



# Geochemical and flow modelling as tools in monitoring managed aquifer recharge



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## ARTICLE INFO

### Article history:

Received 16 February 2016

Received in revised form

1 September 2016

Accepted 3 September 2016

Available online 5 September 2016

### Keywords:

Managed aquifer recharge

Geochemical modelling

Water purification

Isotopes

DIC

DOC

## ABSTRACT

Due to a growing world population and the effects of anthropogenic climate change, access to clean water is a growing global concern. Managed aquifer recharge (MAR) is a method that can help society's response to this increasing demand for pure water. In MAR, the groundwater resources are replenished and the quality of the recharged surface water is improved through effects such as the removal of organic matter. This removal occurs through mechanisms such as microbial decomposition, which can be monitored by studying the isotopic composition of dissolved inorganic carbon (DIC). Nevertheless, the monitoring can be difficult when there are other factors, like dissolving calcite, affecting the isotopic composition of DIC.

The aims of this study were to establish a method for monitoring the decomposition of organic matter (dissolved organic carbon – DOC) in cases where calcite dissolution adds another component to the DIC pool, and to use this method to monitor the beginning and amount of DOC decomposition on a MAR site at Virttaankangas, southwestern Finland. To achieve this, we calculated the mean residence times of infiltrated water in the aquifer and the fractions of this water reaching observation wells. We conducted geochemical modelling, using PHREEQC, to estimate the amount of DOC decomposition and the mineral reactions affecting the quality of the water.

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## 1. Introduction

Access to clean water is a growing global concern (Gale, 2005). In many countries, a growing population leads to both a higher need for food production and an increased demand for drinking water. These two pressures produce an increased demand for pure water and an increased use of groundwater reserves (Falkenmark and Widstrand, 1992; Shah et al., 2000). Replenishing groundwater reserves with surface water is a viable way of maintaining groundwater resources (Freeze and Cherry, 1979; Asano, 1985; Ma and Spalding, 1997; Gale, 2005). Managed aquifer recharge (MAR) is a general term for any engineering process where surface water is introduced into groundwater (Dillon, 2005; Page et al., 2012; Dillon et al., 2009). The main benefits of MAR are natural subsurface treatment for impurities, storage of water supplies (Grove and

Wood, 1979), and groundwater replenishment, which may help reduce salinity (Dillon et al., 2002).

Untreated surface water is generally not suitable for communal water supply use, often due to its high organic carbon content (Vartiainen et al., 1987; Lindroos et al., 2002; Grünheid et al., 2005; Kortelainen and Karhu, 2006). Organic matter can facilitate unwanted bacterial growth in water supply systems leading to odour and taste problems (Miettinen et al., 1999; Lindroos et al., 2002). Combining dissolved organic carbon (DOC) with chlorine disinfection can lead to the formation of mutagenic or carcinogenic compounds (Lindroos et al., 2002).

MAR is widely used in Europe: for example, in Germany, Finland, Sweden and Hungary to remove DOC from surface water and make it more suitable for human consumption (Sundlöf and Kronqvist, 1992; Hatva, 1996; Van Breukelen et al., 1998; Kuehn and Mueller, 2000; Lindroos et al., 2002; Balderer et al., 2004; Grünheid et al., 2005; Kortelainen and Karhu, 2006; Kolehmainen et al., 2009). In North America, Australia and Asia the benefits of MAR for water quality have also been reported (Herczeg et al.,

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2004; Dillon et al., 2002; Vanderzalm et al., 2006; Moon et al., 2012; Graham et al., 2015). During artificial recharge, surface water is infiltrated into the topsoil of an aquifer by direct infiltration through infiltration ponds (Kortelainen and Karhu, 2006; Kolehmainen et al., 2009) or wells (Vanderzalm et al., 2006; Pavelic et al., 2007), by bank filtration (Grünheid et al., 2005) or by sprinkling (Lindroos et al., 2002). Previous studies have shown that the DOC content of the infiltrated surface water decreases most significantly early on along the flowpath (Frycklund, 1995, 1998; Greskowiak et al., 2005; Kortelainen and Karhu, 2006; Vanderzalm et al., 2006).

During MAR, DOC concentration declines as a function of distance from the infiltration site (Kortelainen and Karhu, 2006; Kolehmainen et al., 2009; Grünheid et al., 2005; Lindroos et al., 2002). This is due to two possible processes: oxidative decomposition due to microbial activity in the aquifer, and sorption on the sediment without decomposing activity (Kortelainen and Karhu, 2006; Kolehmainen et al., 2009). Knowing the amount of oxidative decomposition of DOC, as opposed to DOC removal by sorption to the sediment, is important for understanding the purification process and the effects of MAR to the environment. In previous studies, 40–50% of the total DOC decrease has been attributed to oxidative decomposition (Frycklund, 1995, 1998; Kortelainen and Karhu, 2006; Kolehmainen et al., 2009).

The oxidative decomposition of DOC can be monitored by examining the isotopic composition of dissolved inorganic carbon (DIC) in the MAR water, since the naturally occurring DIC and the DIC produced by the decay of organic material have a different isotopic signal. Decaying organic material adds a significantly lighter component into the DIC pool (Le Gal La Salle et al., 2005; Kortelainen and Karhu, 2006; Kolehmainen et al., 2010). This can be achieved by simple mass balance calculations when there are no external sources of carbon contributing to the DIC pool.

Calcite-rich sediment and limestone are preferable environments for MAR for two reasons. Calcite dissolution is a beneficial process in MAR applications as the higher pH of water prevents corrosion of the water distribution pipes (Kortelainen and Karhu, 2009). Moreover, it has been shown by Pavelic et al. (2007) that calcite dissolution prevents aquifer clogging in MAR systems. Clogging leads to loss in permeability which shortens the lifespan of a MAR site (Vanderzalm et al., 2006; Pavelic et al., 2007). Treating the infiltrated water to prevent aquifer clogging is possible, but costly, and therefore the natural prevention provided by calcite dissolution is a definite asset (Pavelic et al., 2007).

Calcite dissolution complicates the quantification of DOC decomposition as it introduces a third end-member to the carbon budget. The DIC in the infiltrating water is typically derived from the soil or the atmosphere and depleted in  $^{13}\text{C}$  compared to dissolved sedimentary calcite and also enriched in  $^{13}\text{C}$  compared to DOC (Veizer and Hoefs, 1976; Deines, 1980; Vogel, 1993; Schiff et al., 1997; Kortelainen and Karhu, 2009). Therefore, there are two opposing processes contributing to the change in the isotopic composition of DIC. Isotopic evidence can be used in geochemical modelling to constrain these opposing processes and their effect on the composition of DIC. In modelling the MAR system, the contribution of carbon from different sources can be identified if the isotopic compositions of the different sources are known. The model uses the isotopic compositions together with the chemical composition of the source and resulting waters to produce mixing ratios between the two types of carbon.

A MAR site infiltrating surface water from the Kokemäenjoki River located north of the city of Turku was commissioned in 2010 at Virttaankangas. Prior to the startup of the site, thorough studies were conducted on the sedimentological background and water chemistry (Kortelainen et al., 2007; Kortelainen and Karhu,

2009) and a three-dimensional model of the sedimentological and hydrogeological units containing the aquifer was developed (Artimo et al., 2003).

