

Isotopic Fingerprints In Surficial Waters: Stable Isotope Methods Applied In Hydrogeological Studies

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**ISOTOPIC FINGERPRINTS IN SURFICIAL WATERS:
STABLE ISOTOPE METHODS APPLIED IN HYDROGEOLOGICAL STUDIES**

by
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Geological Survey of Finland
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ACADEMIC DISSERTATION
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Isotope partitioning of elements in the course of physicochemical processes produces isotopic variations to their natural reservoirs. Tracer property of the stable isotope abundances of oxygen, hydrogen and carbon has been applied to investigate hydrogeological processes in Finland. The work described here, has initiated the use of stable isotope methods in the hydrogeology of the shallow glacial formations in Finland. The natural isotopic variations of oxygen and hydrogen in the local atmospheric precipitation and the relationship between the isotopic composition of precipitation and the present day groundwaters in Finland have been studied. The geochemical evolution of groundwater and sources of dissolved carbon have been investigated using carbon isotope records in dissolved inorganic carbon (DIC).

The isotopic composition of oxygen and hydrogen in Finnish groundwaters and atmospheric precipitation was determined in water samples collected during 1995–2005. Prior to this study, no detailed records existed on the spatial or annual variability of the isotopic composition of precipitation or groundwaters in Finland. The regional precipitation and groundwater records presented here supplement the global precipitation station network above the latitude of 60°N. The most distinct spatial isotope pattern of precipitation and groundwaters in Finland is the decrease in $\delta^{18}\text{O}$ and δD with increasing latitude. No significant differences were observed between the mean annual $\delta^{18}\text{O}$ and δD values in precipitation and those in local groundwaters. The spatial decline in the $\delta^{18}\text{O}$ and δD values is closely paralleled by a decrease in the mean annual temperature. The spatial relation of $0.53\text{‰} / ^\circ\text{C}$ presented for $\delta^{18}\text{O}$ of Finnish groundwaters is very close to that ($0.59\text{‰} / ^\circ\text{C}$) reported for $\delta^{18}\text{O}$ of precipitation in Sweden and Europe. These results suggest that the link between the spatial variability in the isotopic composition of precipitation and local temperature is preserved in groundwaters.

Artificial groundwater recharge to glacial formations offers many possibilities to apply the isotopic ratios of oxygen, hydrogen and carbon as natural isotopic tracers. In this study the systematics of dissolved carbon have been investigated in two geochemically different glacial groundwater formations: a carbonate-free aquifer at Tuusula, in southern Finland, and a carbonate-bearing aquifer with a complex internal structure at Virttaankangas, in southwest Finland.

Reducing the concentration of dissolved organic carbon (DOC) in water is a primary challenge in the process of artificial groundwater recharge and the $\delta^{13}\text{C}_{\text{DIC}}$ in the recharged water provides a tool to trace the role of redox processes in the decomposition of DOC. Determinations of $\delta^{13}\text{C}_{\text{DIC}}$ and the content of DIC and DOC in water provided new information on the removal of DOC at the Tuusula artificial groundwater plant. In addition, the $\delta^{18}\text{O}$ and δD values of water have been applied to calculate mixing ratios between the local groundwater and the infiltrated surface water. Three distinct processes in the reduction of the DOC content were traced: 1) the decomposition of dissolved organic carbon, 2) adsorption of DOC on mineral matter, and 3) the dilution of artificially recharged water by mixing with local groundwater. The largest decrease (44%) in the DOC content occurred during the early stage of subsurface flow and this change has been attributed to the oxidative decomposition of DOC. A further 23% decrease in DOC has been attributed to adsorption and a final drop of 14% to dilution with local groundwater.

Groundwaters in the Virttaankangas aquifer are characterized by high pH values exceeding 9, which are exceptional for shallow aquifers on glaciated crystalline bedrock. The Virttaankangas

sediments were discovered to contain trace amounts of fine grained, dispersed calcite, which has a high tendency to increase the pH of local groundwaters. Understanding the origin of the unusual geochemistry of the Virttaankangas groundwaters is an important issue for constraining the operation of the future artificial groundwater plant. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values in sedimentary carbonate minerals have been successfully applied to constrain the origin of the dispersed calcite in the Virttaankangas sediments. The isotopic and chemical characteristics of the groundwater in the distinct units of aquifer were observed to vary depending on the aquifer mineralogy, groundwater residence time and the openness of the system to CO_2 . The high pH values of > 9 have been related to dissolution of calcite into groundwater under closed or nearly closed system conditions relative to soil CO_2 , at a low partial pressure of CO_2 .

Keywords (GeoRef Thesaurus, AGI): hydrogeology, stable isotopes, $^{18}\text{O}/^{16}\text{O}$, D/H, $^{13}\text{C}/^{12}\text{C}$, atmospheric precipitation, ground water, recharge, surface water, organic carbon, degradation, glaciofluvial features, aquifers, hydrochemistry, carbonates, Finland.

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LIST OF ORIGINAL PUBLICATIONS

This study is based on the following four papers.

- I 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. *Journal of Hydrology* 285, 143-157.
- II Kortelainen, N. M. & Karhu, J. A. 2006. Tracing the decomposition of dissolved organic carbon in artificial groundwater recharge using carbon isotope ratios. *Applied Geochemistry* 21, 547-562.
- III Kortelainen, N. M., Korkeakoski, P. J. & Karhu, J. A. 2007. Origin of calcite in the glacial complex Virttaankangas. *Bulletin of Geological Society of Finland* 79, 5-15.
- IV Kortelainen, N. M. & Karhu, J. A. Geochemical and isotopic evolution of high-pH groundwater in a carbonate bearing glacial aquifer, SW Finland. Submitted to *Nordic Hydrology*.

For Paper I, N. M. Kortelainen participated in two nationwide groundwater sampling programmes, collected precipitation in team work, processed the data and examined the background data. Both authors were responsible for planning the study and isotopic interpretations. The studies presented in Papers II and IV were planned and carried out by N. M. Kortelainen. The geochemical and isotopic data was processed, visualized, and mostly interpreted by the first author. J. A. Karhu contributed to geochemical modelling and interpretation. N. M. Kortelainen and P. J. Korkeakoski planned and conducted the carbonate study of Paper III. P. J. Korkeakoski was responsible for the mineralogical data presented in Paper III. All three authors were responsible for interpretations. N. M. Kortelainen was responsible for the isotope laboratory work for all four papers.

1. INTRODUCTION

1.1. Environmental isotopes as tracers

Naturally-occurring isotopes of oxygen, hydrogen and carbon are widely applied in environmental studies (e.g. Clark & Fritz 1997; Kendall & McDonnell 1998; Faure & Mensing 2005). These are among the most abundant elements on Earth and are the principal components of various compounds in the hydro-, geo- and biosphere. Characteristic of these light elements is a relatively large mass difference between their isotopes. Isotopes differing in mass have slightly different chemical and/or physical properties (Hoefs 1997; Faure & Mensing 2005), which leads to isotope partitioning or the *frac-*

tiation of isotopes of the same element in the course of physicochemical processes. In the circulation of water and carbon, isotopic compositions change in predictable ways. This isotopic tracer property is widely used in hydrological studies to track, for example, different water sources, groundwater recharge processes, subsurface processes, geochemical reactions and reaction rates (e.g. Clark & Fritz 1997; Kendall & McDonnell 1998). In this investigation the stable isotopes of oxygen ($^{18}\text{O}/^{16}\text{O}$), hydrogen (D/H) and carbon ($^{13}\text{C}/^{12}\text{C}$) were applied to explain hydrogeological processes.

1.2. Isotope notations and expressions

The isotopic composition of the stable nuclides of oxygen, hydrogen and carbon are measured as isotope ratios. The isotope ratios are reported using the δ notation as a per mil (‰) difference relative to the international VSMOW (Vienna Standard Mean Ocean Water) standard for oxygen and hydrogen and the VPDB (Vienna Pee Dee Belemnite) standard for carbon. The δ value is defined as

$$\delta = (R_{sa} / R_{std} - 1) \cdot 1000,$$

where R is the $^{18}\text{O}/^{16}\text{O}$, D/H or $^{13}\text{C}/^{12}\text{C}$ ratio of the sample (*sa*) or standard (*std*) and δ is $\delta^{18}\text{O}$, δD or $\delta^{13}\text{C}$.

The radioactive isotopes of hydrogen and carbon, *tritium* (^3H) and *radiocarbon* (^{14}C), respectively, are formed in the upper atmosphere by cosmic radiation. Tritium has a half-life of 12.32 years (Lucas & Unterwieser 2000). Tritium concentrations are expressed as tritium units (TU), where the ^3H activity of 1 TU denotes 0.118 Bq/kg of water in the SI system. The half-life of ^{14}C is 5730 years (Godwin 1962). ^{14}C activities are expressed as percent modern carbon (pmC).

1.3. Hydrological cycle

Meteoric water refers to the waters circulated through the atmosphere, including precipitation, groundwater, surface water, pore water, ice caps and glaciers. Fresh waters account for only 3% of the Earth's total water supply, whereas seawater composes over 97% of the total (e.g. Schlesinger 1997). By definition, the isotopic compositions of oxygen and hydrogen in ocean water are 0‰, but in reality vary slightly as a function of salinity (Craig & Gordon 1965). Isotopic fractionation during the evaporation of ocean water and subsequent condensation of water in clouds leads to isotope compositions depleted in ^{18}O and D in fresh waters compared

to ocean waters. Fractionation results from the small differences in vapour pressure of water molecules depending on their isotope masses (Friedman 1953).

1.3.1. Atmospheric moisture and precipitation

Atmospheric moisture is produced by evaporation at the surface of oceans. According to a model developed by Craig & Gordon (1965), the isotopic difference between the ocean water and the adjacent water vapour in the atmosphere results from a combination of *equilibrium*

and *kinetic (nonequilibrium) fractionation* processes. Isotopic equilibrium prevails at the thin boundary layer of the water-air interface, where the isotopic differences between the liquid (*l*) and vapour (*v*) phases are directly related to the equilibrium fractionation factors (α) of the $\alpha^{18}O_{l-v}$ (αD_{l-v}) at a given temperature (Majoube 1971). Further isotopic depletion of the water vapour is generated by the kinetic transport of humidity from the boundary layer to the mixed open atmosphere. The kinetic isotope effect is strongly dependent on the humidity (*h*), while the surface temperature, wind speed and salinity may also affect the fractionations. At a low humidity the magnitude of the kinetic isotope effect increases. The fractionation of ^{18}O between water and vapour in equilibrium varies from 11.6 to 9.3‰ (given as $10^3 \ln \alpha^{18}O_{l-v}$) within the temperature range of 0 to 25 °C (Majoube 1971). The magnitude of the kinetic effect between the boundary layer and vapour varies from 14.2‰ to 0‰ in the humidity range from 0 to 100%, respectively (Gonfiantini 1986).

Most of the atmospheric water vapour is formed over the subtropical oceans (Craig & Gordon 1965), from where air masses are transported polewards with gradual rainout and a decrease in their water content. The condensation of water in clouds occurs as a consequence of decreasing temperature, and it is an equilibrium process ($h = 100\%$). The process preferentially removes ^{18}O and D from the air mass, leading to a depletion of ^{18}O and D in the remaining vapour phase (Craig & Gordon 1965). The rainout of an air mass may be modelled as a *Rayleigh process*, where the equilibrium condensate is immediately removed from the vapour after formation (Dansgaard 1964). This process leads to the enrichment of ^{16}O and 1H in the remaining air mass. Dansgaard (1964) recognized a *latitude effect*, which means a gradual decrease in the $\delta^{18}O$ and δD values in atmospheric vapour and precipitation as an air mass moves towards the poles. A similar depletion of the heavier isotopes takes place as moist air masses move inland or to a higher altitude, known as the *continental effect* and *altitude effect*, respectively (Dansgaard 1964; Siegenthaler & Oeschger 1980; Fritz et al. 1981; Rozanski et al. 1982; Ingraham & Taylor 1991; Aravena et al. 1999; Kurita et al. 2004). In tropical marine regions the *amount effect* leads to a strong depletion of ^{18}O and D in connection with intense rain events (Dansgaard 1964; Rozanski et al. 1993). The amount effect is a form of *seasonality* in equatorial areas. In the mid- and high lati-

tudes of the northern hemisphere the most distinctive source of seasonal variation is related to temperature, which causes a greater depletion of ^{18}O and D in precipitation during the cold winter months (Rozanski et al. 1982). Re-evaporation, evapotranspiration, evaporative enrichment of raindrops and seasonally changing vapour source areas may also induce seasonal differences in the isotopic compositions of the atmospheric waters (Zimmerman et al. 1967; Sonntag et al. 1983; Schoch-Fischer et al. 1984; Ingraham & Taylor 1991; Jacob & Sonntag 1991). In the continental interiors the seasonal variations in the isotopic composition of precipitation are much more pronounced compared to the coastal areas (Rozanski et al. 1993).

1.3.2. Groundwater

Groundwater is formed from local atmospheric precipitation. In groundwaters the seasonal $\delta^{18}O$ and δD variations in precipitation are generally smoothed out during the infiltration process by means of mixing and isotope change (Zimmerman et al. 1965, 1967). Some seasonality may exist depending on the hydrological properties, size and thickness of the vadose zone of the aquifer (Clark & Fritz 1997). Groundwater may become isotopically distinct from the precipitation by *selective recharge* or *isotopic fractionation* effects related to *evapotranspiration* and *runoff* (e.g. Gat & Tzur 1967; Clark & Fritz 1997). The evaporation of moisture from soil and vegetation surfaces is a fractionating process (Gonfiantini 1986), whereas the uptake of soil water by plant roots and its further removal by transpiration is a non-fractionating process (e.g. Zimmerman et al. 1967; Allison et al. 1984). A significant proportion of the annual rainfall ends up in surface water reservoirs and the oceans by subsurface and overland flow during strong rain events or as snowmelt, rather than recharging the groundwater system. The hydrogeological properties of soils and aquifer deposits, such as the total and effective porosity, affect the infiltration rates (Zimmerman et al. 1965, 1967; Fontes 1980). Evapotranspiration and runoff mechanisms are tightly connected to climate and, especially in higher latitudes, to changing seasons. Only evaporation may change the isotopic composition of the average rainfall. However, evapotranspiration and runoff are able to cause seasonal imbalances in groundwater recharge, and thereby change the isotopic com-

position of groundwater compared to that of the mean annual precipitation. Despite the numerous processes affecting the amount and the isotopic composition of the percolating water (Gat & Tzur 1967; Fontes 1980; Rozanski 1984), the shallow groundwaters in temperate climates closely follow the isotopic composition of the local mean annual precipitation (e.g. Rozanski 1984, 1985; Fritz et al. 1987; Darling et al. 2003; Darling 2004). This suggests that the seasonal cumulative biases are roughly balanced in annual recharge. In low temperature shallow aquifers, the isotopic compositions of oxygen and hydrogen are conservative parameters, which can only generally be changed by mixing with isotopically different water masses (Payne 1981; Faure & Mensing 2005).

1.3.3. Global meteoric water line

Craig (1961) recognized a predictable relationship between $\delta^{18}\text{O}$ and δD in meteoric waters. Based on a large set of fresh water samples, collected from different latitudes, he noticed a global linear correlation between the $\delta^{18}\text{O}$ and δD values, which is called the *global meteoric water line (GMWL)*. The line is defined by the equation:

$$\delta\text{D} = 8\delta^{18}\text{O} + 10\text{‰ VSMOW}.$$

The relationship has been confirmed in many later studies, including that of Rozanski et al. (1993). The *deuterium excess* (*d*-excess) value is defined as:

$$d = \delta\text{D} - 8\delta^{18}\text{O}\text{‰ VSMOW (Dansgaard, 1964)}.$$

A *d*-excess of 10‰ is the average value for global precipitation and derived waters formed from the vapour that was evaporated in the global average humidity of 85% over oceans (Merlivat & Jouzel 1979; Gonfiantini 1986). Essentially, the *d*-excess is a measure that characterizes the meteoric conditions prevailing in the initial moisture source (Merlivat & Jouzel 1979). In addition, it is affected by secondary processes such as the evaporation of raindrops beneath a cloud or evaporation of continental water bodies adding extra moisture to the air mass (Rozanski 1984; Froehlich et al. 2002). The latter would increase the *d*-excess in precipitation, whereas sub-cloud evaporation, induced for example by the lowered relative humidity of terrestrial areas, would decrease the *d*-excess. Seasonal variations in *d*-excess values are distinctive, especially for the precipitation

of the northern hemisphere. Through the combination of all primary and secondary processes, the *d*-excess in global atmospheric precipitation generally varies from -2‰ to 15‰ (Froehlich et al. 2002).

