundwater. Under open system conditions, calcite dissolution takes place in the presence of a constant supply of soil CO_2 (e.g. Clark & Fritz 1997; Drever 1997; Appelo & Postma 1999). Replenishment of CO_2 in the open system allows more calcite to dissolve and thereby the final concentrations of DIC become much higher than those reached under closed system conditions. In a closed system the flow of CO_2 into or out of the system is restrained and the initial CO_2 will be used up as calcite is dissolved. As a result, the P_{CO_2} drops and only a moderate addition of DIC into the water is recorded. In the closed system a significant rise in pH is observed, exceeding that in an open system (Figure 6).

The isotopic composition of carbon in DIC can be used to evaluate the availability of CO_2 in the groundwater system (e.g. Deines *et al.* 1974; Deines 1980; Clark & Fritz

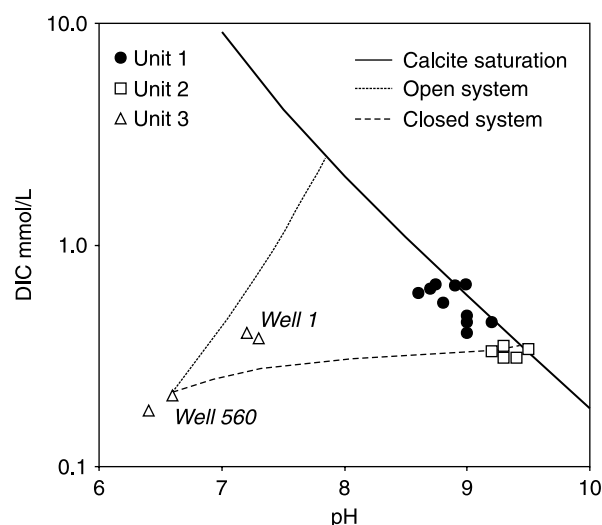


Figure 6 | Modelled evolution of DIC and pH in groundwater as calcite is dissolved, compared to analytical data. The initial water composition is assumed to be that in observation well 560. The model trails were calculated using the PHREEQC program (Parkhurst & Appelo 1999). The open system evolution represents equilibrium with soil P_{CO_2} of $10^{-2.8}$.

1997). Both the $^{13}\text{C}/^{12}\text{C}$ ratios and the activities of $^{14}\text{C}_{\text{DIC}}$ are useful. Soil CO_2 is mainly derived from microbially decomposed organic matter. In high-latitude regions, the $\delta^{13}\text{C}$ value of the C_3 vegetation is around -27‰ (e.g. Deines 1980; Vogel 1993). The diffusive loss of soil CO_2 from soil profiles fractionates carbon, and therefore the $\delta^{13}\text{C}$ values of soil CO_2 generally record a value of about -23‰ (Cerling *et al.* 1991; Aravena *et al.* 1992). The modern $^{14}\text{C}_{\text{DIC}}$ activity is ~ 100 pmC (Deines 1980). The $\delta^{13}\text{C}$ value of the detrital calcite in the Virttaankangas aquifer is $-4.8 \pm 0.5\text{‰}$ (Kortelainen *et al.* 2007). A ^{14}C activity of 0 pmC can be assumed for the clastic calcite derived from old bedrock sources. Under both open and closed system conditions, calcite dissolution increases the $\delta^{13}\text{C}_{\text{DIC}}$ values of water (Figure 2b). Besides this, the enrichment is due to a high fractionation of carbon between soil CO_2 and DIC species as a function of increasing pH. Regardless of calcite dissolution, the soil CO_2 prevails in the open system and ^{14}C remains at around 100 pmC. Under closed system conditions, the modern ^{14}C composition is considerably diluted by the ^{14}C free carbon source (Figure 3).

Three water types differing in hydrogeochemical evolution can be identified in the Virttaankangas aquifer. All water types are ultimately derived from the local precipitation. Open system conditions prevail as rainwater

moves through the soil layer into the unsaturated zone, in all cases. An effective diffusion of CO_2 into soil carried by the percolating water can be expected because of the generally high permeability of aquifer sediments. A fairly constant initial P_{CO_2} is also likely, due to the uniformity of the forest vegetation and soil morphology.