The MAR site meets the main water supply needs of the Turku region with approximately 285 000 inhabitants (Artimo et al., 2003). The Virttaankangas site was selected to host the MAR site because of the vast groundwater reservoir in the aquifer, its proximity to the Turku area and the naturally high pH of the water, which is due to calcite dissolution (Kortelainen and Karhu, 2009).

The main goal of this study was to quantify the oxidative decomposition of DOC and the dissolution of calcite to estimate the effectiveness of the MAR site at Virttaankangas. As a part of this, we had to determine the point in time when DOC decomposition commenced. To achieve these goals, we used a groundwater flow model to determine the flow routes from infiltration areas to the production wells and then the hydrogeochemical modelling program *PhreeqC* (Parkhurst and Appelo, 2013) to determine the onset and the amount of DOC decomposition in the aquifer.

## 2. Study site

### 2.1. Hydrogeological setting

The Virttaankangas esker is part of the glaciofluvial Säkylänharju-Virttaankangas complex, located in south-western Finland (Fig. 1). The area features a boreal climate. The complex was formed during the late Weichselian and early Holocene deglaciation as a meltwater deposit between two sublobes of the retreating Baltic Sea ice-lobe (Punkari, 1980; Kujansuu et al., 1995; Artimo et al., 2003). The esker contains sub-surface kettle hole structures. Because of these structures the travel time cannot be estimated only by the distance and sediment permeability as water entering these kettle hole structures can make the flow take longer than anticipated.

The complex can be divided into three units: The lowermost part is a result of repeated deposition of subaqueous fans containing glaciofluvial sands and gravels (Artimo et al., 2003). The intermediate part is composed of glaciofluvial sand and silt and associated glaciolacustrine silt and clay deposits of a proglacial water body. The uppermost 10–20 m of the complex represent littoral sands and gravels formed by the regression of the water level in the Baltic Basin about 11 000–10 500 years ago (Artimo et al., 2003). The calcite in the Virttaankangas aquifer is located in the two lowermost units. The concentration of calcite is highest in the <0.2 mm fraction, with 3.7–5 wt % calcite, 0.5–1.4 wt % of the total sediment (Kortelainen et al., 2007). The  $\delta^{13}\text{C}$  value of the calcite is  $-4.8 \pm 0.5\text{‰}$  (Kortelainen et al., 2007). Calcite dissolution increases the pH of natural groundwater to 8–9.5 (Kortelainen and Karhu, 2009). Other minerals present in the Virttaankangas sediment are feldspar, quartz, muscovite, talc, chlorite and hematite (Kortelainen et al., 2007).

### 2.2. The MAR system

The MAR site at Virttaankangas consists of seven infiltration areas, each of which comprises of two to four infiltration ponds (Fig. 1). The site can be divided into western and eastern sides. The western side consists of three infiltration areas (IA301, IA303 and IA400), and four production wells (VIK32, VIK33, VIK42 and VIK43), and the eastern side four infiltration areas (IA401, IA500, IA501 and IA503) and three production wells (VIK51, VIK53 and VIK54). The natural groundwater flow is from northwest to southeast, but pumping can reverse the flow direction. Surface water is first treated with poly-aluminium chloride (PACl) to remove some of the DOC before infiltrating into the aquifer.

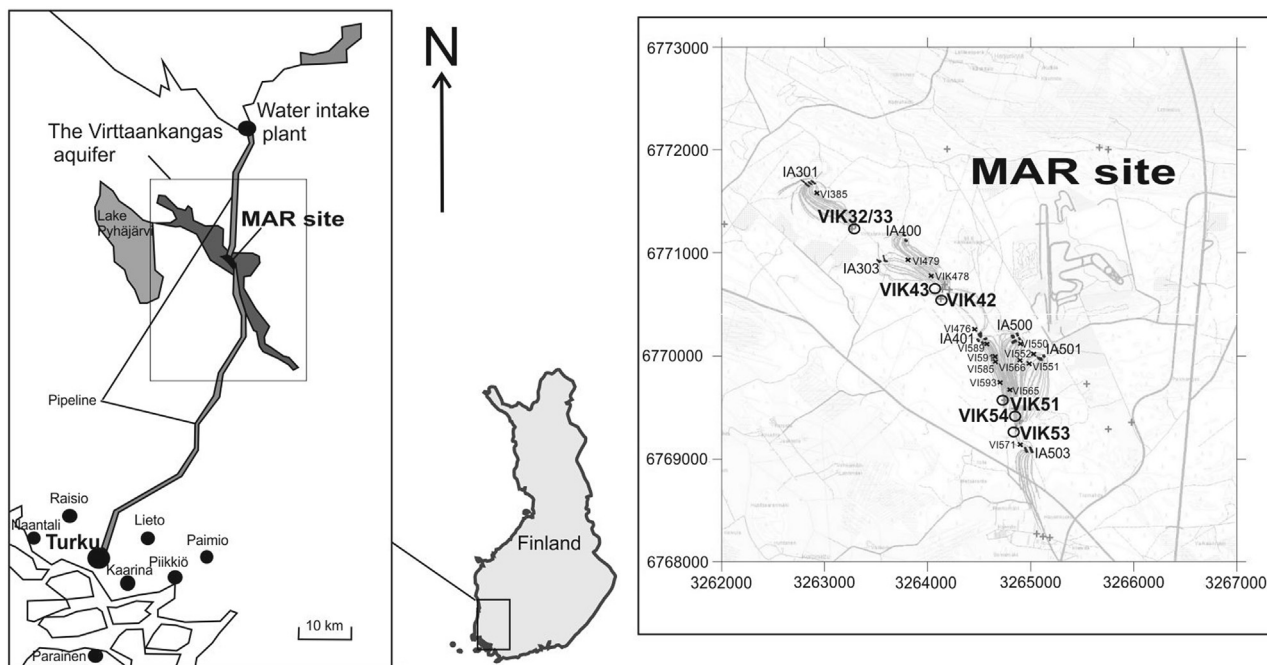


Fig. 1. The location of the study area, the infiltration water intake plant, AR site and the distribution area in southwestern Finland.

Prior to the actual test phase of MAR where the surface water was recharged to the Virttaankangas aquifer, the infiltration process was tested by circulating the local groundwater in the system. This was done by pumping water out and infiltrating it again into the esker by sprinkling. Test infiltrations (Phase I, Table 1) took place in two parts: firstly, the infiltration ponds in the eastern side of the aquifer received pre-treated river water for six months and then the infiltration ponds in the western side received water for another six months (Fig. 1, Table 1). Then the daily infiltration volume was gradually increased (Phases II and III, Table 1) reaching the intended production capacity of the site.

### 3. Methods

#### 3.1. Sampling and analysis

Altogether, 200 samples were collected for chemical analyses, and 162 samples for isotope analyses. The isotopic composition of local natural groundwater was monitored during the period of 2007–2015 inclusive.

Temperature, pH and dissolved oxygen were measured in the field using an YSI water quality meter equipped with a 6562 Rapid Pulse Sensor (dissolved oxygen, precision ±0.2 mg/L), pH 6561 sensor (±0.2) and a temperature sensor (±0.15 °C). The contents of DOC were analysed in the field with an S-CAN meter, with precision of 1% and in the Labtium Oy laboratory by using the method described by the standard SFS-EN 1484, with ±20% precision and 0.4 mg/L detection limit.