Waters with low $\delta^{18}\text{O}$ and δD values are fairly systematically encountered in cold regions and those with high values in warm regions (Craig 1961). Dansgaard (1964) demonstrated a striking correlation between the long-term annual averages of $\delta^{18}\text{O}$ in precipitation and the mean annual surface air temperature (*T* in °C) in middle and high latitudes, given as:

$$\delta^{18}\text{O} = 0.695T_{\text{annual}} - 13.6\text{‰ VSMOW}.$$

Later studies have demonstrated that on a regional basis, the *T* - $\delta^{18}\text{O}$ relationship varies depending on the spatial and temporal scale of the data in question (Rozanski et al. 1992, 1993).

In isolated surface water reservoirs, such as lakes and rivers, the water mass is exposed to evaporation, which leads to isotopic enrichment and to an offset of the $\delta^{18}\text{O}$ and δD values below the meteoric water line. Compared to the GMWL, the slope of the evaporation line varies from 3.9 to almost 8, depending on the relative humidity, *h* (Gonfiantini 1986). In practice, significant differences are often recorded in $\delta^{18}\text{O}$ and δD between local groundwater and surface water reservoirs.

1.3.4. Tritium

The radioactive isotope tritium has commonly been used to estimate the residence time of water. Tritium is produced in the atmosphere and enters the hydrological circulation in atmospheric precipitation. The concentration of ^3H in meteoric waters varies according to the latitude (Eriksson 1965) and is dependent on the production rate of ^3H in the stratosphere, the decay of ^3H to stable helium (^3He) nuclei and the seasonal variations of injected ^3H from the stratosphere to the troposphere (e.g. Faure 1986; Gat et al. 2001). In addition to the natural production of tritium, the thermonuclear bomb tests between 1951 and 1963 led to the release of anthropogenic ^3H into the atmosphere. This raised the tritium levels by tens to hundreds of orders of magnitude in the northern hemisphere compared to those existing prior to 1951 (Suess 1969; Gat 1980; Meijer et al. 1995). Thereafter, the average atmospheric ^3H level has decreased to close to the natural level of approximately 10 TU (Fontes

1980; Meijer et al. 1995; Gat et al. 2001). The bomb-produced tritium signal has effectively been used for qualitative dating of young groundwaters based on the existence or absence of the bomb anomaly (e.g. Fontes

1980; Clark & Fritz 1997). Tritium activities have also been successfully applied in tracing water movements in the unsaturated zone (Zimmerman et al. 1965, 1966, 1967; Saxena & Dressie 1984).

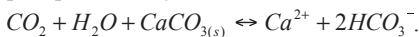
1.4. Carbon in natural waters

1.4.1. Carbonate equilibrium

Rainwater in equilibrium with atmospheric CO_2 records a low P_{CO_2} of $10^{-3.5}$ and a pH of 5.6 (Stumm & Morgan 1996; Appelo & Postma 1999). As the rainwater percolates into the ground, it equilibrates with soil CO_2 , which increases its CO_2 content. Soil CO_2 is mainly derived from the decomposition of organic matter and respiration, and as a consequence, significantly higher P_{CO_2} levels of 10^{-1} to 10^{-3} compared to that of the present atmosphere are observed (Langmuir 1971; Stumm & Morgan 1996; Drever 1997; Appelo & Postma 1999). As CO_2 dissolves in water, carbonic acid (H_2CO_3) is formed. H_2CO_3 further dissociates to bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). The total dissolved inorganic carbon (DIC) is expressed as

$$\sum \text{CO}_2 = m\text{H}_2\text{CO}_3 + m\text{HCO}_3^- + m\text{CO}_3^{2-}.$$

The concentration of DIC in subsurface water may be further increased by carbonate dissolution, which raises the pH and shifts the equilibrium between the carbonate species towards a higher content of CO_3^{2-} . The overall reaction describing carbonate (calcite) dissolution and precipitation may be written as:



The solubility of calcite can be evaluated with the solubility index, $\text{SI}_{\text{calcite}}$, which is defined as:

$$\text{SI}_{\text{calcite}} = [\text{Ca}^{2+}] \cdot [\text{CO}_3^{2-}] / K_{\text{calcite}},$$

$\text{SI}_{\text{calcite}}$ denotes the ion activity product of Ca^{2+} and CO_3^{2-} divided by the solubility product of the calcite, $K_{\text{calcite}} = [\text{Ca}^{2+}] \cdot [\text{CO}_3^{2-}]$ for a saturated solution (Clark & Fritz 1997). The mineral does not have to be present in the system. Natural waters having log $\text{SI}_{\text{calcite}}$ values within ± 0.1 units of zero are considered to be saturated with calcite (Langmuir 1971).

1.4.2. Dissolved organic carbon

The geochemical evolution of dissolved organic carbon (DOC) is closely related to DIC. DOC and DIC are involved in important redox reactions taking place in hydrogeochemical processes. These include the photosynthetic uptake of atmospheric CO_2 by plants and the release of CO_2 by respiration in microbially-mediated processes (e.g. Vogel 1993; Schlesinger 1997). The simplest formula to describe the carbon uptake by photosynthesis and inversely in respiration is as follows:



Respiration controls the soil CO_2 level in the ground, which is generally clearly higher than that in the present atmosphere. Total organic carbon (TOC) is composed of particulate organic carbon (POC) and dissolved organic carbon (DOC), the latter generally amounting to ~90% of TOC in surface waters (Thurman 1985). In groundwaters the DOC content is generally below 1–2 mgC/L.

1.4.3. Carbon isotope signatures of DIC

The $\delta^{13}\text{C}$ values of DIC are dependent on the source of carbon in natural waters. In rainwater, the predominant DIC species is carbonic acid. Thereby, the expected $\delta^{13}\text{C}_{\text{DIC}}$ value for rainwater and surface waters in equilibrium with atmospheric CO_2 is -8‰, as the $\delta^{13}\text{C}$ for the present atmospheric CO_2 is -7‰ (Deines et al. 1974). In subsurface waters, the two main isotopically distinct sources of DIC are the soil CO_2 derived from respiration and microbially-decomposed organic matter and the dissolved carbonate species resulting from the dissolution of carbonate minerals. In addition, the $\delta^{13}\text{C}_{\text{DIC}}$ value of groundwater is dependent on the fractionation between the dissolved carbonate species and soil CO_2 .

In terrestrial high-latitude regions the $\delta^{13}\text{C}$ value of

C_3 vegetation is typically around -27‰ (Deines 1980; Vogel 1993; Schiff et al. 1997). Diffusive loss of soil CO_2 from soil profiles fractionates carbon, and the $\delta^{13}C$ values of soil CO_2 are thereby generally about -23‰ (Cerling et al. 1991; Aravena et al. 1992). Groundwaters in crystalline bedrock terrains have a low pH (< 7), and they generally record nearly the same $\delta^{13}C$ as that in soil CO_2 (Aravena et al. 1992). The existence of carbonate minerals in the aquifer material brings an additional carbon source to the DIC pool. The carbon isotope composition of sedimentary marine carbonates has generally remained at 0(±3)‰ throughout geological history (Schidlowski et al. 1983). In diagenetic carbonates the $\delta^{13}C$ values are typically lower than those in marine carbonates. Generally, the dissolution of carbonate minerals tends to shift the $\delta^{13}C_{DIC}$ to higher values compared to those of the initial DIC in water.

Activities of radiocarbon can be used in constraining the sources of DIC in the geochemical evolution of groundwaters. The fractions of CO_2 , DIC and DOC derived from the living biomass record ^{14}C activities close to the modern atmospheric level of ~100 pmC (Deines 1980). The ^{14}C method has been widely used to date groundwaters from the late Quaternary period (Clark

& Fritz 1997). Carbon matter older than this is generally free of ^{14}C , i.e. the ^{14}C activity of “dead carbon” is 0 pmC.

The $\delta^{13}C_{DIC}$ values and the activities of $^{14}C_{DIC}$ can be used to evaluate the degree of openness of the groundwater system with respect to soil CO_2 (e.g. Deines 1980; Clark & Fritz 1997). In a carbonate-free environment, under both open and closed system conditions, the isotopic composition of soil CO_2 defines the $^{14}C_{DIC}$ activity and the $\delta^{13}C_{DIC}$ value in groundwater (Aravena et al. 1992). In carbonate terrains, however, DIC is derived from isotopically distinct carbon sources. Under both open and closed system conditions, the dissolution of calcite increases the $\delta^{13}C_{DIC}$, but the magnitude of the shift in $\delta^{13}C_{DIC}$ is dependent on the amount of calcite dissolved (Fig. 1). In open systems, regardless of calcite dissolution, the soil CO_2 prevails, and the $^{14}C_{DIC}$ activities remain at around 100 pmC. Under closed system conditions, however, the modern $^{14}C_{DIC}$ composition is diluted by the ^{14}C -free carbon source. Similarly, the decomposition of organic matter with a distinct ^{14}C signature would affect the activity of $^{14}C_{DIC}$ in groundwater. In addition, the decay of DOC may add isotopically light DIC to groundwater, thus raising $\delta^{13}C_{DIC}$. Mixing

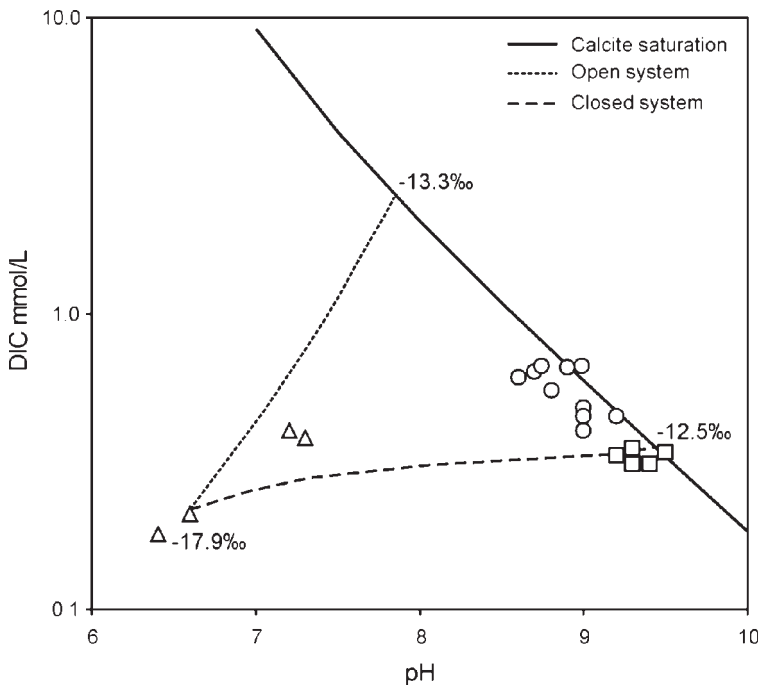


Figure 1. The evolution of DIC, $\delta^{13}C_{DIC}$ and pH in groundwater as calcite ($\delta^{13}C = -4.8\text{‰}$ for the detrital calcite in Virttaankangas sedimentary deposits) is dissolved to the point of saturation under open and closed system conditions. The initial water composition is assumed to be at equilibrium with a soil P_{CO_2} of $10^{-2.8}$ and with the assumed $\delta^{13}C_{CO_2}$ of -23‰ . The model trails for open and closed systems were calculated using the program PHREEQC (Parkhurst & Appelo 1999). The larger the difference between $\delta^{13}C_{CO_2}$ and $\delta^{13}C_{calcite}$, the more diagnostic is the $\delta^{13}C_{DIC}$ to evaluate whether saturation with respect to calcite was attained under open or closed system conditions. The illustration is modified from Figure 6 of Paper IV. Symbols illustrate the composition of groundwater in the Virttaankangas aquifer; circles represent a lowermost unconfined esker core aquifer unit, squares a semi-confined glaciofluvial aquifer unit and triangles an uppermost unconfined perched aquifer unit.

of waters with distinct $^{14}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{DIC}}$ may also affect the isotopic composition of DIC. All these processes

may be investigated and quantified using analyses of $\delta^{13}\text{C}_{\text{DIC}}$ and $^{14}\text{C}_{\text{DIC}}$.

1.5. Aims of the study

Paper I addresses the natural isotopic variations of oxygen and hydrogen in the local atmospheric precipitation and the relationship between the isotopic composition of precipitation and present day groundwaters in Finland. The dataset was complemented with water monitoring data presented in Chapter 4 of this thesis. The aim of the study was to provide isotopic background data for hydrological studies and to supplement the isotopic records of global precipitation.

The sources of dissolved carbon and the geochemical evolution of groundwater were investigated using carbon isotope ratios in dissolved inorganic carbon (DIC). Paper II presents data from an artificially recharged glacial groundwater formation at Tuusula, located north of Helsinki in southern Finland. The

study aimed to trace redox processes associated with the decomposition of DOC using the isotopic composition of DIC in water. Papers III and IV considered a carbonate-bearing, glacial aquifer in a natural state at Virttaankangas, located north of Turku in southwest Finland. Groundwaters in the Virttaankangas aquifer are characterized by exceptionally high pH values exceeding 9. The goal of the investigation reported in Paper III was to determine the mode of occurrence of calcite in the Virttaankangas sedimentary material and to identify its sources. The study reported in Paper IV aimed to determine the interaction of groundwater with solid carbonates and soil CO_2 , and to evaluate the origin of the unusual hydrogeochemical characteristics of the Virttaankangas groundwaters.

2. METHODS

2.1. Water sampling

The precipitation collection devices were placed in an open undisturbed location. The sampling period for monthly precipitation was from the beginning to the end of the month. Rainwater was collected in a 2-litre Teflon® separatory funnel. To prevent evaporation, a layer of paraffin oil was added to the funnel (IAEA/WMO 2006a). The collector was covered by aluminium foil. Snow was collected in a thick-walled plastic cylinder sealed at one end. A plastic bag inside the cylinder was replaced after every snow event. Paraffin oil was added to the plastic bag when thawing. At the end of the month the sub-samples were combined. The monthly precipitation in mm was calculated from the total volume of the collected rainwater.

Groundwater was lifted from dug wells and springs with a clean plastic bucket. Drilled bedrock wells and production wells were sampled from taps. Any filters were removed and the water was allowed to run for a few minutes in order to obtain a fresh sample. Sampling was restricted to wells in intensive use and in good condition to ensure representative groundwater samples. Observation wells (tubes) were sampled using a frequency-controlled electric submersible pump. Prior to sampling the wells were pumped for 20 minutes or more in order to replace the water volume in the well several times.

2.2. Chemical 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 ion chromatography method. Both cations and anions were analysed in the Geolaboratory at the Geological Survey of Finland (GTK). The concentration of DOC was determined using a Shimadzu 5000 TOC analyser in the Laboratory of Environmental Microbiology, National Public Health Institute, Kuopio. The detection limit of the method was 0.3 mg C/L with a total error of $\pm 15\%$. To check the DOC measurements (Paper II), the content of TOC was determined with an Apollo 9000 analyser at the Environment Centre of the City of Helsinki. The measurement uncertainty was $\pm 20\%$. Temperature, pH, electrical conductivity (EC), alkalinity and the dissolved O_2 content in water were determined in the field.

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 areas have low alkalinity values ($< 50 \text{ mg/L}$), 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^- . To verify the field measurements, alkalinity, pH and EC were also analysed in the laboratory. For alkalinity, the titration end point at a pH value of 4.5 (standard method: SFS-EN ISO 9963-1/1996-08-26) was used in the laboratory, which generated a small, systematic shift to higher alkalinity values compared to the field measurements. The speciation of the dissolved carbonate components and the total content of DIC were calculated using the program PHREEQC (Parkhurst & Appelo 1999).