As the littoral sands on the Virttaankangas plain are predominantly lacking calcite, the first step in the geochemical evolution of the rainwater is weathering of silicate minerals. Weathering reactions tend to increase the rainwater pH of 5.6 (Drever 1997; Appelo & Postma 1999). This is observed in Well 560 of the shallowest perched sub-aquifer of Unit 3 (Figure 1(b); Table 1), where a pH of 6.6 was observed. A $^{14}\text{C}_{\text{DIC}}$ activity of 110 pmC and a $\delta^{13}\text{C}$ value of -22.3‰ in the perched water confirm the prevailing open system conditions, and no evidence for calcite dissolution can be observed. This water type represents the most primitive groundwater in the Virttaankangas aquifer, and its composition appears to represent the starting point for further evolution of the groundwater compositions at Virttaankangas. The calculated initial P_{CO_2} in the soil is $10^{-2.8}$, which is low compared to the P_{CO_2} levels of 10^{-2} to 10^{-1} , generally recorded in the soil zone (Langmuir 1971; Stumm & Morgan 1996; Drever 1997; Appelo & Postma 1999). Figure 6 illustrates modelled reaction pathways for the evolution of DIC and pH in groundwater as calcite is dissolved to the point of saturation under a relatively low initial P_{CO_2} of $10^{-2.8}$ under open and closed system conditions.

A water type representing calcite dissolution under closed system conditions was found below the perched aquifer in the confined part of Unit 2, where the most diluted ^{14}C activity of 70 pmC was measured in Well 561 (Figures 1(b) and 3). Groundwaters of Unit 2 are, without exception, saturated with respect to calcite (Figure 3). Figure 6 illustrates the closed system evolution trend that is compatible with a P_{CO_2} of $10^{-2.8}$ for the initial groundwater before calcite dissolution. Calcite dissolution under closed system conditions is supported by carbon isotope data. Groundwaters in Unit 2 show a range of $\delta^{13}\text{C}_{\text{DIC}}$ values varying from -17.1‰ to -12.7‰ (Figure 2(b)). Based on the $\delta^{13}\text{C}$ value of -4.8‰ for the Virttaankangas calcite (Kortelainen *et al.* 2007) and assuming a $\delta^{13}\text{C}_{\text{CO}_2}$ value of -23‰ for soil CO_2 , the $\delta^{13}\text{C}_{\text{DIC}}$ values can be calculated

to change to -12.5‰ at the point of saturation. As a conclusion, the unusually high pH values observed in Unit 2 can be understood to result from the dissolution of calcite and the chemical evolution of groundwaters under closed system conditions at a relatively low P_{CO_2} .

A third water type observed in Well 1 of Unit 3 gives evidence for minor calcite dissolution under predominantly open system conditions. This water type is found in the central perched aquifer, in the Lake Kankaanjärvi area (Figure 1(b)). Although Unit 3 is not known to contain any calcite (Kortelainen *et al.* 2007), a distinct increase in the $\delta^{13}\text{C}$ values as well as in the Ca and DIC concentrations relative to the values observed in other sub-aquifers of Unit 3 can be observed in Well 1 (Figure 2). These characteristics suggest a local presence of calcite in Unit 3.

The groundwaters of the unconfined esker core aquifer of Unit 1 are close to equilibrium with calcite. Their compositions cannot be explained by simple closed or open system calcite dissolution with an initial P_{CO_2} at $10^{-2.8}$. Characteristic of these waters is considerable variability in pH and DIC concentrations scattering along the calcite saturation curve (Figure 6). Apparently, these waters represent calcite dissolution under partially closed conditions. It is possible that they formed under closed system conditions from evolved waters represented by Well 1 of Unit 3. Other scenarios are also possible. The addition of soil CO_2 into the system, e.g. by diffusion from the high porosity gravels, will generate more calcite to be dissolved. As a consequence, the composition of waters may move along the calcite saturation curve. This phenomenon has been noted, for example by Langmuir (1971).