The samples for the analysis of the isotopic composition of

oxygen and hydrogen were collected in HDPE plastic bottles and analysed by Picarro cavity ring-down spectrometer (CRDS) at the Geological Survey of Finland. Laboratory standards were used, calibrated against the international reference standards VSMOW and SLAP. The precision of the measurements of the analysis was 0.1‰ for oxygen and 0.5‰ for hydrogen. Alkalinity and the concentrations of calcium, potassium, sodium, magnesium, chloride, nitrate and sulphate were analysed by Lounais-Suomen Vesi-ja ympäristötutkimus Oy (The Water and Environment Research of Southwestern Finland Ltd.) and the contents of silica by The Water Protection Association of the River Kokemäenjoki.

The isotopic composition of DIC was analysed in the Department of Geosciences and Geography at the University of Helsinki. In the field, 5 ml samples were filtered through 0.8/0.2 µm Supor membrane syringe filters into Exetainer tubes filled with helium and containing 85% phosphoric acid. The samples were analysed by isotope-ratio mass spectrometry (IRMS), using DELTA plus Advantage IRMS (Thermo Finnigan). The laboratory standards used had been calibrated against an international standard (NBS19). The precision for the analysis was 0.1‰. The standards were prepared using an identical procedure as the one utilized for the samples and were both left standing for 24 h in room temperature before analysis.

The isotopic composition of DOC was measured from two samples of the infiltrated water at the University of Jyväskylä. Freeze-dried water samples were incubated in HCl fume at room temperature for 16 h, after which they were kept in desiccator until 0.5 mg of the samples was weighed in tin cups and analysed with DELTA plus Advantage IRMS (Thermo Finnigan) and run against IAEA CH3, NBS-19 and the fish muscle carbon standards in the University of Jyväskylä isotope laboratory. The standard deviation between replicates was smaller than 0.2‰.

The isotopic composition is given as δ values which are calculated from isotope ratios (the heavier isotope against the lighter one):

$$\delta_{\text{sample}} = R_{\text{sample}}/R_{\text{std}} - 1 \tag{1}$$

Table 1  
The different stages of the Virttaankangas MAR site startup and their durations.

Phase	Infiltration rate m <sup>3</sup> /s	Duration
I	20 000	September 2010–October 2011
II	45 000	November 2012–December 2013
III	65 000	March 2014–August 2014

where  $R_{\text{sample}}$  is the isotope ratio in the sample and  $R_{\text{std}}$  is the same isotope ratio in a standard. For waters the standard used here is Vienna Standard Mean Ocean Water (VSMOW) and for carbon Vienna PeeDee Belemnite (VPDB).

### 3.2. The groundwater flow model

The flow model was constructed using the Modflow 2005 code (Harbaugh, 2005). The modelling program used was Processing Modflow for Windows (PMWIN, Chiang and Kinzelbach, 1991, 1993), and the code Modpath (Pollock, 2012). The model consisted of 60 layers, all with a thickness of 2 m, except the topmost layer, the thickness of which varies between 10 and 30 m at the unconfined aquifer areas (Table 2). The grid consists of  $201 \times 161$  cells, each  $50 \times 50$  m in size. The modelling was executed as a steady state with the unit of time as days. The initial hydraulic head for the model was the natural groundwater level. The distribution of the horizontal hydraulic conductivity (K) values in the flow model represents the six units of the 3-D hydrogeological model (Artimo et al., 2003). The K-values were also used to depict the locations of the esker core and the kettle hole structures in the flow model. This allowed a more detailed representation of the hydraulic conductivity within the glaciofluvial coarse hydrogeological unit, where most of the artificially infiltrated water flows. Horizontal and vertical hydraulic conductivity (m/d) were assumed to be equal. Effective porosity varied between 0.05 and 0.27. The flow packages used were: DRAIN, GENERAL HEAD BOUNDARY, RECHARGE and WELL. Groundwater recharge was deduced from the amount of precipitation infiltrating through the topmost hydrogeological unit.

The model was calibrated to fit the observed groundwater levels at 46 observation wells and the measured flow volumes of the two springs in the area before including artificial recharge simulations. To simulate the effects of the water infiltration, the infiltration ponds were simulated as positive flow cells in the highest active model layer. For water pumping wells, the depth of the negative flow cells depict the locations of the screened intervals of the wells. The total volume of water intake from each well was divided by the screen length for each well.

### 3.3. Geochemical modelling

For establishing the onset and amount of DOC decomposition in the aquifer, and the conditions affecting it, the first step was determining the mean residence time (MRT) of the infiltrated water. This was achieved by fitting a sinusoidal curve on the seasonal variations in the isotopic composition of the infiltrated river

water (Burgman et al., 1987). These values were compared to the shortest travel times (STT) given by the flow model to establish the variation and complexity of the travel routes of the MAR water in the aquifer and the effect of residence time on the oxidative decomposition of DOC. The isotopic composition of oxygen was also used to determine the percentage of MAR water (RW%) in the wells. These fractions were subsequently used for modelling the oxidative decomposition of DOC.

Quantifying oxidative decomposition of DOC was achieved by inverse modelling using PHREEQC (Parkhurst and Appelo, 2013). The basic procedure is described in short in Fig. 2. First an initial solution was defined. In the case of Virttaankangas, the initial solution is a mixture of the natural groundwater of the area, and the infiltrated surface water. Mixing ratios were established by using the isotopic composition in oxygen. In Phases I and II, this was the mean isotopic composition of infiltrated river water and the composition of the well water sample. In Phase III, for wells VIK32/33, VIK54 and VIK42 the annual mean of the well water as well as the annual mean of the river water were used. The starting solution was then allowed to react with the mineral assemblage from Virttaankangas (Kortelainen et al., 2007). The average isotopic composition of the calcite dissolving from the sediment was then used in the model. Also, secondary minerals kaolinite and illite were allowed to form to produce a realistic simulation. The chemical composition of the infiltrated water was relatively stable throughout the year, so annual mean composition was used (Table 3). The precision of 0.05 was used for all analysis results, except for the isotope results, which were given the precision of the analysis method to make sure that precision limitations of the analysis equipment would not prevent the acquisition of modelling results.

The program was asked to find possible models on how the given starting solution would, going through the mineral assemblage given (Fig. 2), end up being the observed water in the observation and production wells. The modelling was first done without adding the effect of DOC decomposition. If results were not obtained, a carbon component was added. This was achieved by adding carbon dioxide gas with the isotopic composition of the organic carbon typical for the Kokemäenjoki River. In cases where models could not be obtained without the addition of  $\text{CO}_2$  balancing the  $\delta^{13}\text{C}$  value with this addition yielded results.

When satisfactory models were found, the mineral reactions were quantified. Models with the fewest amount of reacting phases were chosen. From them the minimum and maximum amounts of  $\text{CO}_2$  addition, or DOC decomposition, were taken, as were the amounts of reacting minerals, and the saturation indices for calcite.

**Table 2**  
The hydrogeological units, K values and calibration methods used in the flow modelling. (\* Different K-values within the glaciofluvial coarse unit depict the phases of the esker sedimentation, e.g. ice tunnel deposits, esker fans, distal sands. \*\*Calibration zones were defined on the basis of the variation of the depositional environments of the esker core. E.g. open channel, high elevation bedrock, bedrock fracture depression.)