2.3. Isotope methods

Unfiltered samples for isotope analyses of oxygen and hydrogen were poured into 50 ml HDPE bottles and stored in the dark and cold. For the analysis of $\delta^{18}\text{O}$ the water samples were equilibrated with CO_2 gas and the isotopic composition of CO_2 was analysed (Epstein & Mayeda 1953). The isotopic composition of hydrogen was analysed after the reduction of water to H_2 using zinc metal (Coleman et al. 1982). The zinc reagent was prepared from pure metal by adding Na as an impurity (Karhu 1997).

For the analysis of $\delta^{13}\text{C}$ in DIC, a phosphoric acid reaction technique was applied, modified from that published by Atekwna & Krishnamurthy (1998). In the field, the duplicate water samples were filtered (< 0.45 or $< 0.20 \mu\text{m}$) or injected without filtering into pre-evacuated glass septum tubes (20 or 60 ml), loaded with 85% phosphoric acid and a magnetic stir bar. The evolved CO_2 gas was extracted in a vacuum line, with the sample vessel stirred in a water bath at 50°C for 10 minutes. CO_2 gas was purified cryogenically and the yield was measured. To examine the reliability of the $\delta^{13}\text{C}_{\text{DIC}}$ measurements, a test solution of $9.4 \text{ mM Na}_2\text{CO}_3$ was prepared by dissolving dried Na_2CO_3 (200°C under vacuum for 4 hours) into distilled water (CO_2 degassed by boiling under N_2 gas). The solution was sampled and

prepared as described above and analysed for $\delta^{13}\text{C}_{\text{DIC}}$. The dried Na_2CO_3 powder was also analysed for $\delta^{13}\text{C}$ (and $\delta^{18}\text{O}$). The carbonate samples were reacted at 50°C for 50 to 100 minutes. Otherwise, the same preparation method was followed as for calcite given below. The mean $\delta^{13}\text{C}_{\text{DIC}}$ value measured in the Na_2CO_3 test solution was $-5.73 \pm 0.09\text{‰}$ (1SD, $n = 5$), while the mean $\delta^{13}\text{C}$ determined in the solid Na_2CO_3 was $-5.61 \pm 0.07\text{‰}$ (1SD, $n = 4$). The isotope values measured in the solution and in the solid carbonate therefore agreed well.

Prior to isotopic analysis of carbonate samples, the carbonate mineral in question was identified by XRD analysis. For the determination of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in calcite, the sample was reacted with supersaturated phosphoric acid. The sample vessels were kept in a water bath at 50°C for 2 hours to ensure a complete reaction, and the evolved CO_2 was removed from the vessels by vacuum extraction and cryogenic collection.

Isotopic ratios of the produced CO_2 and H_2 were measured by a Finnigan MAT 251 gas source mass spectrometer at GTK. $\delta^{18}\text{O}$ and δD values are given normalized to values of -55.5‰ and -428‰ , respectively, for SLAP (Standard Light Antarctic Precipitation) relative to VSMOW (Coplen 1994). The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of calcite and $\delta^{13}\text{C}$ of DIC are given relative to

the VPDB and VSMOW standards calibrated through the NBS-19 standard. The repeatability of analyses was $\leq 0.1\%$ for oxygen and $\leq 1.0\%$ for hydrogen in water, $\leq 0.2\%$ for carbon in DIC, and $\leq 0.05\%$ for carbon and oxygen in calcite. During this study, the reference standard GISP yielded $\delta^{18}\text{O}$ and δD values of $-24.94 \pm 0.07\%$ and $-189.4 \pm 1.3\%$ (1SD, $n = 8$), respectively. This agrees well with the $\delta^{18}\text{O}$ and δD values of -24.75% and -189.9% , respectively (Hoefs 1997).

Filtered groundwater samples ($< 0.45 \mu\text{m}$) were taken for strontium analyses. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were determined in a dynamic mode on a VG SECTOR 54 mass spectrometer at GTK. The isotopic ratios were normalized to a $^{86}\text{Sr}/^{88}\text{Sr}$ value of 0.1194. The 2SD uncertainty

of the measurements varied within $\pm 0.00002 - 0.00009$. The average value for the SRM987 standard over the analysis period was 0.710261 ± 0.000011 (2 SD, $n = 12$) for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio.

Tritium and ^{14}C in water samples were analysed at CIO, the University of Groningen, the Netherlands. Tritium was determined from enriched samples by liquid scintillation counting (LSD). The analytical error was $\pm 0.2 \text{ TU}$. ^{14}C in water samples was measured by accelerator mass spectrometry (AMS). ^{14}C activities were normalised to a common $\delta^{13}\text{C}$ value of -25% in order to correct the ^{14}C value distorted by isotopic fractionation. The analytical errors varied within $\pm 0.4 - 0.9 \text{ pmC}$.

3. REVIEW OF PAPERS

3.1. Paper I

The isotopic composition of oxygen and hydrogen in Finnish groundwaters and in precipitation were determined to examine the relationships between groundwater, precipitation and mean surface temperature. No previous detailed studies existed on the isotopic composition of precipitation or groundwater in Finland, and the regional groundwater data and precipitation records presented in Paper I gave the first approximation of the spatial variability in the isotopic composition of precipitation in Finland.

Monthly precipitation was collected at a precipitation station in Espoo, on the southern coast of Finland. The data set covers a two-year monitoring period from November 2000 to October 2002. Due to the lack of precipitation data from northern Finland, published data from adjacent areas in northern Sweden were used for the comparison of groundwater (Burgman et al. 1983, 1987). Paper I also presents two comprehensive groundwater data sets collected in two nationwide hydrogeological research programmes during 1995 to 2001. The first one comprises a 7-year monitoring record of groundwater at 19 sites sampled four times a year. The $\delta^{18}\text{O}$ value was analysed in 451 groundwater samples and the δD in 433 samples. The groundwater sites represent shallow unconsolidated aquifers of glaciogenic origin, generally consisting of unconfined basal till and moraine formations, eskers and ice-marginal formations. Besides these,

confined clay-covered and bedrock aquifers were also included in the second groundwater research programme. The regional data set is based on one sampling occasion conducted during the field season of 1999. In total, 983 water samples with a good geographical coverage were analysed for the isotopic composition of oxygen, and 70 samples out of these for that of hydrogen.

The $\delta^{18}\text{O}$ and δD values for monthly precipitation in Espoo varied from -6.64% to -15.85% and from -44.4% to -114.4% , respectively. The weighted mean annual $\delta^{18}\text{O}$ and δD values for the two-year precipitation collecting period were -11.62% and -81.6% , respectively. The isotopic ratios of oxygen and hydrogen were highly correlated and yielded a regression line of $\delta\text{D} = 7.84\delta^{18}\text{O} + 9.35$ ($r^2 = 0.99$), which is very close to the line defined by GMWL. Monthly $\delta^{18}\text{O}$ values correlated linearly with mean monthly surface temperatures, defining a line of $\delta^{18}\text{O} = 0.29T - 13.83$ ($r^2 = 0.86$; $T \text{ } ^\circ\text{C}$). The isotopic composition of oxygen and hydrogen in both groundwater data sets showed a systematic and gradual depletion of heavy isotopes from south to north, the difference in the long-term means being approximately 4% for oxygen and 34% for hydrogen. The highest δ -values measured in southwest Finland were -11.56% for oxygen and -82.3% for hydrogen. The most negative $\delta^{18}\text{O}$ and δD values recorded in the north were -15.56% and -116.2% , respectively. The correla-

tion line for $\delta^{18}\text{O}$ and δD in the long-term monitoring data is defined by the equation $\delta\text{D} = 8.51\delta^{18}\text{O} + 16.65$ ($r^2 = 0.99$). A strong linear correlation was also recorded between the mean $\delta^{18}\text{O}$ (or δD) value of groundwaters and the local mean annual temperatures, defining a line $\delta^{18}\text{O} = 0.53T - 14.42$. Significant regional variations are encountered in the Finnish mean annual surface temperature with a gradual change from +5 °C in the south to -3 °C in the north. Apart from eastern Finland, the isotope shift in groundwaters almost parallels the change in the mean annual surface temperature.

The mean weighted annual composition of precipitation in the limited data set of Paper I displayed no significant differences from the isotopic composition of local groundwater, even though several climatic and hydrogeological factors potentially affect the isotopic composition of infiltrating water. The attenuation of the strong seasonal isotopic variations seen in precipitation is the most distinctive feature in the formation of groundwater. In the southern Finland the total range of 9‰ for the $\delta^{18}\text{O}$ in precipitation is reduced to less than 1‰ and in the north the total variation of 11‰ for oxygen has decreased to 1–2.5‰. The proportion of water that actually recharges the groundwater system is small

compared to the annual amount of rainfall. In Finland this is mainly dependent on the infiltration rates of the soil deposits and the existing seasonal imbalance in recharge, decreasing the proportion of winter and summer precipitation in groundwater recharge. The annual cumulative bias in the isotopic composition of groundwater is, however, small, suggesting that the seasonal biases are roughly similar in magnitude but opposite in sign.

Groundwaters in Finland display a distinct spatial distribution of the isotopic ratios of oxygen and hydrogen. The depletion of the heavier isotopes as a function of increasing latitude is closely related to the local mean surface temperature. Using the mean $\delta^{18}\text{O}$ values of the long-term monitoring data and local mean annual temperatures, the spatial isotope-temperature coefficient of 0.53‰ / °C was observed for Finnish groundwaters. This value is close to the spatial relation of 0.59‰ / °C reported for the $\delta^{18}\text{O}$ of precipitation in Sweden by Burgman et al. (1987) and for European stations by Rozanski et al. (1992). These results suggest that the link between the spatial variability in the isotopic composition of precipitation and local temperature is preserved in groundwaters.

3.2. Paper II

Paper II considers the role of redox processes in the decomposition of dissolved organic carbon (DOC) in water as surface water with a high DOC content is infiltrated into an aquifer. The isotopic composition of DIC in the infiltration water was used to trace the reduction of DOC in subsurface processes. The method was applied at the Tuusula artificial groundwater plant, southern Finland.

Reducing the concentration of DOC in surface water to a recommended level is the main challenge for managed groundwater recharge in Finland. A general observation is that the infiltration of surface water through mineral soil leads to a significant decrease in the DOC content, and especially the early stage of subsurface flow is critical. Two distinct processes are suggested for the reduction of the DOC content in infiltrated water during artificial recharge: (1) DOC may be adsorbed as organic matter on the surfaces of soil particles, and (2) DOC could be oxidized and decomposed

by bacterially-mediated processes. In earlier attempts to quantify the removal of DOC, measurements of the consumption of O_2 and the production of CO_2 have been the only methods applicable for reaction rate calculations. A few studies have been published on the use of isotope methods to trace geochemical reactions in managed aquifer recharge. In Paper II, isotopic methods are used for the first time to quantify the processes of DOC removal in artificial groundwater recharge.

At the Tuusula artificial groundwater plant, surface water derived from Lake Päijänne, about 100 km NNE of the plant, is recharged into a glaciofluvial esker aquifer by a pond infiltration method. The volume of artificially recharged water accounts for 70% of the water intake from the groundwater system. The distance between the farthest intake well and the infiltration ponds is 700 m. The time span from infiltration to intake of water is approximately 36 to 51 days.

Water samples were collected from 10 sites, outside

and within the artificial recharge system, and analysed for the isotopic composition of oxygen, hydrogen and DIC, for the DOC and TOC contents and for basic hydrochemical parameters. The total DIC content was calculated from the chemical composition of the water. Besides the samples collected in August 2001, a few additional samples taken in 1999 and 2005 were included, and the data were complemented by geochemical monitoring data from the same observation sites between 1998 and 2001 provided by Tuusula District Waterworks.

The $\delta^{18}\text{O}$ value of $-12.20 \pm 0.12\text{‰}$ ($\pm 1\text{SD}$) and δD value of $-86.6 \pm 0.9\text{‰}$ for local groundwater and the respective values of $-9.47 \pm 0.07\text{‰}$ and $-74.5 \pm 0.7\text{‰}$ for the infiltrated surface water are based on the monitoring period of two years. The distinctive $\delta^{18}\text{O}$ and δD signatures of the end member waters were used to trace mixing in the system. The waters determined in the area within the first 480 m of groundwater flow included a 95 to 100% proportion of infiltration water. Thereafter, the proportions of infiltration water decreased to 48 to 71%.

Based on the determinations of $\delta^{13}\text{C}_{\text{DIC}}$ and the content of DIC and DOC, the hydrogeochemical evolution of the infiltrated water can be divided into three successive stages, where different processes dominate in the removal of DOC.

(1) The initial DOC content decreased by 44% during the first 330 m of groundwater flow. At the same time, the content of total dissolved carbon (DIC + DOC) remained constant, indicating that the system was closed to external carbon sources. The sources of DIC include atmospheric and soil CO_2 , the admixture of local groundwater with a high DIC content, and carbonate dissolution. The recharge water recorded a considerable decrease in $\delta^{13}\text{C}_{\text{DIC}}$ from -10.7‰ to -16.3‰ at the first observation well next to the infiltration ponds. The change in $\delta^{13}\text{C}_{\text{DIC}}$ is attributed to the mixing of carbon

from two isotopically distinct sources, i.e. from the oxidation of DOC in the infiltrated water with terrestrial carbon ($\delta^{13}\text{C} = -27\text{‰}$, e.g. Deines, 1980) and from DIC initially present in the infiltration water ($\delta^{13}\text{C}_{\text{DIC}} = -10.7\text{‰}$). The mean $\delta^{13}\text{C}_{\text{DIC}}$ value of -20.8‰ was measured for the local groundwater. The measured $\delta^{13}\text{C}_{\text{DIC}}$ values in waters agree with the modelled change in the $\delta^{13}\text{C}$ values as a function of increasing DIC content. It can be concluded that oxidative decomposition is the main process reducing the content of DOC and producing DIC in the first stage of groundwater flow to a distance of 330 m from the infiltration ponds.

(2) Between 330 and 450 m from the infiltration ponds the concentration of DOC decreased by 23% relative to the initial value. However, the DIC content simultaneously decreased. As a result, total dissolved carbon was removed from the system, suggesting that organic carbon was adsorbed on mineral surfaces. Oxygen isotope ratios indicated no significant mixing with local groundwater.

(3) The final decrease of 14% in the DOC content was observed between a distance of 450 and 700 m from the ponds. At the farthest intake well (700 m) the proportion of local groundwater had increased to 52%, adding an additional carbon source to the system. This is seen as a significant rise in the concentration of DIC and a decrease in the $\delta^{13}\text{C}_{\text{DIC}}$ value in water. The $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{18}\text{O}_{\text{water}}$ values were consistent with a modelled change in the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, when two end member waters with different DIC contents and isotope ratios were mixed in varying proportions. The results suggested that the shift in $\delta^{13}\text{C}_{\text{DIC}}$ and in dissolved carbon contents observed at the final stage can be mostly attributed to mixing between infiltrated water and local groundwater.

The total drop in DOC observed at the artificial plant was 0.35 mmol/L or 81% relative to the level in the infiltrated water.

3.3. Paper III

Paper III addresses the mineralogy, the isotope geochemistry and the origin of the aquifer sediments in the glacial Virttaankangas complex, SW Finland. Groundwaters in the Virttaankangas aquifer are characterized by high pH values up to 9.5, which are exceptional for an unconsolidated aquifer composed of

silicate minerals. These high pH values have apparently been derived from reactions between the sediments and groundwater, but they are in strong contrast to the pH normally recorded in shallow groundwaters of the Fennoscandian shield, averaging 6.4. Virttaankangas sediments were discovered to contain small amounts of fine

grained, dispersed calcite, which has a high tendency to increase the pH of local groundwaters. The aim of this study was to determine the occurrence, dispersal and the source of carbonate minerals in the Virttaankangas sedimentary material. The mineralogical composition of the aquifer material and the potential sources of carbonate bearing rocks in the surrounding areas were examined. The isotope ratios of carbon and oxygen in calcite were used to provide evidence for the origin of dispersed calcite in the Virttaankangas complex.