CONCLUSIONS

The following conclusions can be drawn from the geochemical and isotope study of the Virttaankangas aquifer in SW Finland.

1. Some groundwater units in the glacialic Virttaankangas aquifer are characterized by high pH values of >9 . These values are exceptional for shallow aquifers on glaciated crystalline bedrock.
2. Groundwaters in the Virttaankangas aquifer system show a considerable range in water pH from 6.4 to 9.5.

The chemical composition, the ^{14}C and ^3H activities, the $\delta^{13}\text{C}_{\text{DIC}}$ values and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of groundwater in separate aquifer units vary according to the aquifer mineralogy, the residence time of groundwater and the openness of the system to CO_2 exchange.

- The high pH values of groundwater in the glaciofluvial and glaciolacustrine sediments are related to dissolution of calcite into groundwater under closed or nearly closed system conditions relative to soil CO_2 . The rise in pH is paralleled by increases in the contents of Ca and DIC and in the values of $\delta^{13}\text{C}_{\text{DIC}}$. The saturation with respect to calcite and the diluted $^{14}\text{C}_{\text{DIC}}$ activities are compatible with calcite dissolution.
- Shallow groundwaters in glacial aquifers on crystalline bedrock may attain high pH values of >9 as a result of calcite dissolution under closed system conditions at a low P_{CO_2} .

ACKNOWLEDGEMENTS

This study was supported by the Geological Survey of Finland (GTK), the Finnish Graduate School of Geology and Turku District Water Ltd. We are grateful to A. Henttinen and the staff of the Laboratory for Isotope Geology, GTK, for help with isotopic analyses and field-work. We are grateful to Dr A. Artimo and his research group in Turku District Water Ltd. and at the University of Turku for providing technical, hydrogeological and sedimentological data, for help in the field and for useful discussions concerning the hydrogeology of the study site. Dr J. Kääriä from Turku University of Applied Sciences is appreciated for initiating this study as part of the research programme of Turku District Water Ltd. We acknowledge an anonymous reviewer who significantly improved the previous versions of the manuscript. The authors wish to thank two anonymous reviewers of the journal for their constructive and useful comments.