Hydrogeological unit*	Note	K (m/d)	Calibration
Littoral sand	Only perched groundwater. Omitted from the flow model	–	–
Silt and clay	Acquiclude (inactive)	0	–
Glaciofluvial fine	K-values vary due the bedrock elevation and vicinity of the GF coarse unit	3.49–14.63	manual
Glaciofluvial coarse**	The esker core having the best hydraulic conductivity	625–1500	automatic
Glaciofluvial coarse	Esker core flanks	752–900	automatic
Glaciofluvial coarse		400	manual
Glaciofluvial coarse	Esker core, open channel sedimentation	375–500	man & auto
Glaciofluvial coarse	Esker core flanks, open channel sedimentation	300	manual
Glaciofluvial coarse	Open channel sedimentation	200	manual
Till		2	manual
Bedrock	Inactive	0	–
MUKH	Morphologically undetectable kettle holes in the vicinity of the esker core	499	manual



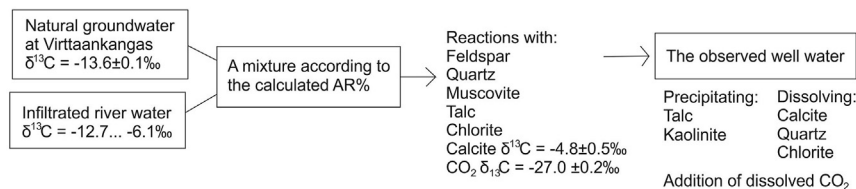


Fig. 2. The geochemical modelling steps used in PhreeQC. The composition of Virttaankangas sediments is taken from Kortelainen et al. (2007).

Table 3

The isotopic composition of DIC and the DOC content in the studied water samples.

Site	Date	$\delta^{13}\text{C}_{\text{DIC}}$ ‰ VPDB	DOC mg/L	Site	Date	$\delta^{13}\text{C}$ ‰ VPDB	DOC mg/L
Inf.	20.9.2010	-9.2	4.0	VIK42	17.1.2013	-12.5	1.6
Inf.	23.9.2010	-9.0	3.6	VIK42	18.3.2013	-12.2	2.0
Inf.	12.10.2010	-7.7	3.8	VIK42	30.5.2013	-12.2	2.3
Inf.	8.12.2010	-7.6	5.6	VIK42	10.7.2013	-12.0	2.5
Inf.	11.1.2011	-8.7	4.9	VIK42	18.9.2013	-12.2	2.1
Inf.	14.2.2011	-9.3	4.9	VIK42	6.11.2013	-12.3	2.6
Inf.	14.3.2011	-10.8	4.4	VIK42	4.3.2014	-12.2	1.9
Inf.	19.11.2012	-8.6	4.4	VIK43	21.5.2014	-10.5	2.2
Inf.	4.2.2013	-10.4	4.2	VIK43	13.8.2014	-10.3	2.0
Inf.	18.3.2013	-10.7	4.3	VIK43	5.11.2014		2.8
Inf.	16.1.2013	-9.6	4.3	VIK51	2.9.2010	-14.5	0.5
Inf.	10.4.2013	-12.7	4.1	VIK51	21.5.2014	-11.5	1.8
Inf.	29.5.2013	-8.3	5.1	VIK51	13.8.2014	-11.6	1.2
Inf.	18.6.2013	-9.1	5.1	VIK51	4.11.2014		2.6
Inf.	9.7.2013	-9.9	5.2	VIK53	11.10.2010		0.5
Inf.	12.8.2013	-9.9	4.9	VIK53	20.11.2012	-14.0	1.2
Inf.	1.10.2013	-9.0	4.2	VIK53	17.1.2013	-13.7	1.2
Inf.	18.9.2013	-9.6	4.5	VIK53	18.3.2013	-13.0	2.6
Inf.	5.11.2013	-8.7	4.2	VIK53	30.5.2013	-12.8	2.5
Inf.	2.12.2013	-7.3	3.8	VIK53	10.7.2013	-12.4	2.7
Inf.	4.3.2014	-8.3	4.0	VIK53	18.9.2013	-12.4	2.3
Inf.	20.5.2014	-6.1	4.3	VIK53	6.11.2013	-12.6	3.3
Inf.	12.8.2014	-9.7	2.3	VIK53	4.3.2014	-12.2	2.4
Inf.	4.11.2014		3.7	VIK53	21.5.2014	-11.5	1.6
VIK32	20.11.2012	-10.6	2.5	VIK53	13.8.2014	-11.3	2.3
VIK32	18.3.2013	-10.7	2.9	VIK53	4.11.2014		2.7
VIK32	17.1.2013	-11.3	2.8	VIK54	20.11.2012	-12.0	2.5
VIK32	18.9.2013	-11.1	3.3	VIK54	17.1.2013	-11.7	2.7
VIK33	6.11.2013	-11.8	3.6	VIK54	18.3.2013	-11.1	2.5
VIK32	4.3.2014	-11.3	2.7	VIK54	30.5.2013	-11.4	3.4
VIK33	21.5.2014	-10.8	1.5	VIK54	10.7.2013	-11.4	3.6
VIK32	13.8.2014	-10.7	2.5	VIK54	18.9.2013	-11.3	3.1
VIK32	5.11.2014		2.7	VIK54	6.11.2013	-11.4	3.6
VIK42	20.11.2012	-13.1	1.5	VIK54	4.3.2014	-12.1	2.5

#### 4. Results

The results of the isotopic analysis for DIC and DOC contents of the infiltrated water and production well samples are given in Table 2. The  $\delta^{13}\text{C}_{\text{DOC}}$  values in the two samples were  $-27.0\%$  and  $-26.9\%$ , and the  $\delta^{13}\text{C}$  value for DIC in the infiltrated water varied between  $-12.7$  and  $-6.1\%$  (Table 3). The contents of DOC varied between 2.3 and 5.6 mg/L in the infiltrated water and between 0.5 and 3.6 mg/L in the wells (Table 3). The  $\delta^{18}\text{O}$  values in the infiltrated river water followed a sinusoidal pattern (Niinikoski et al., 2016), with maxima in the summer at  $-8.9\%$  and minima in the spring at  $-9.9\%$  (Fig. 3). The average of the  $\delta^{18}\text{O}$  values for the river water was  $-9.2\%$ . The isotopic composition of hydrogen followed a similar pattern. The mean  $\delta^{18}\text{O}$  value of natural groundwater in the area was  $-12.1 \pm 0.2\%$  in 2007–2015 (Fig. 3). The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values are given in the Supplementary Material.

The chemical analysis results are also given in the Supplementary Material. Before infiltration, the infiltrated river water is treated with polyaluminium chloride (PACl) which raises

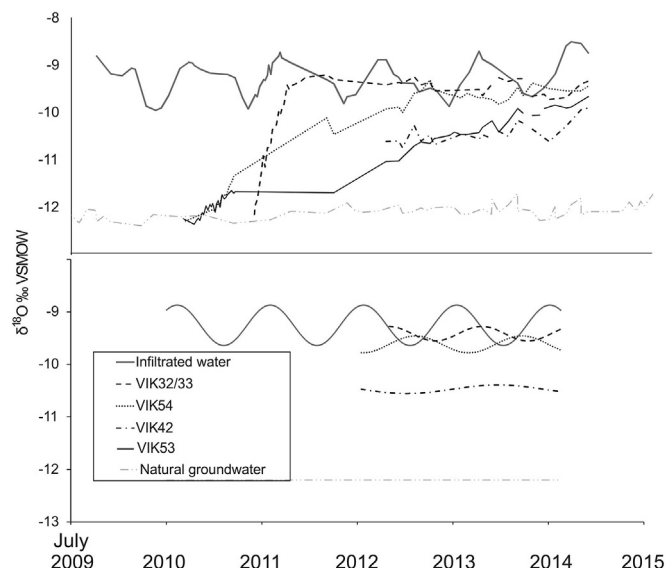


Fig. 3. The annual variations of the isotopic compositions of natural groundwater, infiltrated and well waters and the sinusoidal functions fitted into these variations when possible. The values for natural groundwater are means from several sampling locations (see Supplementary Data Table).

its Cl contents to 9–12 mg/L. In natural groundwater in Virttaankangas, the Cl concentrations are below 2 mg/L. Calcite dissolution raises the pH of the infiltrated water from neutral to 8 or even 9. Dissolution can also be observed in the Ca concentration, which rises from 5 mg/L to as high as 26.4 mg/L. Fig. 4 illustrates the differences between infiltrated river water, natural and artificial groundwater.