Calcite could be present in the Virttaankangas sediments as an in-situ precipitate or as a detrital phase transported from the source area. The presence of an in-situ precipitate was considered, as post-depositional carbonate precipitation in the porous media of carbonate aquifers has been reported e.g. by McMahon & Chapelle (1991). The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the Virttaankangas dispersed calcite were compared with those resulting from precipitation under modern conditions, which, however, showed that in-situ precipitation of calcite was not an option. The presence of detrital carbonate in the glacial sediments appeared to be unlikely also, as no obvious source for carbonate minerals is available in the Virttaankangas area, as the Säkylänharju–Virttaankangas complex has been deposited on the Paleoproterozoic basement consisting mainly of plutonic quartz-diorite and tonalite. The Mesoproterozoic Satakunta sandstone is known to be the principal source of sedimentary material for the Virttaankangas complex, but previous studies have not reported the presence of carbonate minerals in the sandstone material. The southeast contact of the Satakunta Formation is met approximately 10–15 km W and NW from the Virttaankangas study area.

The mineralogy of the glacial Virttaankangas complex was studied using material from 21 sediment drill cores. The mineralogical composition, soil type, grain size and sorting of the sediment samples were investigated. The total amount of carbon in the sediment cores was determined using a carbon analyser (Leco) in order to obtain a rough estimate of carbonate contents in the cores. Selected samples were analysed by XRD and SEM/EDS. In order to constrain the source of calcite, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of five calcite samples were compared to those from five carbonate rock erratics and eight crystalline bedrock samples from the

region. The erratics and bedrock samples were studied micro- and macroscopically. Additionally, the chemical composition of calcite in two bedrock samples from the Satakunta sandstone and in one sediment sample from the Virttaankangas complex was analyzed using electron probe microanalysis (EPMA).

The fine-grained clastic calcite in the Virttaankangas formation 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 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 EPMA, the grains are practically stoichiometric calcite (CaCO_3). The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of detrital calcite vary from -5.67 to -4.45‰ and from 23.20 to 23.53‰, respectively.

Three of the investigated Satakunta sandstone drill cores were observed to contain a significant amount of calcite, representing diagenetic cement in grain inter-spaces, concretions and interlayers. Six samples from these drill cores and one from the erratic boulder yielded $\delta^{13}\text{C}$ values varying from -11.38‰ to -5.13‰ and $\delta^{18}\text{O}$ values from 20.68‰ to 25.02‰. In the SE corner of the sandstone formation the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values were more tightly constrained from -5.84 to -5.13‰ and from 24.43 to 25.02‰, respectively. These isotope values compared well with those measured from detrital calcite in the Virttaankangas complex. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in carbonate rock erratics, carbonate bedrock samples and Phanerozoic marine carbonates excluded them from the list of the possible sources of detrital calcite.

The isotope records of carbon and oxygen, the angular morphology of the grains and the uniform dispersion of calcite in the Virttaankangas complex suggest a clastic origin for calcite. Based on $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values and elemental compositions, the dispersed calcite of the Virttaankangas complex has been derived from diagenetic calcite locally abundantly present in the Mesoproterozoic Satakunta sandstone, some 30 km NW of the Virttaankangas area. The results support the earlier suggestion that the Satakunta Formation is the main source of clastic material in the Virttaankangas complex.

3.4. Paper IV

Paper IV presents a groundwater formation with unusual hydrogeochemical properties. Very high pH values of up to 9.5 are encountered in the Virttaankangas glacial aquifer, southwest Finland. This is in strong contrast to the average pH of 6.4 in Finnish shallow groundwaters. Chemical and isotopic compositional parameters were determined in order to evaluate the origin of the unusual chemical characteristics of the groundwater. Mineralogical investigations, presented in Paper III, revealed trace amounts of dispersed calcite in the aquifer sediments. The isotopic composition of carbon in DIC was applied as a key variable to study the interaction of the groundwater system with solid carbonates and soil CO₂.

The Virttaankangas aquifer is located in a NW–SE esker chain composed of Quaternary deposits. The total thickness of unconsolidated sediments generally varies from 20 to 50 m, but reaches 90 m locally in a bedrock fault zone. Three distinct aquifer units were recognized in the Virttaankangas groundwater system based on their hydrogeologic properties and sedimentation history. These are an esker core aquifer (Unit 1), a semi-confined aquifer (Unit 2) and a perched aquifer (Unit 3). Water samples were collected from 17 sites in Units 1–3 and analysed for $\delta^{18}\text{O}$, δD and $\delta^{13}\text{C}_{\text{DIC}}$, and for basic hydrochemical parameters. The activities of ^3H and ^{14}C and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were determined for selected samples.

Mineralogical investigations of the Virttaankangas sediments revealed trace amounts of calcite, predominantly in the < 0.2 mm fraction. Calcite is present in the glacial Units 1 and 2. However, the littoral sands of Unit 3 are practically devoid of calcite. The mean $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for clastic calcite were $-4.8 \pm 0.5\text{‰}$ and $23.4 \pm 0.1\text{‰}$, respectively. In a relatively limited area within the same aquifer system, considerable variation in the water pH values from 6.4 to 9.5 was observed. The separate aquifer units have distinct hydrogeochemical and isotope geochemical characteristics. The groundwater of Unit 3 is highly undersaturated with respect to calcite. Chemically, it represents typical shallow groundwaters in calcite-poor Precambrian shield areas, with a low pH value of < 7, low electrical conductivity and generally low $\delta^{13}\text{C}_{\text{DIC}}$ of < -20‰. Somewhat higher $\delta^{13}\text{C}_{\text{DIC}}$ values of up to -17‰ were encountered in groundwater taken from one of the perched sub-aqui-

fers, in the Lake Kankaanjärvi area. The groundwater in Unit 2 is saturated with respect to calcite and the 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 respect to calcite. The $\delta^{13}\text{C}_{\text{DIC}}$ values in Units 1 and 2 vary from -17.2‰ to -12.7‰.

The contents of tritium and ^{14}C in groundwaters were used to determine qualitative age constraints for the waters in the different aquifer units. The thermonuclear “bomb” tritium label of about 20 TU was strongest in Unit 2, recognisable in Unit 1 and decreased down to the present atmospheric level of about 10 TU in Unit 3, which suggests that the residence time of groundwater decreases in this order. An inverse pattern exists for ^{14}C in relation to tritium. In Unit 2 the $^{14}\text{C}_{\text{DIC}}$ signal is diluted by the dissolution of old ^{14}C -free carbonate minerals, whereas the atmospheric level of 100 pmC is measured in Unit 3. The $\delta^{18}\text{O}_{\text{water}}$ and $\delta\text{D}_{\text{water}}$ in all units are typical for groundwater formed under the present climatic conditions. Sr concentrations and isotope ratios also showed systematic differences between the aquifer units. In the main formation of Units 1–3 the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr concentrations increased as a function of increasing residence time of waters in the aquifer. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the Virttaankangas groundwater are relatively radiogenic, varying approximately in the range of 0.718–0.752.

Calcite dissolution appears to have an essential role in the evolution of hydrochemical and isotope geochemical characteristics of the Virttaankangas aquifer. Three distinct evolution paths were recognized depending on the openness of the system with respect to soil CO₂ and the occurrence of calcite in the aquifer sediments. An open system without detrital calcite prevailed in the perched aquifer of Unit 3. Calcite dissolution in open system conditions is found in the deepest parts of the perched aquifer of Unit 3, which adds more DIC to the water prior to closing of the system with respect to soil CO₂. Thereby, a combination of closed and open system calcite dissolution is observed in the unconfined esker core aquifer of Unit 1, leading to variability in the pH values and DIC concentrations of groundwaters. Finally, closed system calcite dissolution is suggested to be responsible for the chemical composition of the waters in

the semi-confined aquifer of Unit 2 with extreme pH values. A relatively low P_{CO_2} of $10^{-2.8}$ is estimated to prevail in the system prior to calcite dissolution. It can be con-

cluded that a high pH was reached as a result of calcite dissolution at a low P_{CO_2} . Calcite dissolution was verified by $\delta^{13}C_{DIC}$ values and decreasing $^{14}C_{DIC}$ activities.

4. RESULTS OF WATER MONITORING

This chapter presents recent results from the precipitation and groundwater monitoring programs, not included in Papers I, II, III or IV.

4.1. Precipitation

Cumulative monthly precipitation has been collected for isotopic determinations at a southern coastal station in Espoo, continuing from November 2000. The isotopic data from 2000 to 2002 were published in Paper I. In order to expand the coverage of the precipitation records in Finland, two new inland stations were established, one at Kuopio in eastern and the other at Rovaniemi in northern Finland. Precipitation collection at the Rovaniemi station started at the end of 2003 and at the Kuopio station at the beginning of 2005. The locations of the three stations are shown in Figure 2. The stations are active parties of the Global Network for Isotopes in Precipitation (GNIP) programme operated by the International Atomic Energy Agency (IAEA) in cooperation with the World Meteorological Institute (WMO).

The isotopic composition of oxygen and hydrogen of the cumulative monthly precipitation at the Espoo, Rovaniemi and Kuopio stations was analysed in samples collected during monitoring periods from November 2002 to October 2005, November 2003 to October 2005, and January to December 2005, respectively. The $\delta^{18}O$ and δD values, the d -excess, the amount of precipitation at the collection site, the collecting period and the mean monthly temperatures at the closest meteorological observation stations of the Finnish Meteorological Institute (FMI) are presented in Appendix 1. The monthly and annual mean amount of precipitation and the monthly and annual averages of air temperature, $\delta^{18}O$, δD and d -excess are summarized in Table 1. Both the arithmetic and weighted mean of $\delta^{18}O$, δD and d -excess values are provided. To consider the seasonality in $\delta^{18}O$ and δD , the monthly minimum and maximum and the amplitude

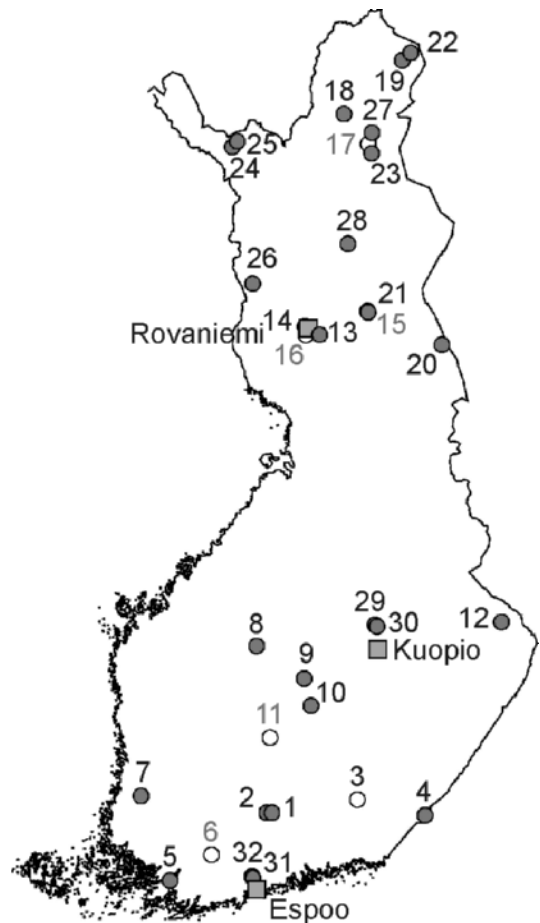


Figure 2. Locations of the groundwater monitoring sites (closed circles = active sites, open circles = monitoring ended in 2001) and the precipitation collection stations in Espoo, Kuopio and Rovaniemi.

Table 1. Annual and monthly mean $\delta^{18}\text{O}$, δD and d -excess in precipitation.

STATION	Month	T °C	Prec mm	$\delta^{18}\text{O}$, ‰ VSMOW		δD , ‰ VSMOW		d -excess	
				arithmetic	weighted	arithmetic	weighted	arithmetic	weighted
ESPOO									
Monthly means (5 years)	Jan	-3.6	63	-14.55	-13.79	-105.6	-100.4	10.8	10.0
	Feb	-4.1	38	-15.80	-14.58	-116.1	-106.8	10.3	9.8
	Mar	-1.7	28	-12.32	-12.89	-89.5	-94.3	9.1	8.8
	Apr	4.4	23	-12.35	-12.35	-90.8	-87.9	8.0	10.9
	May	10.2	39	-8.88	-9.07	-63.7	-65.7	7.3	6.9
	Jun	14.1	77	-10.26	-10.49	-74.9	-76.5	7.2	7.4
	Jul	19.2	83	-8.91	-9.59	-62.4	-67.5	8.9	9.2
	Aug	17.3	92	-9.36	-10.03	-66.0	-69.7	8.8	10.6
	Sep	12.5	53	-8.61	-9.72	-59.4	-67.4	9.5	10.3
	Oct	5.9	58	-13.26	-12.77	-94.4	-90.6	11.7	11.5
	Nov	1.9	76	-13.19	-12.79	-90.9	-87.6	14.7	14.7
	Dec	-2.0	62	-13.94	-13.07	-99.7	-93.2	11.9	11.3
Annual mean		6.2	Σ 692	-11.79	-11.54	-84.4	-82.0	9.8	10.3
Min		-4.1		-15.80	-14.58	-116.1	-106.8	7.2	6.9
Max		19.2		-8.61	-9.07	-59.4	-65.7	14.7	14.7
Amplitude		23.3		7.18	5.52	56.7	41.2	7.5	7.9
KUOPIO (1 year)									
Annual mean		4.6	Σ 625	-14.12	-13.43	-102.7	-97.0	10.3	10.5
Min		-8.4		-21.46		-167.1		4.6	
Max		18.7		-9.47		-68.2		14.9	
Amplitude		27.1		11.99		98.9		10.3	
ROVANIEMI									
Monthly means (2 years)	Jan	-8.0	32	-19.18	-18.46	-142.1	-136.7	11.4	11.0
	Feb	-9.5	21	-18.51	-18.73	-138.0	-139.5	10.0	10.3
	Mar	-6.8	13	-13.88	-14.05	-105.2	-106.5	5.8	5.9
	Apr	2.0	22	-15.15	-15.15	-116.4	-116.4	4.8	4.8
	May	6.8	63	-12.56	-12.89	-89.4	-92.2	11.1	10.9
	Jun	13.2	56	-12.11	-12.34	-91.5	-93.4	5.4	5.3
	Jul	17.6	71	-10.02	-10.02	-73.1	-73.1	7.1	7.1
	Aug	14.3	96	-10.59	-10.47	-76.1	-75.0	8.6	8.8
	Sep	8.7	90	-12.90	-12.87	-91.9	-91.7	11.3	11.3
	Oct	2.7	22	-13.46	-13.14	-95.0	-92.2	12.7	12.9
	Nov	-4.0	21	-17.59	-17.54	-125.2	-125.0	15.5	15.3
	Dec	-7.1	43	-15.32	-14.84	-109.4	-106.0	13.1	12.7
Annual mean		2.5	Σ 550	-14.23	-13.04	-103.9	-94.8	9.9	9.5
Min		-9.5		-19.18	-18.73	-142.1	-139.5	4.8	4.8
Max		17.6		-10.02	-10.02	-73.1	-73.1	15.5	15.3
Amplitude		27.1		9.17	8.71	69.0	66.4	10.8	10.5

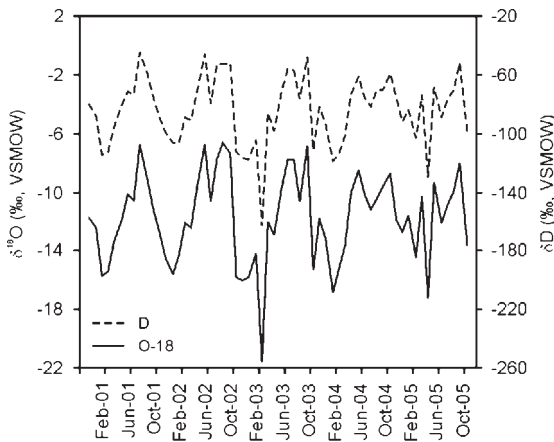


Figure 3. Time series of $\delta^{18}\text{O}$ and δD values in the monthly precipitation at the Espoo station.

are also presented in Table 1. The highest $\delta^{18}\text{O}$ and δD in precipitation were recorded at the Espoo station, where the weighted (and arithmetic) annual mean $\delta^{18}\text{O}$ and δD values were -11.54‰ (-11.79‰) and -82.0‰ (-84.4‰), respectively. At the Kuopio station the mean $\delta^{18}\text{O}$ value of -13.43‰ (-14.12‰) and the δD value of -97.0‰ (-102.7‰) were recorded, and at the Rovaniemi station the respective values for $\delta^{18}\text{O}$ and δD were -13.04‰ (-14.23‰) and -94.8‰ (-103.9‰). The time series of the monthly $\delta^{18}\text{O}$ and δD values at the Espoo station with the longest monitoring period are presented in Figure 3. Inter annual variations occur, and the weighted mean $\delta^{18}\text{O}$ and δD values of separate monitoring years at Espoo record standard deviations (1SD) of 0.3‰ and 3.4‰ , respectively. The seasonal isotopic variations of the average (arithmetic) monthly precipitation at the monitoring sites are illustrated in Figure 4. The amplitudes of the $\delta^{18}\text{O}$ and δD variations in precipitation increase towards north, at Espoo being 7.2‰ for oxygen and 57‰ for hydrogen, and at Rovaniemi 9.2‰ and 69‰ , respectively. Inland stations typically record higher seasonal amplitudes compared to coastal stations (Rozanski et al. 1993). Based on the one year data, the amplitudes of $\delta^{18}\text{O}$ and δD for Kuopio rainfall were 12.0‰ for oxygen and 99‰ for hydrogen. The overall d -excess patterns at all stations were similar: the highest values of $\geq 12\text{‰}$ were recorded during late autumn and early winter, whereas the lowest values of $\leq 8\text{‰}$ were generally attained between April and June. This is a typical d -excess pattern in the northern hemisphere (Froehlich et al. 2002). The

mean annual d -excess was roughly 10‰ at all stations. At the time of the low d -excess, the lowest mean monthly relative humidity of $< 75\%$ is also recorded in Finland (Drebs et al. 2002). The highest d -excess values exceed the expected maximum of 15‰ (Froehlich et al. 2002). Similar high values of up to 18‰ were systematically recorded in November at Espoo and Rovaniemi stations. During this period, additional moisture is given up from the Baltic Sea (Alalammi 1987).