REFERENCES

- Åberg, G., Jacks, G. & Hamilton, P. J. 1989 Weathering rates and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios: an isotopic approach. *J. Hydrol.* **109**, 65–78.
- Appelo, C. A. J. & Postma, D. 1999 In: Balkema, A. A. (ed.) *Geochemistry, Groundwater and Pollution*, 1st edition, Rotterdam, p. 536.
- Aravena, R., Schiff, S. L., Trumbore, S. E., Dillon, P. L. & Elgood, R. 1992 Evaluating dissolved carbon cycling in a forested lake watershed using carbon isotopes. *Radiocarbon* **34**(3), 636–645.
- Artimo, A., Mäkinen, J., Berg, R. C., Abert, C. C. & Salonen, V.-P. 2003a Three-dimensional geologic modeling and visualization of the Virttaankangas aquifer, southwestern Finland. *Hydrogeol. J.* **11**, 378–386.
- Artimo, A., Berg, R. C., Abert, C. C. & Mäkinen, J. 2003b Methods for constructing a three-dimensional geologic model of the Virttaankangas aquifer, southwestern Finland. *Illinois State Geological Survey, Circular* 562, pp. 1–9.
- Atekwana, E. A. & Krishnamurthy, R. V. 1998 Seasonal variations of dissolved inorganic carbon and $\delta^{13}\text{C}$ of surface waters: application of a modified gas evolution technique. *J. Hydrol.* **205**, 265–278.
- Cerling, T. E., Solomon, D. K., Quade, J. & Bowman, J. R. 1991 On the isotopic composition of carbon in soil carbon dioxide. *Geochimica et Cosmochimica Acta* **55**, 3403–3405.
- Cipolli, F., Gambardella, B., Marini, L., Ottonello, G. & Zuccolini, M. V. 2004 Geochemistry of high-pH waters from serpentinites of the Gruppo di Voltri (Genova, Italy) and reaction path modeling of CO_2 sequestration in serpentinite aquifers. *Appl. Geochem.* **19**, 787–802.
- Clark, I. & Fritz, P. 1997 *Environmental Isotopes in Hydrogeology*. Lewis Publishers, New York, p. 328.
- Coleman, M. L., Shepherd, T. J., Durham, J. J., Rouse, J. E. & Moore, G. R. 1982 Reduction of water with zinc for hydrogen isotope analysis. *Anal. Chem.* **54**(6), 993–995.
- Coplen, T. B. 1994 Reporting of stable hydrogen, carbon and oxygen isotopic abundances. *Pure Appl. Chem.* **66**, 273–276.
- Deines, P. 1980 The isotopic composition of reduced organic carbon. In: Fritz, P. & Fontes, C. H. (eds) *Handbook of Environmental Isotope Geochemistry, The Terrestrial Environment*, (Vol. 1A). Elsevier, Amsterdam, pp. 329–406.
- Deines, P., Langmuir, D. & Harmon, R. S. 1974 Stable carbon isotope ratios and the existence of a gas phase in the evolution of carbonate ground waters. *Geochimica et Cosmochimica Acta* **38**, 1147–1164.
- Drever, J. I. 1997 *The Geochemistry of Natural Waters*, 3rd edition. Prentice-Hall, Upper Saddle River (N.J.), p. 436.
- Gat, J. R. 1980 The isotopes of hydrogen and oxygen in precipitation. In: Fritz, P. & Fontes, C. H. (eds) *Handbook of Environmental Isotope Geochemistry, The Terrestrial Environment*, (Vol. 1A). Elsevier, Amsterdam, pp. 21–47.
- Gat, J. R., Mook, W. G. & Meijer, A. J. 2001 *Environmental isotopes in the hydrological cycle. Principles and applications*. UNESCO, Paris, IHP-V, Technical Documents in Hydrology, No. 39, Vol. II, p. 113.
- Hämäläinen, A. 1994 *Kokemäki. Geological map of Finland 1:100 000, Pre-Quaternary Rocks, Sheet 1134*. Geological Survey of Finland.
- Jacks, G., Åberg, G. & Hamilton, P. J. 1989 Calcium budgets for catchments as interpreted by strontium isotopes. *Nordic Hydrol.* **20**, 85–96.