Natural groundwater flow direction in the western side of the Virttaankangas aquifer is from northwest to southeast, while in the eastern part groundwater flows towards south. The flow routes given by the flow model are shown in Figs. 5 and 6. In the eastern side, well VIK54 receives water from the infiltration areas 401, 500 and 501, and against the natural groundwater flow gradient from infiltration area 503 (Fig. 5). In the western side of the aquifer, wells VIK32/33 receive their water from infiltration area 301, well VIK42 is fed mostly by infiltration areas 303 and 400 and to a lesser extent against the natural gradient by 401 (Fig. 6). The water in the wells is therefore always a mixture of different aged infiltrated water from different infiltration areas.

The flow model gives the shortest travel times (STT). STT is the minimum time taken for the infiltrated water to arrive at the well in question. A simulation for the eastern part of the aquifer (Fig. 5) shows that the infiltrated water reaches the wells in 14 weeks (Table 4). The model also indicates that the infiltrated water travels as a distinct plume within the aquifer. This leaves some narrower paths for the natural groundwater to travel. Some of these paths may be faster than the plume of infiltrated water. In the western

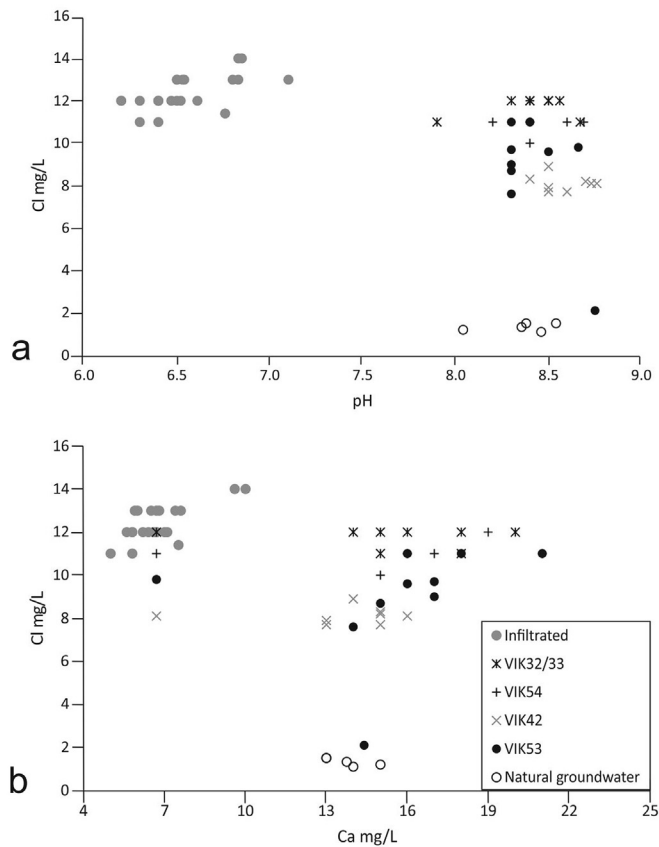


Fig. 4. Chemistry of the natural groundwater, infiltrated river water and well waters. A shows pH against Cl concentration, b Ca against Cl concentration.

side of the aquifer, the model simulates the infiltrated water arriving first at wells VIK32/33, in 12 weeks, and later at well VIK42 in 18 weeks (Table 4).

The start of DOC decomposition and the decomposing amount was modelled with Phreeqc. In Phase I (Table 1) the models showed no oxidative decomposition of DOC except for a few isolated cases. These few exceptions were: during December in wells VI589 and VI591, during May in well VI479, during June in well VI486 and during July in well VI552 (Fig. 1). In Phase II (Table 1) PHREEQC could no longer provide models without a CO<sub>2</sub> addition. This was also true for Phase III (Table 1). All groundwater samples obtained from the production wells were close to calcite-saturation.

The reacting mineral phases are given in Table 5. In most cases the dissolving mineral phases were quartz, calcite, muscovite and feldspar, and the precipitating ones were chlorite, kaolinite and talc. The reacting amounts of these minerals varied between none, to as high as 5.5 mol/L in the case of quartz in one of the samples from well VIK42 (Table 5). The amount of dissolving calcite remained constant at 0.3 mmol/L.

## 5. Discussion

### 5.1. The mean residence time of water

To determine the MRT of MAR water in the wells the stable isotopic composition of MAR water was used. The Kokemäenjoki shows an annual fluctuation of the isotopic composition of oxygen and hydrogen which follows a sinusoidal pattern (Niinikoski et al.,

2016). The same fluctuation is reflected in the well water and is used to determine the MRT of the MAR water. This was achieved once the portion of the infiltrated water had become stable in the wells reflecting the clear seasonal variation in the composition (Fig. 3). A sinusoidal curve was fitted on the isotopic curve and MRT was determined using the phase displacement method (Stichler, 1980). The MRT of the infiltrated water was assumed to be less than one year, based on the shortest travel times simulated by the flow model (Table 3).

Because of the highly complex nature of the flow routes in the aquifer, it is difficult to assess the MRT of the infiltrated water in the aquifer by using the flow model. Only a fraction of the infiltrated water can fit onto the fastest routes, given by the flow model. The rest follows longer paths, sometimes reaching the well slower than the natural groundwater flows. This means that not only is the well water composed of water of varying age and from different infiltration areas, but also the age of the water from the same infiltration area can differ greatly in the same well.