The isotope ratios of oxygen and hydrogen in precipitation are strongly correlated. The monthly $\delta^{18}\text{O}$ and δD values of precipitation are illustrated in Figure 5. Table 2 summarizes the slope, intercept and correlation coefficient of the local meteoric water lines at each monitoring station. The use of local lines is recommended, as the study area is close to the particular precipitation station. The isotope ratios of oxygen and hydrogen measured in snow are clearly depleted in ^{18}O and D compared to those in rain, as illustrated in Figure 6. The correlation line for the precipitation received as rain is $\delta\text{D} = 7.54 \delta^{18}\text{O} + 4.30\text{‰}$ and that for the rainfall received as snow or mixed rain and snow is $\delta\text{D} = 7.80 \delta^{18}\text{O} + 7.71\text{‰}$. In practice, the difference between the meteoric water lines for rain and snow, as well as the local lines according to the station, are insignificant. The combined monthly $\delta^{18}\text{O}$ and δD values in Finnish precipitation can therefore be used to derive an equation for the national scale meteoric water line (Fig. 5):

$$\delta\text{D} = 7.67 \delta^{18}\text{O} + 5.79\text{‰}$$

with a correlation coefficient (r^2) of 0.99 ($n = 95$). The monthly $\delta^{18}\text{O}$ and δD values in precipitation correlate with the mean monthly temperature (Fig. 4). At each station, the slope of the temporal relationship is $0.28\text{‰} / ^\circ\text{C}$ for oxygen and varies from $2.1\text{‰} / ^\circ\text{C}$ to $2.3\text{‰} / ^\circ\text{C}$ for hydrogen (Table 2). The intercept varies according to the station. The temperature dependence is illustrated in Figure 7.

At the Espoo station, a mean annual amount of precipitation of 692 mm with high interannual variations from 467 to 883 mm was recorded during the 5-year monitoring period. At the Kuopio station, the amount of rainfall in 2005 was 625 mm , and at the Rovaniemi station, the annual mean for the 2-year precipitation collecting period was 550 mm . The distribution of rainy months varied according to the monitoring site. In the south, precipitation was attained rather evenly throughout the year. In the east and north the rainiest months were from May to August in Kuopio and from May to

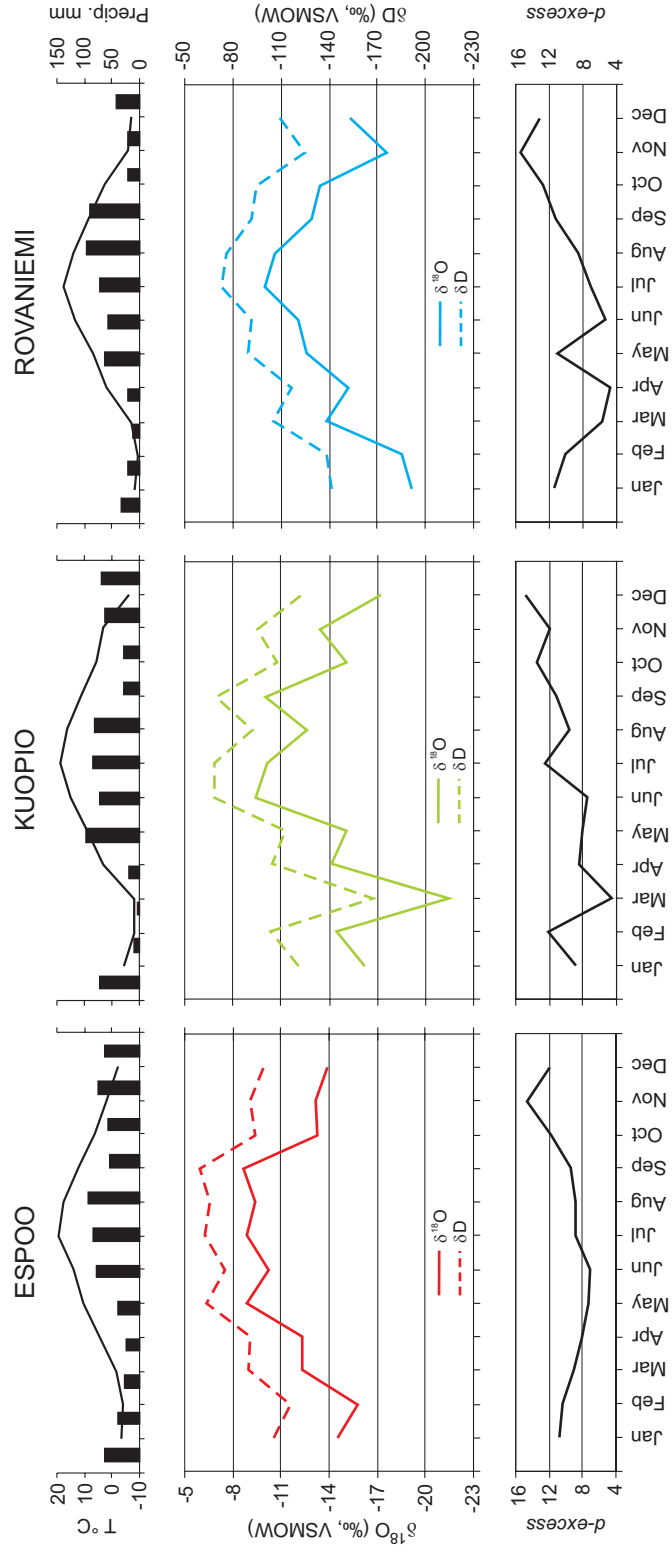


Figure 4. Monthly arithmetic mean $\delta^{18}\text{O}$, δD and d -excess values of precipitation, the mean amount of precipitation (columns) and mean monthly temperature at the Espoo, Kuopio and Rovaniemi stations. In case of the Kuopio station, only one year precipitation data are presented. The climate data is from the closest meteorological observation station and provided by the Finnish Meteorological Institute.

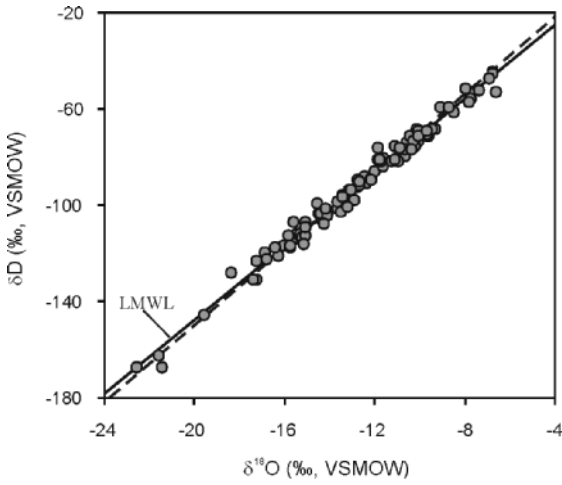


Figure 5. Monthly $\delta^{18}\text{O}$ and δD values of precipitation. The local meteoric water line (LMWL) defined by the data is $\delta\text{D} = 7.67 \delta^{18}\text{O} + 5.79\text{‰}$. The global meteoric water line (GMWL, dashed) is shown for comparison.

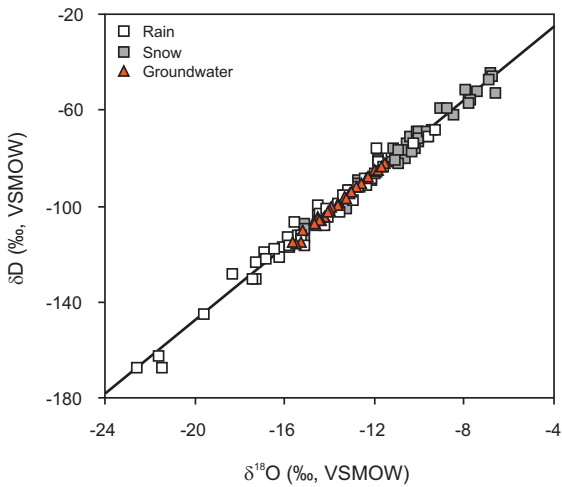


Figure 6. $\delta^{18}\text{O}$ and δD values in monthly precipitation (rain and snow separated) and in groundwater. The data is shown against LMWL ($\delta\text{D} = 7.67 \delta^{18}\text{O} + 5.79\text{‰}$).

September in Rovaniemi. In Kuopio another rainy period was recorded in mid-winter from November to January. The precipitation was attained totally or partially in the form of snow at all sites from November to April. During this period, the monthly cumulative precipita-

Table 2. Slope, intercept and correlation coefficients of the local meteoric water lines and the temporal isotope-temperature relations for $\delta^{18}\text{O}$ and δD at each monitoring station.

Site	Slope a	Intercept b	Correlation coefficient, r^2
<i>Local meteoric water lines</i> [#]			
Espoo	7.56	4.71	0.98
Kuopio	8.23	13.47	0.99
Rovaniemi	7.50	2.89	0.98
<i>Temporal isotope-temperature relation for $\delta^{18}\text{O}$</i> [□]			
Espoo	0.28	-13.50	0.56
Kuopio	0.28	-15.41	0.65
Rovaniemi	0.28	-14.94	0.70
<i>Temporal isotope-temperature relation for δD</i> [□]			
Espoo	2.1	-97.3	0.52
Kuopio	2.1	-109.2	0.68
Rovaniemi	2.3	-113.1	0.62

[#] Equation of the line is $\delta\text{D} = a \delta^{18}\text{O} + b$.
[□] Equation of the line $\delta = a T ^\circ\text{C} + b$, ($\delta = \delta\text{D}$ or $\delta^{18}\text{O}$) .

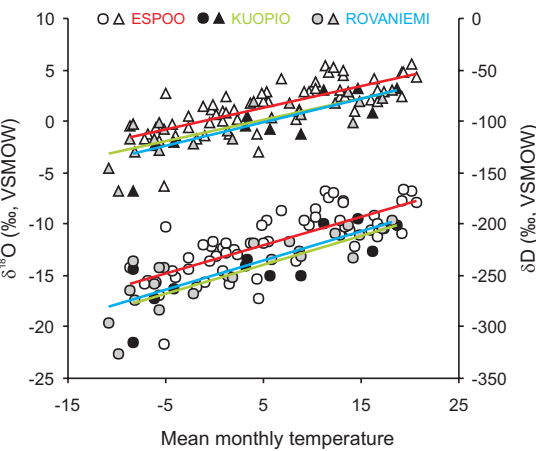


Figure 7. Covariation of the monthly values of $\delta^{18}\text{O}$ (circles) and δD (triangles) in precipitation and the monthly mean surface temperature. The equations of the lines are given in Table 2.

tion sample was usually composed of both rainwater and snow in the south, whereas in the east and north the precipitation of at least 2 to 3 months was attained completely in the form of snow.

Table 3. Site codes, locations, hydrogeological characteristics of the groundwater monitoring sites, and mean $\delta^{18}\text{O}$, δD and d -excess values of the groundwaters.