- Kaitanen, V. & Ström, O. 1978 Shape development of sandstone cobbles associated with the Säkylä-Mellilä esker, southwest Finland. *Fennia* **155**, 23–67.
- Karhu, J. A. 1997 Catalytical reduction of water to hydrogen for isotopic analysis using zinc containing traces of sodium. *Anal. Chem.* **69**, 4728–4730.
- Kortelainen, N. 2007 Isotopic fingerprints in surficial waters: stable isotope methods applied in hydrogeological studies. Espoo: Geological Survey of Finland. 41 p. 55. Full text available in: <http://arkisto.gtk.fi/ej/ej66synopsis.pdf>
- Kortelainen, N. M. & Karhu, J. A. 2004 Regional and seasonal trends in the oxygen and hydrogen isotope ratios of Finnish groundwaters: a key for mean annual precipitation. *J. Hydrol.* **285**, 143–157.
- Kortelainen, N. M. & Karhu, J. A. 2006 Tracing the decomposition of dissolved organic carbon in artificial groundwater recharge using carbon isotope ratios. *Appl. Geochem.* **21**(4), 547–562.
- Kortelainen, N. M., Korkeakoski, P. J. & Karhu, J. A. 2007 Origin of calcite in the glacialic Virttaankangas complex. *Bull. Geol. Soc. Finland* **79**, 5–15.
- Lahermo, P., Ilmasti, M., Juntunen, R. & Taka, M. 1990 The Geochemical Atlas of Finland, Part 1. Geological Survey of Finland, Espoo. p. 66.
- Langmuir, D. 1971 The geochemistry of some carbonate ground waters in central Pennsylvania. *Geochimica et Cosmochimica Acta* **35**, 1023–1045.
- Manning, M. R., Lowe, D. C., Melhuish, W. H., Sparks, R. J., Wallace, G., Brenninkmeijer, C. A. M. & McGill, R. C. 1990 The use of radiocarbon measurements in atmospheric studies. *Radiocarbon* **32**(1), 37–58.
- Meijer, H. A. J., van der Plicht, J., Gislefoss, J. S. & Nydal, R. 1995 Comparing long-term atmospheric ^{14}C and ^3H records near Groningen, The Netherlands with Fruholmen, Norway and Izaña, Canary Islands ^{14}C stations. *Radiocarbon* **37**(1), 39–50.
- Mäkinen, J. 2003 The development of depositional environment within the interlobate Säkylänharju–Virttaankangas glaciofluvial complex in SW Finland. *Annales Academiae Scientiarum Fennicae. Geologica–Geographica* **165**, p. 65.
- Mäkinen, J. & Räsänen, M. 2003 Early Holocene regressive spit-platform and nearshore sedimentation on a glaciofluvial complex during the Yoldia Sea and the Ancylus Lake phases of the Baltic Basin, SW Finland. *Sed. Geol.* **158**, 25–56.
- Negrel, P., Casanova, J., Blomqvist, R., Kaija, J. & Frape, S. 2003 Strontium isotopic characterization of the Palmottu hydrosystem (Finland): water-rock interaction and geochemistry of groundwaters. *Geofluids* **3**, 161–175.
- Nurmi, P. A., Kukkonen, I. & Lahermo, P. W. 1988 Geochemistry and origin of saline groundwaters in the Fennoscandian Shield. *Appl. Geochem.* **3**(2), 185–203.
- Parkhurst, D. L. & Appelo, C. A. J. 1999 *User's guide to PHREEQC (Version 2)–A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations*. USGS, Water-Resources Investigation Report 99–4259.
- Pitkänen, P., Snellman, M. & Vuorinen, U. 1996 *On the origin and chemical evolution of groundwater at the Olkiluoto site*. Posiva Oy, Helsinki, Report POSIVA 1996–04, p. 41.
- Pitkänen, P., Luukkonen, A., Ruotsalainen, P., Leino-Forsman, H. & Vuorinen, U. 1999 *Geochemical modelling of groundwater evolution and residence time at the Olkiluoto site*. Posiva Oy, Helsinki, Report POSIVA 1998–10, p. 184.
- Punkari, M. 1980 The ice lobes of the Scandinavian ice sheet during the deglaciation in Finland. *Boreas* **9**(4), 307–310.
- Salli, I. 1953 *Loimaa. Geological map of Finland 1:100 000, Pre-Quaternary Rocks, Sheet 2111*. Geological Survey of Finland.
- Stumm, W. & Morgan, J. J. 1996 *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd edition. Wiley & Sons, New York, p. 1022.
- Suess, H. E. 1969 Tritium geophysics as an international research project. *Science* **163**(3874), 1405–1410.
- Tarvainen, T., Lahermo, P., Hatakka, T., Huikuri, P., Ilmasti, M., Juntunen, R., Karhu, J., Kortelainen, N., Nikkarinen, M. & Väisänen, U. 2001 Chemical composition of well water in Finland–main results of the “one thousand wells” project. In: Autio, S. (ed.) *Geological Survey of Finland, Current Research 1999–2000*. Geological Survey of Finland, Special Paper 31, 57–76.
- Vogel, J. C. 1993 Variability of carbon isotope fractionation during photosynthesis. In: Ehrlinger, J. R., Hall, A. E. & Farguher, G. D. (eds) *Stable Isotopes and Plant Carbon–Water Relations*. Academic Press, San Diego, CA, pp. 29–38.

First received 14 October 2007; accepted in revised form 19 June 2008