The isotopic composition of precipitation depends on temperature (Dansgaard, 1964; Gat, 1996). In boreal regions, the isotopic composition of precipitation has an annual periodicity with the heaviest composition during the warm months of summer and the lightest during winter. To establish the residence time of groundwater, a sinusoidal function can be fitted to this annual fluctuation of the isotopic composition of precipitation, and on similar fluctuations found in groundwater (Stichler, 1980; Burgman et al., 1987). The sinusoidal fluctuations disappear after approximately three years, so the method is only applicable to dating young groundwaters and surface waters with homogenous catchments (Kirchner, 2015). In the case of MAR, the mean residence time can be established by this method if the source water still shows the sinusoidal fluctuations. This is possible, because there are no more than one component with these annual fluctuations in the mix (Kirchner, 2015). There were three wells where the isotopic composition of water was stable enough to be used for quantifying residence times by fitting the sinusoidal curves on them (Fig. 3). The results were as follows (Niinikoski et al., 2016):

$$\text{VIK32/VIK33: } \delta^{18}\text{O} = 0.138 \times \sin(-0.018t - 2.22) - 9.41(\text{‰}) \quad (2)$$

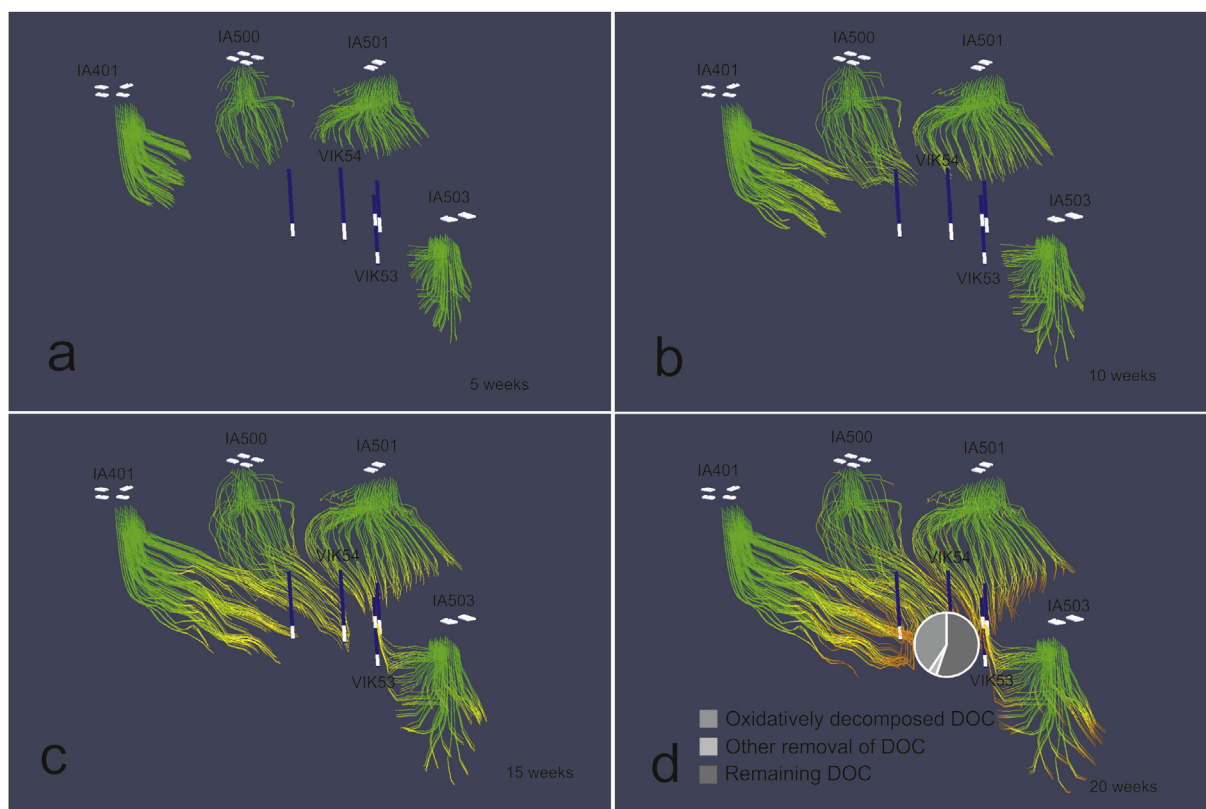
$$\text{VIK54: } \delta^{18}\text{O} = 0.161 \times \sin(-0.015t - 8.84) - 9.62(\text{‰}) \quad (3)$$

$$\text{VIK42: } \delta^{18}\text{O} = 0.081 \times \sin(-0.009t + 0.42) - 10.5(\text{‰}) \quad (4)$$

The equation for infiltrated water was:

$$\delta^{18}\text{O} = -0.36 \sin(0.017t - 3.47) - 9.41(\text{‰}) \quad (5)$$

The MRT's, RW% and distances from the infiltration sites are given in Table 3. The MRT's do not correlate very well with distance. Longer MRT does not necessarily correlate to longer simulated STT (Table 4). This reflects the complexity of the system. In the case of well VIK42 the flow model shows two flow routes: One in the direction of natural groundwater flow from infiltration area IA400 and the other one against the natural gradient from IA401 (Fig. 6). As there are two different residence times the MRT simulated by Equation (4) may not be valid, as combining two sinusoidal functions may not always lead to the right conclusion (Kirchner, 2015). In the cases of the other two wells the flow direction given by the model is less complex. Wells VIK32 and VIK33 get their water from IA301. The MRT and STT are similar indicating that the flow route is quite straight forward. In the case of well VIK54, MRT is almost three times STT.



**Fig. 5.** The flow routes given by the flow model, shows the flow routes and travel times in the eastern part of the aquifer. A shows the routes at 5 weeks after infiltration, b in 10 weeks, c in 15 and d in 20 weeks. The colour of the flow routes corresponds to the travel time changing gradually from green to red with increasing time. Green indicated water which has been in the aquifer for less than 10 weeks, yellow less than 15 weeks, and orange less than 20 weeks. The amount of DOC reduction is indicated in figure d. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

## 5.2. The oxidative decomposition of DOC and the mineral reactions in the aquifer

### 5.2.1. Determining the RW%

The MAR component in the well water (RW%) was determined by using the mean annual  $\delta^{18}\text{O}$  values of the infiltrated and the well waters, and that of the natural groundwater in the area. The annual mean could only be determined in the wells where the isotopic composition of oxygen in the water did not show a rising trend, but only reflected the annual fluctuations of the infiltrated water (wells VIK32/33, VIK42 and VK54 in Fig. 3). From these values, the amount of infiltrated water in the wells could be calculated following a mass balance approach. In cases where the fraction of infiltrated water was still increasing in the well water (Fig. 3), the RW% could not be determined with enough accuracy to produce credible numeric data from the geochemical modelling. For individual groundwater samples the RW% was calculated using the isotopic composition of that particular sample. This gave a good estimate of the RW% but due to the annual fluctuations in the isotopic composition of the river water, only gave  $\pm 15\%$  accurate results.

The difficulty in determining the RW% in the well water in cases where the isotopic composition of groundwater has not stabilized, caused problems in determining the true amount of DOC decomposition in Phases I and II. The isotopic composition of DIC was also subject to change following a seasonal pattern. Therefore using the annual mean value for  $\delta^{13}\text{C}$  of DIC resulted in a high uncertainty. In Phase I the few isolated cases showing DOC decomposition are more likely due to uncertainty in the calculations than simulating actual DOC decomposition.