Code	Site name	Location (monitoring area, municipality)	Type of gw-monitoring site	Altitude	Aquifer material	Formation (= fm.)	Catchment area		$\delta^{18}\text{O}$, ‰, VSMOW		δD , ‰, VSMOW		d -excess		
							Coverage	Thickness of sediments, m	Mean ^a	Stdev ^b	n	Mean		Stdev	n
Southern Finland															
1	PEHKU1	Kaikkälä, Hämeenkoski	Spring	114	Till	Basal till	0.13	4 - 28	-12.36	0.16	37	-88.4	1.6	37	10.5
2	PEHTA1	Tammikvaivo, Lammii	Dug well	123	Till	Basal till	0.05	6 - 8	-12.25	0.25	35	-87.8	2.5	35	10.2
3	PEKKA1	Käivänkylä, Mäntyharju	spring	97	loose till	Moraine fm.	≤ 0.05	≤ 7	-12.59	0.10	22	-90.9	1.9	22	9.8
4	PEKPE1	Penttilä, Joutseno	Spring	50	Sand, gravel	Glaciofluvial fm.	0.20	6 - 15	-12.82	0.19	34	-91.7	1.2	34	10.8
5	PELAN1	Kiila, Kemiö	Spring	7	Sand, fine sand	Glaciofluvial fm.	0.17	10 - 21	-11.55	0.14	37	-82.0	0.9	37	10.4
6	PELJA1	Jakkula, Somero	Spring	72	Sand, gravel	Ice-marginal fm.	6.6	10 - 65	-11.94	0.08	22	-85.6	1.0	22	9.9
7	PESU1	Jumilla, Eura	Spring	35	Loose till	Basal till/moraine fm.	0.10	6 - 10	-11.99	0.21	33	-85.2	2.1	33	10.7
8	PKKIL1	Haapakangas, Karstula	Spring	171	Till	Basal till/moraine fm.	0.32	4 - 10	-13.34	0.21	38	-96.5	2.8	38	10.2
9	PKKIS1	Isomäki, Suolahti	Spring	112	Till	Basal till	0.13	7 - 20	-13.61	0.23	36	-99.1	2.5	36	9.8
10	PKKOL1	Onaslähde, Jyväskylä	Spring	87	Till	Basal till	0.16	7 - 15	-13.11	0.28	39	-94.8	2.3	39	10.1
11	PKKRU1	Ruuhikangas, Jämsä	Spring	140	Sand, gravel	Ice-marginal fm.	2.0	4 - 60	-12.99	0.14	22	-94.1	1.5	22	9.8
31	ESP	Kalajärvi, Espoo	Drilled well	n.d. ^e	Sand, gravel	Sorted sands at hill feet	n.d.	clay and silt covered	-11.82	0.08	17	-84.7	0.8	8	9.9
32	ESP	Lahus, Espoo	Drilled well	n.d.	Sand, fine sand	Sorted sands at hill feet	0.11	clay and silt covered	-11.71	0.04	6	-83.7	1.2	6	10.0
29	KUO	Mikka, Siilinjärvi	Observation well	129	Sand, gravel	Glaciofluvial fm.	n.d.	25 - 26	-13.22	0.06	4	-96.7	0.7	4	9.1
30	KUO	Pöjä, Siilinjärvi	Drilled well	103	Sand, gravel	Glaciofluvial fm.	n.d.	3 - 4	-13.65	0.03	4	-99.8	0.8	4	9.3
12	PKIH6	Hietajärvi, Lieksa	Observation well	167	Sandy till	Moraine fm.	0.13	~15	-13.91	0.27	31	-100.3	2.3	31	11.0
Northern Finland															
13	PLEOI1	Jokkavaara, Rovaniemi	Dug well	85	Sand, gravel	Glaciofluvial fm.	0.60	5 - 40	-14.25	0.35	38	-104.7	2.3	36	9.6
14	PLEKO1	Korkovaara, Rovaniemi	Spring	105	Till, bedrock	Basal till	0.15	n.d.	-14.26	0.37	39	-104.3	3.1	37	9.7
15	PLEPO2	Pöyliövaara, Kemijärvi	Dug well	170	till (stony)	Basal till	0.15	< 10	-14.62	0.50	23	-107.9	4.0	21	9.1
16	PLETA1	Tavivaara, Rovaniemi	Dug well	105	sand	Glaciofluvial fm.	0.3	~10	-14.39	0.23	20	-106.1	2.3	19	9.0
17	PLPKE1	Kentävaara, Inari	Dug well	143	till	Basal till	0.2	n.d.	-15.28	0.63	19	-114.7	5.1	16	8.1
18	PLPKU1	Kuutsamo, Inari	Dug well	150	Sand	Glaciofluvial fm.	0.25	19	-15.50	0.56	40	-115.7	3.9	37	8.3
19	PLPSE1	Sevettijärvi, Inari	Dug well	100	Stony till, sand	Moraine/glaciofl. fm.	0.15	7	-14.00	0.78	39	-102.0	6.4	37	9.6
20	PLEPE2	Pesojärvi, Kuusamo	Spring	265	Fine till	Moraine fm.	0.07	4 - 5	-14.51	0.13	15	-104.8	1.2	15	11.3
21	PLEPT1	Pitkavaara, Kemijärvi	Spring	193	Till, bedrock	Basal till	0.10	n.d.	-14.50	0.67	13	-105.5	4.6	13	10.5
22	PLPKR1	Krakkaajärvi, Inari	Bedrock well	99	Bedrock (Br)	Glaciofluvial fm. + Br	0.18	n.d.	-14.07	0.31	15	-102.1	1.8	15	10.5
23	PLPKU2	Kuukkelinlampi, Inari	Spring	270	Till	Basal till	n.d.	n.d.	-14.64	0.77	15	-106.2	5.9	15	10.9
24	PLPLE2	Leppäjärvi, Enontekiö	Dug well	350	Sand, gravel	Glaciofluvial fm.	0.42	n.d.	-15.21	0.60	13	-110.3	3.7	13	11.4
25	PLPNA1	Nartteit, Enontekiö	Bedrock well	365	Bedrock	Glaciofluvial fm. + Br	n.d.	n.d.	-15.64	0.34	12	-115.2	1.4	12	10.0
26	PLPVI1	Panisar, Pello	Spring	161	Till	Basal till	n.d.	n.d.	-14.53	0.17	15	-105.3	1.3	15	10.9
27	PLPKV1	Viekkalanvaara, Inari	Bedrock well	125	Bedrock	Basal till + Br	0.05	n.d.	-14.47	0.22	14	-105.7	1.4	14	10.1
28	ONNELA	Siurunmaa, Sodankylä	Spring	183	Till	Basal till	n.d.	n.d.	-14.68	0.69	15	-107.1	5.4	15	10.4

^{a)} Arithmetic mean; ^{b)} Standard deviation (1SD); ^{c)} Number of analyses; ^{d)} Isotope monitoring ended in 2001 at sites 3, 6, 11, 15-17; ^{e)} no data.

4.2. Groundwater

The long-term monitoring of the isotopic composition of oxygen and hydrogen in Finnish groundwaters has been conducted since 1995 in association with the GTK's groundwater monitoring programme, comprising 50 aquifers in different parts of Finland (Backman et al. 1999). Isotopic ratios of oxygen and hydrogen were studied at 19 locations during 1995 to 2001 and at 22 locations during 2002 to 2004. Additionally, at the beginning of 2005, groundwater monitoring was started at 4 sites near the Espoo and Kuopio precipitation stations. In total, 32 sites were monitored. The locations of the monitoring sites are presented in Figure 2. Table 3 summarizes the hydrogeologic information from each monitored groundwater formation and the mean $\delta^{18}\text{O}$ and δD values and standard deviations of groundwater at both active and closed stations. The dataset of 2002–2004 groundwater monitoring is stored as a file report at the Geological Survey of Finland (Kortelainen 2007). In the south, 8 sites out of 13 active ones, and respectively in the north, 4 sites out of 13 have a 10-year quarterly-sampled oxygen and hydrogen isotope record.

$\delta^{18}\text{O}$ and δD of Finnish groundwaters record a gradual change towards more depleted values moving from south to north. The highest mean $\delta^{18}\text{O}$ and δD values of -11.55‰ and -82.0‰, respectively, were reached in the southernmost coastal station of Kemiö Island (Site 5; Table 3). The most negative $\delta^{18}\text{O}$ of -15.64‰ and δD of -115.2‰ were observed at Enontekiö, NW Lapland (Site 25; Table 3). Influenced by the airflows from the Barents Sea, NE of Lapland, the mean annual temperature is inversed towards more positive values (Paper I), which is accompanied by an increase in the $\delta^{18}\text{O}$ and δD values of groundwater in NE Lapland. Values for $\delta^{18}\text{O}$ and δD of approximately -14.0‰ and -102‰, respec-

tively, were measured in northernmost Finland (sites 19 and 22; Table 3). The isotope values of oxygen and hydrogen in groundwater are strongly correlated and agree reasonably well with the local meteoric water line defined above for atmospheric precipitation in Finland.

The isotopic variations of $\delta^{18}\text{O}$ in Finnish groundwaters are illustrated in Figure 8. The seasonal fluctuations in the isotopic composition of groundwater increase when moving from southern Finland towards the north, and are especially distinctive in northern Finland. In the north, a strong input of snowmelt waters is recorded as a pulse of isotopically lighter water into the groundwater system in early summer (Fig. 8). The variation (1SD) of the $\delta^{18}\text{O}$ and δD values in the south was generally < 0.30‰ and < 3.0‰, respectively, whereas in the north the range of deviation was from 0.13‰ to 0.78‰ in $\delta^{18}\text{O}$ and from 1.2‰ to 6.4‰ in δD (Table 3). Besides the seasonal variations, indications of cycles lasting a few years were observed at some sites during the 10-year monitoring record (Fig. 8). Following the study in Paper I, the number of groundwater sampling sites has been increased in Lapland to verify the observations of strong seasonality in the isotopic ratios. In northern Lapland, higher seasonality and more distinctive long-term fluctuations are recorded compared to groundwaters in southern Lapland (Fig. 8). Both features are, however, nearly invisible at sites where groundwater is drawn from a bedrock aquifer, with longer water residence times. Both in southern and northern Finland, the extent of seasonal variation is emphasized in basal till and moraine formations. Glaciofluvial formations in southern Finland are practically devoid of seasonal fluctuations, but longer-term trends with low amplitudes can be observed (Fig. 8).

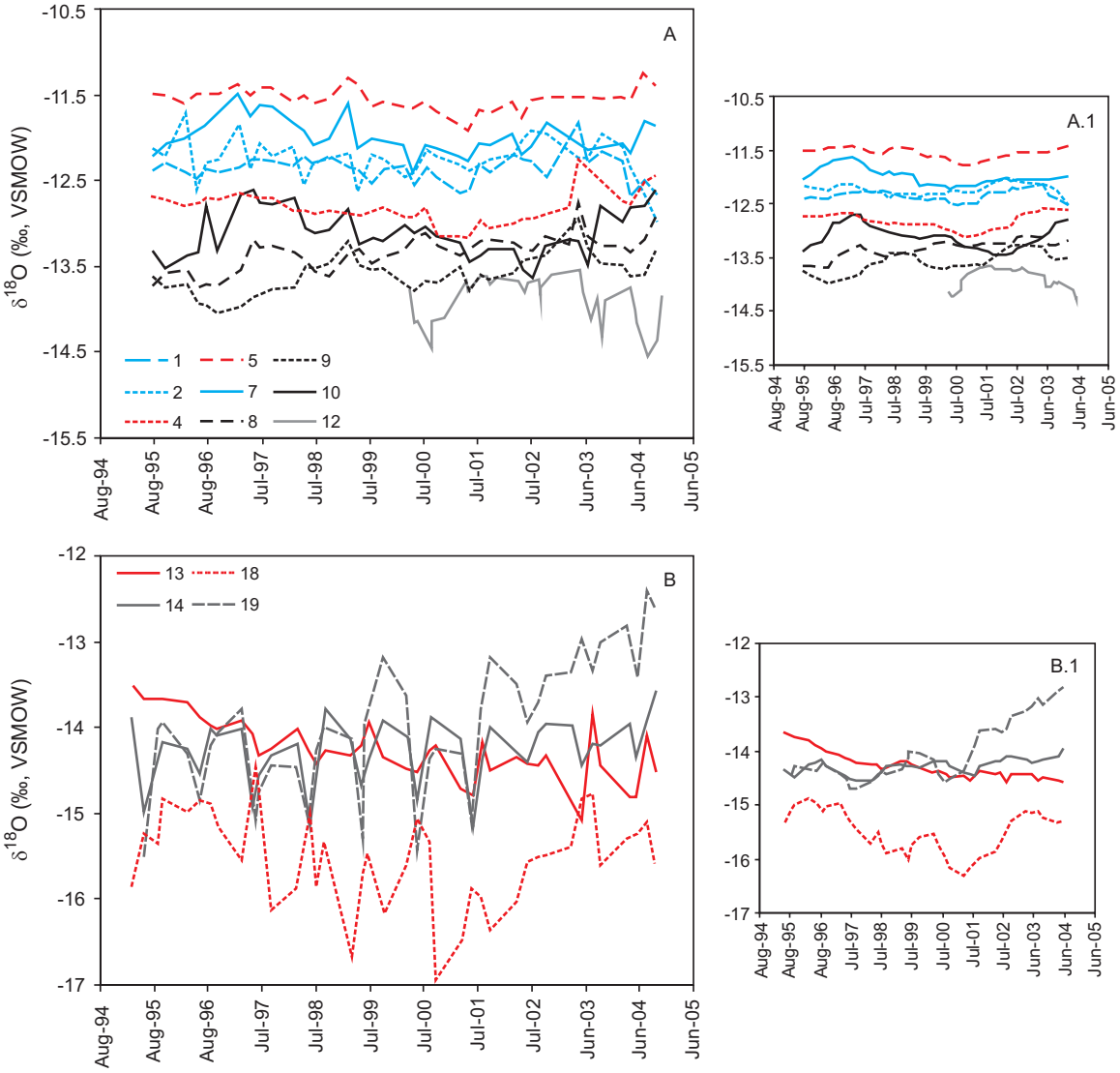


Figure 8. $\delta^{18}\text{O}$ time series of groundwaters in southern (A) and northern (B) Finland. Next to the graphs are illustrated the smoothed trend curves (A.1, B.1), shown as four-point moving averages. Site codes in legends are based on Table 3. Red curves denote glaciofluvial formations and black, blue and grey curves basal tills or moraine formation.

5. DISCUSSION

5.1. Precipitation and groundwater in Finland

Several studies have reported a link between $\delta^{18}\text{O}$ and δD in groundwater and precipitation in temperate climates (e.g. Rozanski 1984, 1985). Prior to this study, no detailed records existed on the isotopic composition of precipitation and modern groundwater or the spatial variability of the isotopic composition of precipitation in Finland. A linear relationship between the mean annual $\delta^{18}\text{O}$ and δD in precipitation and the mean annual surface temperature has been recognized at middle and

high latitudes (Dansgaard 1964; Rozanski et al. 1992, 1993). The best approximation for the regional slope describing the variation of $\delta^{18}\text{O}$ with the mean annual temperature in Finnish precipitation was determined using isotope data from groundwaters (Paper I). The spatial isotope-temperature coefficient of $0.53\text{‰} / ^\circ\text{C}$ for Finnish groundwaters is very close to the spatial relation ($0.59\text{‰} / ^\circ\text{C}$) reported for $\delta^{18}\text{O}$ of precipitation in Sweden and Europe (Burgman et al. 1987; Rozanski et

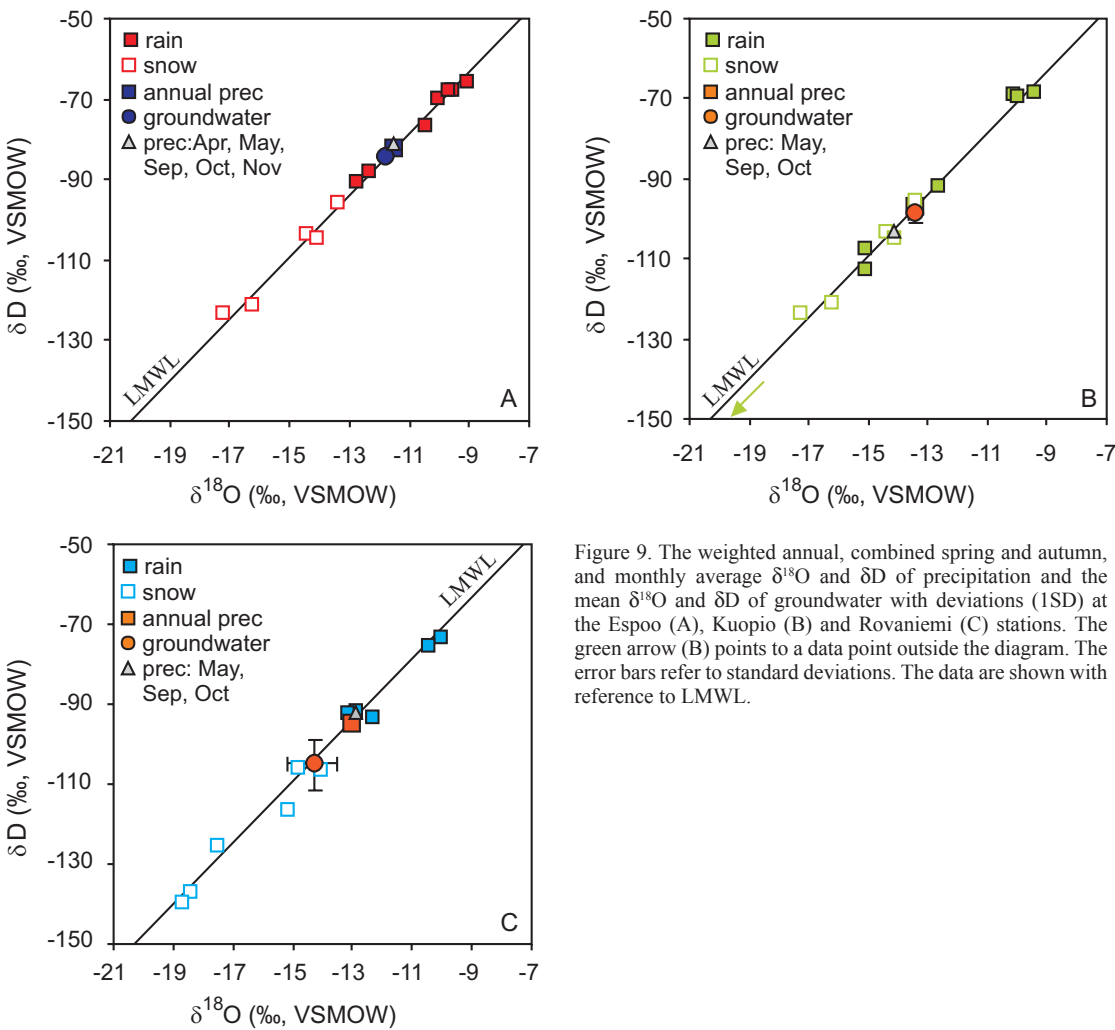


Figure 9. The weighted annual, combined spring and autumn, and monthly average $\delta^{18}\text{O}$ and δD of precipitation and the mean $\delta^{18}\text{O}$ and δD of groundwater with deviations (1SD) at the Espoo (A), Kuopio (B) and Rovaniemi (C) stations. The green arrow (B) points to a data point outside the diagram. The error bars refer to standard deviations. The data are shown with reference to LMWL.