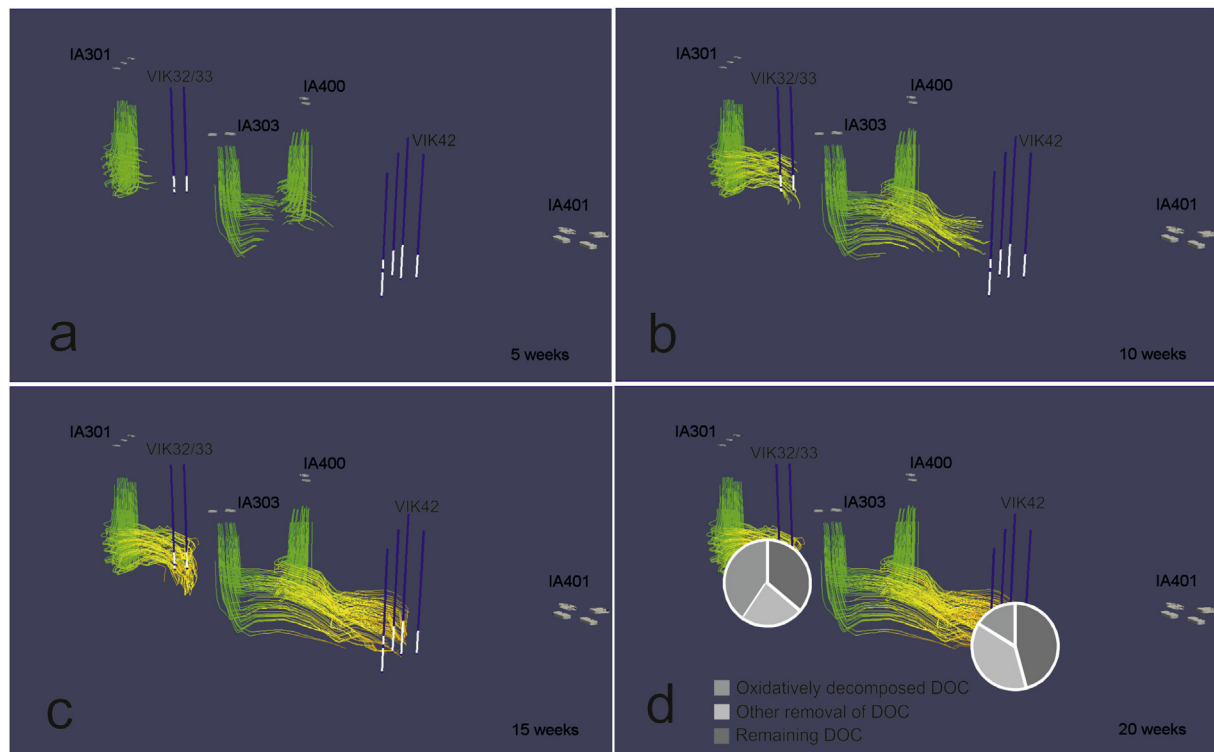
In Phase II the models started showing DOC oxidation in

consecutive samples unlike in the test phase. Running the models with the calculated  $\text{RW}\% \pm 15\%$  yielded results suggesting that the observed composition of the well water in Phase II could not be formed unless there was an addition of an organic carbon component. The full range of the measured  $\delta^{13}\text{C}$  values for the DIC in the infiltrated water were used to validate the results. This did not change the result that some DOC was needed to balance the model. Due to uncertainty in the determination of RW%, and the wide range in the  $\delta^{13}\text{C}$  values for the DIC, the exact amount of DOC decomposition could not be determined. In Phase III, it was possible to determine RW% accurately in cases, where the isotopic composition of the groundwater had stabilized (wells VIK54, VIK32/33 and VIK42). This was achieved by using the mean annual isotopic compositions of both river and well water.

Also, as the MRT of the well water was known, it was possible to use the  $\delta^{13}\text{C}$  value of DIC closest to the time of the year when the majority of the observed well water was first infiltrated. This allowed for more precise modelling. The modelled amount of oxidative decomposition of DOC in the production wells is given in Table 4. The oxidative decomposition of DOC seems to be related to the residence time of the water, as it is highest in well VIK54 with also the longest MRT (Table 4). Also the concentration of DOC seems to play a role, as the amount of decomposition in well VIK42 does not rise quite as high, even though the MRT is comparable.

### 5.2.2. Mineral reactions and DOC decomposition

There is considerable variability in the modelled reacting phases, even within the same sample; the models suggest a vast amount of different outcomes (Table 5). This is most likely due to large uncertainties in the analysis results, and missing input



**Fig. 6.** The flow routes given by the flow model, shows the flow routes and travel times in the western part of the aquifer. A shows the routes at 5 weeks after infiltration, b in 10 weeks, c in 15 and d in 20 weeks. The colour of the flow routes corresponds to the travel time changing gradually from green to red with increasing time. Green indicated water which has been in the aquifer for less than 10 weeks, yellow less than 15 weeks, and orange less than 20 weeks. The amount of DOC reduction is indicated in figure d. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 4**

The shortest travel times (STT) given by the flow model, and the mean residence times (MRT) of water in different wells calculated by the phase shifting method, the RW%, and distance from the infiltration site to the well. The two distances in the case of well VIK42 are from the two different infiltration sites from which the well receives water. The modelled amount of DOC decomposition in the wells is also stated. In the last column the percentage of oxidative decomposition of the total DOC loss is stated.

Well	STT weeks	MRT	RW %	Dist. from inf. site m	Decomposed DOC mg/L	Decomposed/Total reduction %
VIK32/33	12	15	97	670	0.7–1.3	44–81
VIK54	14	40	88	380	1.8	100
VIK42	9/18	36	67	297/450	0.7	30

**Table 5**

PHREEQC modelling results showing the main reacting mineral phases.

Mineral phase	Amount		
	mol/L		
<b>Dissolving</b>	<b>VIK32/33</b>	<b>VIK42</b>	<b>VIK54</b>
Quartz	0–1	0–5.5	0.0001–0.0006
Calcite	0.0002	0.0003	0.0003
Muscovite	0–0.25	0–2	0
Feldspar	0–0.25	0.8–2	0
<b>Precipitating</b>			
Chlorite	0–0.25	0–0.6	0
Kaolinite	0–1	0–2	0
Talc	0.4–1.6	0–2.5	0
<b>SI Calcite</b>	–0.33	–0.25	–0.30

parameters as analysis was executed for the purpose of concentrating on the carbon balance of the water. Based on this variability, the only robust mineral reactions are those of calcite in these results. The modelled calcite reactions are more accurate than the rest of the mineral reactions, since they do not rely solely on the

concentrations of dissolved ions in the waters, but are also based on the isotopic composition of carbon in the calcite and in DIC. The concentration of dissolving calcite is relatively constant, approximately 0.2–0.3 mmol/L and the corresponding saturation index of calcite varies between –0.25 and –0.33. The well water is only slightly undersaturated in calcite (Table 5) compared to the infiltrated river water which is highly undersaturated ( $SI < -3$ ).

The readiness of calcite dissolution at the Virttaankangas site was explained by Kortelainen et al. (2007) as a product of small grain sizes of calcite. Calcite dissolution is beneficial for the operation of the MAR site, as it prevents aquifer clogging (Pavelic et al., 2007). All samples from Virttaankangas are close to calcite saturation from the start of the flow path. This indicates that the dissolution of calcite occurs early along the flow path. In the samples studied, the pH varied between 7.9 and 8.9; considerably higher than in the aquifer clogging study conducted by Pavelic et al. (2007) where the pH of the studied samples never exceeded 8. In a system closed to the atmosphere the pH will rise more than in an open system, the latter being buffered by external  $CO_2$  and therefore remaining close to neutral. The high pH of the Virttaankangas



groundwater therefore indicates a closed or partly closed system.

The amount of CO<sub>2</sub> addition required to produce models in Phase III varied between production wells. It was the highest in the well VIK54 and the lowest in the well VIK42 (Table 4). Since the groundwater system is likely closed to the atmosphere, and the CO<sub>2</sub> changes attributed to calcite dissolution are already taken into account in the modelling, it is probable that this CO<sub>2</sub> addition is due to DOC decomposition.

Examining the DOC concentrations validated the DOC decomposition suggested by the model. By a simple mass balance calculation with the DOC concentrations and the RW%, one can determine the diluting effect of mixing with the natural groundwater of the area. Any DOC loss larger than this could be attributed to either decomposition or adsorption on mineral surfaces. Comparing the DOC concentrations to the modelled CO<sub>2</sub> production by the DOC degradation gives the percentage estimates for DOC decomposition of the total decrease in concentration (Figs. 5 and 6, Table 4).

In the monitored production wells, the percentages of DOC loss through decomposition are provided in Table 4. In other MAR sites, the percentage of decomposition of the total amount of DOC decrease has been reported to be 40–50% (Frycklund, 1995, 1998; Kortelainen and Karhu, 2006; Kolehmainen et al., 2009). The Virttaankangas site shows similar, or even higher numbers (Table 4). The low level of oxidative decomposition of DOC per litre of well water in well VIK42 is explained by the low RW% (67%), resulting in dilution by the natural groundwater (Table 4). In previous studies, and in laboratory experiments, the oxidative decomposition of DOC has been reported to start almost instantaneously if the conditions are suitable (Greskowiak et al., 2005; Vanderzalm et al., 2006; Kolehmainen et al., 2009, 2010). The delay in the DOC decomposition onset at Virttaankangas requires further investigation.

The DOC decomposition initiated at the same time as the infiltration volume was drastically changed, implying that the amount of DOC introduced to the aquifer could play a role in the beginning of oxidative decomposition of DOC. The flow model, however, shows that the MAR water travels as a separate plume in the system (Figs. 5 and 6), in which the concentration of DOC would be constant and only the size of the plume would change with changing infiltration volumes. Even though infiltration rate cannot be completely ruled out as an influencing factor, other reasons for the delay should be taken into account.

High pH can affect DOC decomposition by affecting the microbial community responsible for the DOC decomposition. It is probable that the same microbes responsible for DOC decomposition in close to neutral pH conditions are not as effective in a pH of 8.5 as microbes are very sensitive to pH (Willey et al., 2009). Therefore, it may take a considerably longer time for the microbial community to develop and start decomposing DOC. It has been shown in previous studies that the rate of formation of a microbial biomass is linked to the rate of oxidative decomposition of DOC (Greskowiak et al., 2005). Even after decomposition has started in the aquifer, the decomposition is dependent on the MRT which might be the reason for the delayed onset of the DOC decomposition at Virttaankangas.

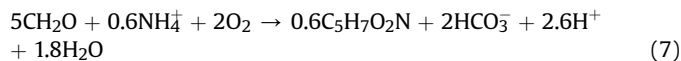
The availability of oxygen for microbial consumption is essential for DOC decomposition (Greskowiak et al., 2005). There are several pathways for oxidative decomposition of DOC to take place. The most common one under aerobic conditions is the simple oxidation reaction with oxygen (Greskowiak et al., 2005; Vanderzalm et al., 2006):



Other reactions involved in the oxidative decomposition of DOC

may involve nitrate, sulphate, or hematite as oxidizing agents, and they commence after the molecular oxygen has been consumed (Vanderzalm et al., 2006). In Virttaankangas there is an abundance of dissolved oxygen available along the flow path, so the anaerobic conditions suitable for these reactions are not likely.

Another reaction is the following which uses up oxygen in the presence of ammonium (Greskowiak et al., 2005):



In solutions with a pH above 8 most of the nitrogen available in a solution is in the form of nitrate (NO<sub>3</sub><sup>-</sup>) whereas at lower pH values other forms of nitrogen, such as nitrite (NO<sub>2</sub><sup>-</sup>) and ammonium (NH<sub>4</sub><sup>+</sup>) are readily available. The high pH of the water at Virttaankangas aquifer does not favour this reaction path. Therefore the only reaction capable of oxidizing DOC in the Virttaankangas conditions is likely to be that represented in Eq. (6). This may have an effect on DOC decomposition in the aquifer.

The overall loss in DOC contents is approximately 1.5–2 mg/L depending on the site and the starting concentration of the infiltrated water. In most cases this corresponds to 30–50% lowering in DOC concentration within the aquifer, mostly due to oxidative decomposition of DOC. This corresponds to the findings in other studies, usually reporting DOC loss of 20–50% (Frycklund, 1995; Kortelainen and Karhu, 2006; Kolehmainen et al., 2009). Previous studies conducted in the presence of carbonates in limestone aquifers, however, produced lower DOC removal rates of between 20 and 24% (Vanderzalm et al., 2006). These results indicate that once the DOC removal process begins at the Virttaankangas MAR site, it is a very efficient process.

Sorption seems to play a minor, if not negligible, role at Virttaankangas aquifer. Graham et al. (2015) discovered in their study on organic carbon mobilisation that intensive pumping can mobilise organic carbon, therefore adding to the overall contents of the water being pumped up from the aquifer. In the case of Virttaankangas, the rate of pumping was increased as the infiltration volume was also increased therefore providing means for this process to occur. It is possible that the actual loss in DOC contents is higher than the perceived loss, since pumping introduces DOC mobilised from the sediment into the water. This process might conceal the effect of sorption in the aquifer.

Further study is required to establish the mechanism(s) responsible for the onset of DOC decomposition coinciding with the higher infiltration volume. It is evident however that the processes by which the MAR removes DOC from the infiltrated water are tied to the pH of the groundwater in the area.

## 6. Conclusions

The main aim of this study was to quantify the oxidative decomposition of DOC and to determine when the oxidative decomposition of DOC started in the aquifer. For this purpose the mean residence time (MRT) and the simulated shortest travel times (STT) of the infiltrated water were determined.

At the Virttaankangas MAR site, the MRT of the infiltrated water was from 15 to 40 weeks. Decomposition of DOC commenced with a higher infiltration volume. The total reduction of the concentration of DOC was 30–50% of the total DOC contents. Of this, between 30 and 80% was due to oxidative microbially induced decomposition. These results show that the Virttaankangas MAR site functions well, and that the amount of DOC decomposition correlates with the MRT. The high pH environment at the Virttaankangas site seem to delay the beginning of DOC decomposition.

It is concluded that seasonality in the δ<sup>18</sup>O content of the

infiltrated water can be used to determine the MRT in the system. The mean residence time can differ significantly from the STT of the infiltrated water and these do not always correlate: a short STT does not necessarily mean a shorter MRT.

In a MAR system where oxidative decomposition of DOC is coupled with calcite dissolution, carbon isotope mass balance combined with geochemical modelling may be applied to estimate the quantities of oxidative decomposition of DOC. The reasons for the delay in the oxidative decomposition of DOC in a high pH environment require further study.

## Acknowledgments

The study was funded by The Turku Region Water Ltd and K. H. Renlund Foundation. The authors would like to thank Osmo Puurunen, Jorma Paavola and Viivi Sillanpää from The Turku Region Water for doing sampling for this study, Marja Tiirola from the University of Jyväskylä for DOC isotope analysis and Arja Henttinen for laboratory analysis. Laura Arppe and Eloni Sonninen from the Finnish Museum of Natural History are thanked for help in DIC isotope analysis. Kirsti Korkka-Niemi and Veli-Pekka Salonen are thanked for their comments on the manuscript. Richard Chopping checked the language. The comments of the two anonymous reviewers helped improve the manuscript.

## Appendix A. Supplementary data

Supplementary data related to this article can be found at doi: 10.1016/j.apgeochem.2016.09.001.

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