Table 4. Comparison of the weighted mean annual $\delta^{18}\text{O}$ and δD values of precipitation with the isotopic composition of local groundwaters.

Site name	Location ^a	Sample type	$\delta^{18}\text{O}$ ‰, VSMOW			δD ‰, VSMOW		
			Mean	Stdev	n	Mean	Stdev	n
<i>Southern Finland</i>								
OTASA	Espoo	Precipitation	-11.54	3.09	60	-82.0	23.6	60
ESP	Espoo (sites 31 & 32)	Groundwater	-11.79	0.09	23	-84.1	1.1	17
<i>Middle Finland</i>								
KUOSA	Kuopio	Precipitation	-13.43	3.40	12	-97.0	28.1	12
KUO	Siilinjärvi (sites 29 & 30)	Groundwater	-13.43	0.23	8	-98.4	1.8	8
<i>Northern Finland</i>								
ROISA	Rovaniemi	Precipitation	-13.04	3.25	23	-94.8	24.6	23
	Rovaniemi (sites 13 & 14)	Groundwater	-14.26	0.36	77	-104.5	2.7	73

^{a)} Code numbers of groundwater monitoring sites are based on Table 3.

al. 1992). The temporal relation between monthly $\delta^{18}\text{O}$ (and δD) and the mean monthly temperature at each precipitation station in Finland is $0.28\text{‰} / ^\circ\text{C}$ (Table 2; Fig. 7), which is clearly different from the spatial value. A systematic difference between temporal and spatial slopes has generally also been recognized in other studies (Rozanski et al. 1993; Jouzel et al. 1997).

The weighted mean annual $\delta^{18}\text{O}$ and δD in atmospheric precipitation are key values in considerations of groundwater recharge. They refer to the annual or perennial isotope signal of the cumulative rainfall that reaches the Earth's surface at a particular location. However, due to evapotranspiration and runoff, there exists a clear difference between the amount of precipitation and the proportion of it that actually replenishes the groundwater reservoirs. The two most favourable periods for groundwater recharge in Finland are in the spring, just after snowmelt, with low evapotranspiration and wet soils, and in the autumn after the cessation of evapotranspiration prior to frost. In southern Finland this is generally from April to May and from September to November. The respective months in the east and north are May, September and October. This also agrees with the weighted mean $\delta^{18}\text{O}$ and δD values of precipitation of the months concerned, being closely consistent with those of the annual precipitation and groundwater (Fig. 9). In contrast, overland flow effectively removes a significant proportion of the cumulated winter precipitation in the spring and strong evapotranspiration during the growing season generally does the same to the rainfall during the summer. Figure 9

presents the monthly (rain and snow months separated), combined spring and autumn and the annual weighted mean $\delta^{18}\text{O}$ and δD values in precipitation and the mean $\delta^{18}\text{O}$ and δD in local groundwater samples with minimum and maximum values at the monitoring stations. Despite the seasonal biases in groundwater recharge, no significant differences between the $\delta^{18}\text{O}$ and δD values of precipitation and those of groundwater were observed when the precipitation and groundwater isotope records were compared at the monitoring sites. The most recent isotope data of precipitation and groundwaters not included in Paper I, supported the observations and interpretations presented in Paper I. Table 4 summarizes the weighted mean annual $\delta^{18}\text{O}$ and δD values of precipitation at the collecting stations and at the closest groundwater monitoring sites. At Rovaniemi in northern Finland, the groundwater is more depleted in ^{18}O and D in comparison to the respective values in precipitation. The two-year precipitation monitoring period at Rovaniemi is, however, fairly short, and the difference has to be considered with caution. The regional correlations between $\delta^{18}\text{O}$ and δD in precipitation are systematic. Based on the isotope data on monthly precipitation collected in this study, the local meteoric water line for precipitation in Finland (LMWL; Fig. 5) is:

$$\delta\text{D} = 7.67 \delta^{18}\text{O} + 5.79\text{‰}.$$

The $\delta^{18}\text{O}$ and δD in Finnish groundwaters plot on the local meteoric water line (Fig. 6), which is also close to the global meteoric water line (GMWL) defined by Craig in 1961.

5.2. Continental scale isotope patterns of precipitation

Systematic data on the isotopic composition of oxygen and hydrogen in modern precipitation provide a fundamental background for hydrological studies from local to global scales. Locally, the isotope data for precipitation provide the basic framework for better understanding of water resources, the recharge of groundwater and the dimensions of hydrological systems and their responses to temporal and seasonal climatic variations.

On the continental scale, various meteorological regimes may control the temporal and spatial patterns observed in the $\delta^{18}\text{O}$ and δD of precipitation as reported, for instance, from Canada (Gibson et al. 2005). In recent years, several new studies on the regional isotopic variation of precipitation have been reported from Italy by Longinelli & Selmo (2003), from Russia by Kurita et al. (2004), from Switzerland by Schürch et al. (2003)

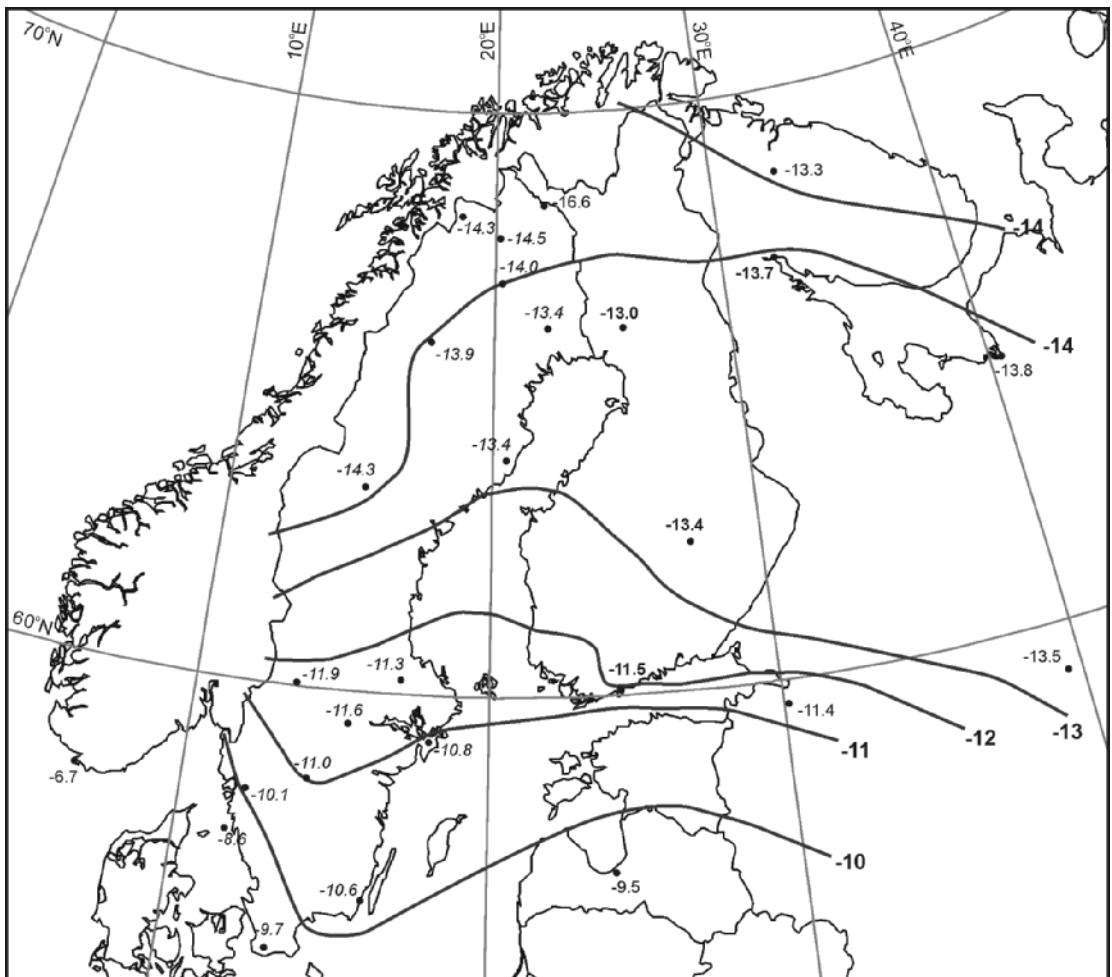


Figure 10. Regional distribution of mean annual $\delta^{18}\text{O}$ in precipitation around the Baltic Sea area and in western Russia. At the station location, the weighted mean annual $\delta^{18}\text{O}$ (bold), the arithmetic mean annual $\delta^{18}\text{O}$ (regular), or the mean annual $\delta^{18}\text{O}$ (italic) of unknown form (Burgman et al. 1987) are given. The map is based on data published by Burgman et al. (1987), Kurita et al. (2004), IAEA/WMO (2006b), and the precipitation and groundwater records of this study. Besides the IAEA Vienna Stable Isotope Lab in Austria, the analyses of oxygen isotopic ratios were provided by the Mass Spectrometry Laboratory / Division of Hydrology / University of Uppsala in Sweden and the Water Problems Institute / Academy of Science / Moscow in the Russian Federation.

and from Great Britain by Darling & Talbot (2003). Through the IAEA/WMO's GNIP programme, isotope data for precipitation have been gathered from hundreds of stations around the world since 1961, including several mentioned in the above studies. The active regional network for isotopes in Finnish precipitation was gradually established after 1999 partly in order to collect data for the GNIP programme. These new stations will supplement the global network with stations located above the latitude of 60°N. As a result of the monitoring programmes, the spatial isotope patterns in precipitation, such as latitude, continental and altitude effects, are well understood. They are related to the primary moisture source, the climatic conditions in the source area and the gradual rainout of moist air masses driven by atmospheric airflows (Rozanski et al. 1993).

The primary source of moisture in Scandinavia and Eurasia is in the North Atlantic air masses carried by the westerlies throughout the year. The climate in northwestern parts of the Eurasian continent, including Finland, is strongly affected by the warming effect of the Gulf Stream. At the latitudes of 60°N and 70°N, in Canada for example, the weighted $\delta^{18}\text{O}$ and δD values of annual precipitation are around -26‰ and -188‰, respectively (CNIP©2004; Gibson et al. 2005). The lowest annual $\delta^{18}\text{O}$ and δD values recorded in Finnish

precipitation were -13.43‰ and -97.0‰ at the Kuopio station. The isotope ratios of oxygen and hydrogen in precipitation become more depleted with respect to ^{18}O and D from the Baltic Sea area towards the east on the Russian platform (Kurita et al. 2004). The continental effect is the primary cause of the eastward-decreasing δ values in Russian precipitation. In addition, temperature and latitude effects are also clearly recognized. The most negative $\delta^{18}\text{O}$ and δD that have been reported for weighted annual precipitation at the latitude of 68°N in Russia are -20.59‰ and -161.9‰, respectively (Kurita et al. 2004). In the Baltic Sea area and in Finland the most notable spatial isotope pattern in precipitation and modern groundwaters is the decrease in $\delta^{18}\text{O}$ and δD with increasing latitude, and to some extent also with distance from the coast (Burgman et al. 1987; Paper I). This regional distribution of mean annual $\delta^{18}\text{O}$ in precipitation around the Baltic Sea area and in western Russia is illustrated in Figure 10. The isolines are drawn based on the precipitation and groundwater data from Finland (Paper I), the precipitation data published from Sweden by Burgman et al. (1987), from Russia by Kurita et al. (2004), and the precipitation data from Russian, Norwegian and Latvian stations reported in the GNIP database (IAEA/WMO 2006b).

5.3. Carbon as a tracer in hydrogeology

Artificially-enhanced aquifer recharge methods are widely used to induce the productivity of the groundwater formation or to store water masses for later recovery (Sundlöf & Kronqvist 1992; Hatva 1996; Mallen et al. 1998, 2005; Herczeg et al. 2002, 2004; Balderer et al. 2004; Vanderzalm et al. 2004; Le Gal La Salle et al. 2005). Simultaneously, the soil provides a medium for natural purification process for surface waters. In regions with abundant surface water resources and common glaciofluvial deposits, the main objective in the use of artificial recharge is the reduction of the total organic carbon content in surface waters to the required drinking-water level (Sundlöf & Kronqvist 1992; Hatva 1996; Mallen et al. 1998, 2005; Balderer et al. 2004). In subsurface waters, the two main isotopically distinct sources of DIC are the soil CO_2 derived from respiration and microbially-decomposed organic

matter and the dissolved carbonate species resulting from the dissolution of carbonate minerals (e.g. Clark & Fritz 1997). Carbon isotopes may thereby act as useful natural tracers for monitoring the state of the hydrogeological system during construction and operation of artificial groundwater recharge plants. However, a few reports have been published on the use of isotope methods in managed aquifer recharge studies. The isotopic composition of carbon in DIC has been applied to trace geochemical reactions related to aquifer storage and recovery studies in Australia (Herczeg et al. 2002, 2004; Vanderzalm et al. 2004; Le Gal La Salle et al. 2005). Mallén et al. (1998) applied the ^{13}C isotope method to study DOC removal in a riverbank filtration study. Here, isotope methods were used for the first time to quantify the processes of DOC removal in an artificial groundwater recharge.

Papers II–IV consider the carbonate system in two geochemically different glacial aquifers. The Tuusula site is a typical non-calcite bearing esker aquifer with a water pH slightly < 7 (Paper II). Instead, the Virttaankangas site is characterized by a complex internal structure with calcite-bearing depositional units (Paper III), leading to a wide variation in groundwater compositions both isotopically and in basic chemistry (Paper IV). Both sites are linked to artificial groundwater recharge with the distinction, however, that the Tuusula site represents a hydrochemically and hydrologically stabilized system that has operated for 30 years, whereas the Virttaankangas site is in a natural state and the artificial recharge plant is under construction.

Tuusula study (Paper II) aimed to trace and quantify redox processes associated with the decomposition of DOC using isotopic composition of DIC in water. At the Tuusula site, artificial recharge leads to a significant decrease in the organic matter content of the infiltrated water. In total, 81% of the initial DOC present in the infiltrated water was removed in three successive stages of subsurface processes. The first stage, extending to a distance of 330 m from the infiltration ponds, appeared to be the most significant part in DOC removal, as 44% of the initial DOC content was removed. Parallel variations in the concentration of DIC place important constraints on the process reducing the DOC content. During the first stage of subsurface flow, a balance between the decrease in DOC and an increase in DIC exists, accompanied by a consistent shift in the $\delta^{13}\text{C}_{\text{DIC}}$ of recharged water. Oxygen isotope ratios suggest no admixture of local groundwater at this stage, and the drop in $\delta^{13}\text{C}_{\text{DIC}}$ cannot therefore be attributed to mixing. No other sources of carbon are present, and the system appears to be closed to atmospheric and soil CO_2 . This suggests that oxidative decomposition is the main process reducing the content of DOC in the first stage, with no evidence of adsorption. Other studies have also emphasized the significance of the early stage of the subsurface flow to the decrease in the organic carbon concentration, and recognized the importance of oxidative degradation of organic carbon (Frycklund 1995, 1998; Mallén et al. 1998; Jacks 2001; Kivimäki 2001; Herczeg et al. 2004; Vanderzalm et al. 2004; Le Gal La Salle et al. 2005). A further decrease of 23% in the DOC content is recorded in the second stage, between 330 and 450 metres from the ponds. Finally, the third stage extends to a distance of 700 m with a further 14% decrease in

DOC. In contrast to the first stage, a further decrease in the DOC content in the second stage is accompanied by a decrease in the DIC content. The concentration of total dissolved carbon is reduced, suggesting that organic carbon is adsorbed on mineral surfaces. In the final stage, the proportion of natural groundwater exceeds that of the infiltration water, adding an external source of carbon into the system. Due to concentration differences in DIC and DOC, the content of DIC increases significantly, whereas dilution in the content of DOC is observed.

The hydrogeochemistry of the Virttaankangas groundwater formation is exceptional, as pH values exceeding 9 are measured in the shallow glacial aquifer (Lahermo et al. 1990; Tarvainen et al. 2001). Hydrological and mineralogical properties vary within the system, and separate aquifer units are thereby traceable by their water chemistry. The units are an unconfined esker core aquifer, a semi-confined aquifer and a perched aquifer. Geochemical evolution of the waters can be constructed based on carbonate species equilibrium and $\delta^{13}\text{C}_{\text{DIC}}$ (Paper IV). The mineralogical investigations (Paper III) revealed trace amounts of detrital calcite dispersed in the esker core and the semi-confined aquifer units of the Virttaankangas formation. Calcite dissolution appears to play an essential role in the evolution of hydrochemical and isotope geochemical characteristics of the Virttaankangas aquifer. The Virttaankangas aquifer will in the future be the site for long-term enhanced groundwater recharge activities (Artimo et al. 2003), and understanding of the natural efficiency of sediment to buffer the pH in infiltrated water is therefore of high priority. Open system conditions lacking calcite prevail in the uppermost perched aquifer with water pH slightly below neutral and low $\delta^{13}\text{C}_{\text{DIC}}$ values. The calculated initial groundwater P_{CO_2} is $10^{-2.8}$, which is only marginally higher than that in the atmosphere. The waters in the esker core and semi-confined units are saturated or close to saturated relative to calcite, and in contrast to the perched unit, higher $\delta^{13}\text{C}_{\text{DIC}}$ values are detected. The high saturation indexes and the low $^{14}\text{C}_{\text{DIC}}$ activities in these units are compatible with calcite dissolution. The residence time of groundwater and the saturation stage of water with respect to calcite increase in the same order, from the perched to the esker core aquifer, and finally, to the semi-confined aquifer. Calcite dissolution in open system conditions is found in the deepest parts of the perched aquifer, which adds more DIC

to the water prior to the system becoming closed with respect to soil CO_2 . A combination of closed and open system calcite dissolution is observed in the unconfined esker core aquifer, leading to variability in pH values and DIC concentrations of groundwaters. The semi-confined aquifer is characterized by a moderate increase in DIC content, high $\delta^{13}\text{C}_{\text{DIC}}$ values and the lowest $^{14}\text{C}_{\text{DIC}}$ activities. In summary, the shallow groundwater in the Virttaankangas aquifer, or in general, in glacial aquifers on crystalline bedrock may attain high pH values of > 9 as a result of calcite dissolution under closed system conditions at low P_{CO_2} .

The study presented in Paper III aimed to determine the mode of occurrence of calcite in the Virttaankan-

gas sedimentary material and to identify its sources. The isotope records of carbon and oxygen, the angular morphology of the grains and the uniform dispersion of calcite in the Virttaankangas complex suggested a clastic origin for calcite. Based on $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values and elemental compositions, the dispersed calcite of the Virttaankangas complex was suggested to be derived from diagenetic calcite locally abundantly present in the Mesoproterozoic Satakunta sandstone, some 30 km NW of the Virttaankangas area. Simultaneously, the results support the earlier suggestion that the Satakunta Formation is the main source of clastic material in the Virttaankangas complex.

6. CONCLUSIONS

The driving force behind this study has been the need to develop and apply methods for investigating the hydrogeochemical processes of significance to water management and artificial groundwater recharge. The work described here has initiated the use of stable isotope methods to achieve a better understanding of these processes in the shallow glacial formations of Finland. In addition, the regional precipitation and groundwater records will supplement the data of global precipitation, but as importantly, provide primary background data for hydrological studies.

Isotope data for oxygen and hydrogen in atmospheric precipitation and groundwaters were collected to provide the first detailed records on the spatial and annual variability of the isotopic composition of precipitation and groundwaters in Finland. The following conclusions can be drawn:

1. No significant difference between the oxygen and hydrogen isotope ratios of weighted mean annual precipitation and groundwater can be observed. The regional $\delta^{18}\text{O}$ distribution derived from the groundwater data gives a valid approximation for the mean annual composition of Finnish precipitation.
2. The $\delta^{18}\text{O}$ and δD values of precipitation decrease with increasing latitude, and to some extent, with the distance from the coast.
3. The spatial drop in the $\delta^{18}\text{O}$ values is closely paralleled by a decrease in the mean annual temperature, with an isotope-temperature coefficient of $0.53\text{‰} / ^\circ\text{C}$.

4. Based on the monthly $\delta^{18}\text{O}$ values of precipitation and the monthly temperatures, the temporal isotope-temperature coefficient is $0.28\text{‰} / ^\circ\text{C}$.
5. Based on the isotope data of precipitation, the local meteoric water line (LMWL) for precipitation in Finland is: $\delta\text{D} = 7.67 \delta^{18}\text{O} + 5.79\text{‰}$.

Determinations of $\delta^{13}\text{C}_{\text{DIC}}$ and the content of DIC and DOC in water provide new information on the removal of DOC at the Tuusula artificial groundwater plant. Here, isotope methods were used for the first time to quantify the processes of DOC removal in an artificial groundwater recharge. The hydrogeochemical evolution of the infiltrated water can be divided into three successive stages, where different processes are responsible for the reduction in DOC in the infiltrated water:

1. The largest decrease of 44% in the DOC content occurred during the early stage of subsurface flow, and it can be attributed to oxidative decomposition of DOC.
2. In the second stage, the concentration of DOC decreased by approximately 23% relative to the initial value. A decrease in the concentration of total dissolved carbon suggested that organic carbon was adsorbed on mineral surfaces.
3. In the final stage of the flow path, the admixture of local groundwater decreased the DOC content of the infiltrated water by 14%.

Groundwaters in the glacial Virttaankangas aquifer record a wide range of pH values from 6.4 to 9.5. As the Virttaankangas sediments contain very fine-grained calcite as an accessory mineral, the isotopic composition of carbon in DIC was applied to study the interaction of the groundwater system with solid carbonates and soil CO₂. The study also aimed to determine the mode of occurrence of calcite and to identify its sources. The main findings of the Virttaankangas studies are:

1. Dispersed calcite of clastic origin 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.
2. Based on constraints from carbon and oxygen isotope ratios, the calcite is implied to have been derived from the Satakunta sandstone, some 30 km NW of the Virttaankangas area.
3. The isotopic and chemical characteristics of the groundwater in the aquifer units vary depending on the occurrence of calcite in the aquifer, the groundwater residence time and the openness of the system to CO₂. Due to the different evolutionary paths of groundwater, a wide range of variability in the DIC content, pH and $\delta^{13}\text{C}$ in DIC was observed.
4. The high pH values of groundwater in the calcite-bearing sediments are related to dissolution of calcite into groundwater under closed or nearly closed system conditions relative to soil CO₂.
5. 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 partial pressure of CO₂.

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APPENDIX 1. MONTHLY ISOTOPIC DATA OF PRECIPITATION.

Sample code	Collecting period		Precip. mm	δD ‰, VSMOW	δ ¹⁸ O ‰, VSMOW	d- excess	T °C ^a	
	start	end						
<i>Espoo station</i>								
SADE-25	Nov-02	01.11.02	02.12.02	52.1	-116.8	-16.06	11.7	-1.9
SADE-26	Dec-02	02.12.02	02.01.03	7.0	-117.4	-15.79	8.9	-7.1
SADE-27	Jan-03	02.01.03	31.01.03	60.5	-104.0	-14.20	9.6	-8.6
SADE-28	Feb-03	31.01.03	28.02.03	8.7	-162.7	-21.62	10.3	-5.1
SADE-29	Mar-03	28.02.03	31.03.03	11.6	-86.0	-12.00	10.0	-1.2
SADE-30	Apr-03	31.03.03	30.04.03	22.3	-97.9	-12.92	5.5	2.4
SADE-31	May-03	30.04.03	30.05.03	70.7	-71.0	-9.70	6.6	9.1
SADE-32	Jun-03	30.05.03	30.06.03	51.5	-55.7	-7.75	6.3	13.2
SADE-33	Jul-03	30.06.03	31.07.03	20.9	-56.9	-7.82	5.7	20.7
SADE-34	Aug-03	31.07.03	01.09.03	96.4	-76.9	-10.64	8.2	16.8
SADE-35	Sep-03	01.09.03	01.10.03	26.0	-47.3	-6.90	7.9	12.1
SADE-36	Oct-03	01.10.03	31.10.03	64.8	-112.1	-15.30	10.3	4.4
SADE-37	Nov-03	31.10.03	28.11.03	57.3	-81.7	-11.81	12.7	3.7
SADE-38	Dec-03	28.11.03	31.12.03	90.6	-93.6	-13.16	11.7	0.2
OTASA0401	Jan-04	31.12.03	30.01.04	26.7	-119.3	-16.88	15.7	-5.7
OTASA0402	Feb-04	30.01.04	01.03.04	56.8	-113.3	-15.24	8.6	-4.0
OTASA0403	Mar-04	01.03.04	31.03.04	44.6	-101.1	-13.66	8.1	-0.5
OTASA0404	Apr-04	31.03.04	30.04.04	7.3	-73.2	-10.06	7.3	4.9
OTASA0405	May-04	30.04.04	31.05.04	36.3	-61.7	-8.50	6.3	10.3
OTASA0406	Jun-04	31.05.04	30.06.04	81.1	-75.6	-10.20	6.0	13.3
OTASA0407	Jul-04	30.06.04	30.07.04	175.8	-81.5	-11.23	8.4	16.6
OTASA0408	Aug-04	30.07.04	31.08.04	117.2	-70.9	-10.44	12.6	17.3
OTASA0409	Sep-04	31.08.04	30.09.04	88.6	-70.2	-9.66	7.1	12.8
OTASA0410	Oct-04	30.09.04	01.11.04	74.5	-59.0	-8.74	11.0	6.8
OTASA0411	Nov-04	01.11.04	01.12.04	82.0	-75.9	-11.89	19.2	1.1
OTASA0412	Dec-04	01.12.04	31.12.04	99.1	-92.2	-12.73	9.7	1.1
OTASA0501	Jan-05	31.12.04	31.01.05	110.6	-83.8	-11.63	9.2	-0.1
OTASA0502	Feb-05	31.01.05	28.02.05	19.3	-103.7	-14.51	12.4	-4.4
OTASA0504	Mar-05	28.02.05	31.03.05	4.2	-73.6	-10.27	8.5	-5.0
OTASA0503	Apr-05	31.03.05	29.04.05	10.7	-130.5	-17.29	7.8	4.5
OTASA0505	May-05	29.04.05	31.05.05	46.7	-68.5	-9.29	5.8	10.3
OTASA0506	Jun-05	31.05.05	30.06.05	88.9	-89.5	-12.13	7.5	14.4
OTASA0507	Jul-05	30.06.05	01.08.05	72.5	-76.3	-10.92	11.1	19.2
OTASA0508	Aug-05	01.08.05	31.08.05	160.5	-70.2	-9.96	9.5	16.7
OTASA0509	Sep-05	31.08.05	30.09.05	29.2	-51.5	-7.96	12.2	13.2
OTASA0510	Oct-05	30.09.05	31.10.05	35.4	-98.9	-13.66	10.4	8.3
<i>Kuopio station</i>								
KUOSA0501	Jan-05	31.12.04	31.01.05	72.6	-121.1	-16.25	8.9	-4.2
KUOSA0502	Feb-05	31.01.05	28.02.05	10.4	-103.2	-14.42	12.2	-8.4
KUOSA0503	Mar-05	28.02.05	31.03.05	4.5	-167.1	-21.46	4.6	-8.4
KUOSA0504.2	Apr-05	31.03.05	02.05.05	18.7	-104.4	-14.11	8.4	3.2
KUOSA0505	May-05	02.05.05	31.05.05	95.7	-112.6	-15.09	8.1	8.8
KUOSA0506	Jun-05	31.05.05	30.06.05	72.5	-68.2	-9.47	7.5	14.7
KUOSA0507	Jul-05	30.06.05	01.08.05	83.7	-68.6	-10.15	12.6	18.7
KUOSA0508	Aug-05	01.08.05	31.08.05	80.4	-91.7	-12.66	9.6	16.2
KUOSA0509	Sep-05	31.08.05	30.09.05	29.3	-69.1	-10.03	11.2	11.1
KUOSA0510	Oct-05	30.09.05	31.10.05	27.4	-107.2	-15.09	13.5	5.7
KUOSA0511	Nov-05	31.10.05	30.11.05	62.8	-95.5	-13.42	11.9	3.4
KUOSA0512	Dec-05	30.11.05	02.01.06	67.4	-123.2	-17.26	14.9	-6.1

Sample code	Collecting period		Precip.	δD	δ ¹⁸ O	d-excess	T °C ^a	
	start	end	mm	‰, VSMOW	‰, VSMOW			
Rovaniemi station								
ROISA0311.2	Nov-03	31.10.03	01.12.03	21.8	-122.2	-16.81	12.2	-2.2
ROISA0312	Dec-03	01.12.03	07.01.04	25.1	-117.7	-16.47	14.0	-8.7
ROISA0401	Jan-04	07.01.04	02.02.04	25.0	-167.5	-22.58	13.1	-9.8
ROISA0402	Feb-04	02.02.04	01.03.04	25.7	-145.4	-19.61	11.5	-10.8
ROISA0403	Mar-04	01.03.04	05.04.04	18.6	-107.9	-14.23	5.9	-5.2
	Apr-04	05.04.04	03.05.04	0.0				2.1
ROISA0405	May-04	03.05.04	31.05.04	39.8	-82.0	-11.68	11.5	7.6
ROISA0406	Jun-04	31.05.04	30.06.04	44.4	-82.0	-10.96	5.7	12.3
ROISA0407	Jul-04	30.06.04	02.08.04	72.6	-77.2	-10.37	5.8	17.1
ROISA0408	Aug-04	02.08.04	31.08.04	118.4	-71.5	-10.08	9.2	13.6
ROISA0409	Sep-04	31.08.04	01.10.04	105.8	-90.4	-12.70	11.3	8.6
ROISA0410	Oct-04	01.10.04	01.11.04	18.2	-109.2	-15.10	11.6	1.4
ROISA0411.2	Nov-04	01.11.04	07.12.04	19.3	-128.1	-18.36	18.8	-5.7
ROISA0412	Dec-04	07.12.04	03.01.05	60.5	-101.1	-14.16	12.2	-5.6
ROISA0501	Jan-05	03.01.05	31.01.05	38.4	-116.6	-15.78	9.6	-6.1
ROISA0502	Feb-05	31.01.05	28.02.05	17.1	-130.6	-17.40	8.6	-8.2
ROISA0503	Mar-05	28.02.05	31.03.05	6.5	-102.5	-13.52	5.6	-8.3
ROISA0504.2	Apr-05	31.03.05	29.04.05	44.7	-116.4	-15.15	4.8	1.9
ROISA0505	May-05	29.04.05	31.05.05	87.2	-96.8	-13.44	10.7	5.9
ROISA0506	Jun-05	31.05.05	01.07.05	67.7	-100.9	-13.25	5.1	14.1
ROISA0507	Jul-05	01.07.05	01.08.05	69.9	-68.9	-9.66	8.3	18.1
ROISA0508	Aug-05	01.08.05	31.08.05	72.9	-80.8	-11.10	8.0	14.9
ROISA0509	Sep-05	31.08.05	30.09.05	74.5	-93.5	-13.10	11.3	8.8
ROISA0510	Oct-05	30.09.05	01.11.05	26.8	-80.8	-11.82	13.8	4.0

^{a)} The monthly mean temperatures are published by the permission of the Finnish Meteorological Institute.

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In this thesis, comprising a synopsis and four papers, tracer property of the stable isotope abundances of oxygen, hydrogen and carbon has been applied to investigate hydrogeological processes in Finland. The work described here has initiated the use of stable isotope methods to achieve a better understanding of these processes in the shallow glacial formations of Finland. In addition, the regional precipitation and groundwater records will supplement the data of global precipitation and provide primary background data for hydrological studies.

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