

The effect of water pre-treatment with poly-aluminium chloride on the decomposition of dissolved organic matter in managed aquifer recharge



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Abstract

This study examines the effect of poly-aluminium chloride (PACl) pre-treatment on the biological purification process taking place during managed aquifer recharge (MAR). PACl treatment is used in waste and surface water treatment to remove organic material. PACl can decrease the organic carbon contents of water significantly. However, aluminium is toxic to microbes, which may be detrimental when the PACl treatment is followed by infiltration into an aquifer (MAR). In this study the effect of pre-treatment with PACl on the water purification process in MAR was examined, by using sediment from a MAR site in four test columns. Two columns were filled with PACl-treated water, and the remaining ones with river water without PACl. The residence time of water in the columns was raised from direct sampling gradually to 64 days. Among the parameters monitored were the pH of the water, microbial activity and the decomposition of dissolved organic carbon (DOC). The results showed active decomposition in all columns. Decomposition of organic matter, and the amount of living/active microbial cells, was marginally higher in the untreated water, which could imply a better functioning MAR system. However, this may also be due to higher DOC starting concentration.

Keywords: PACl, DOC, carbon isotopes, water purification, managed aquifer recharge, isotope hydrology

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1. Introduction

Poly-aluminium chloride (PACl) is used in water purification to remove organic matter. It is commonly used in waste water treatment, and in purifying surface water (Volk et al., 2000; Duan and Gregory, 2003; Yan et al., 2008; Matilainen et al., 2010; Niinikoski et al., 2016). PACl facilitates the precipitation of dissolved organic carbon (DOC) (Volk et al., 2000; Duan and Gregory, 2003; Yan et al., 2008; Matilainen et al., 2010; Niinikoski et al., 2016). The precipitate can be collected by flotation or sedimentation. After the PACl treatment other purification methods can be used, one of which is infiltration into suitable soil for further purification. This process is called managed aquifer recharge (MAR) and it is used in water purification for drinking water purposes to further remove DOC (Vartiainen et al., 1987; Sundlöf and Kronqvist, 1992; Hatva, 1996; Grünheid et al., 2005; Kortelainen and Karhu, 2006; Niinikoski et al., 2016).

MAR is especially effective in removing organic contaminants from the surface water (Kortelainen and Karhu, 2006; Kolehmainen et al., 2009; Niinikoski et al. 2016;). The purification process may include adsorption on mineral surfaces, as well as microbial oxidative decomposition, where organic carbon compounds are oxidized into harmless inorganic forms (Vartiainen et al., 1987; Sundlöf and Kronqvist, 1992; Hatva, 1996; Grünheid et al., 2005; Kortelainen and Karhu, 2006; Niinikoski et al., 2016). The latter process relies on non-harmful microbes within the water and the soil, which use organic carbon as their energy source (Kolehmainen et al., 2009; Niinikoski et al., 2016). Normally there is no pre-treatment required in MAR. Surface water is infiltrated into a suitable soil either by pond, bank or well infiltration, or by sprinkling (Vartiainen et al., 1987; Sundlöf and Kronqvist, 1992; Hatva, 1996; Grünheid et al., 2005; Kortelainen and Karhu, 2006; Niinikoski et al., 2016). However, in some special cases pre-treatment may be done to lower the DOC contents of the infiltrated water, to

prevent “clogging” the aquifer with organic material absorbed onto mineral surfaces (Niinikoski et al., 2016).

The effect of PACl on the microbes required for water purification in MAR has not been studied previously. There are two possible pathways by which it can have a negative effect: Firstly, by adding aluminium into the water, and secondly, by removing nitrate. Aluminium is toxic to many microbes (Silver, 1983). Concentrations of less than 50 µmol/L have been found to cause microbes to work less efficiently. The toxicity of aluminium rises with decreasing pH (Keyser and Munns, 1979; Whelan and Alexander, 1986; Wood et al., 1988; Willey et al., 2009), but it is most mobile in pH higher than 7.4. Secondly, the PACl can remove other nutrients besides DOC (Willey et al., 2009). PAC used in effluent treatment may reduce, not only the contents of DOC but also the nitrate contents of the water, which could be vital to efficient microbial decomposition of DOC (Ayyasamu et al., 2007; Aghapour et al., 2016). The purpose of this study was to examine, how PACl treatment affects the decomposition of DOC by microbial activity, by using water and soil from an operational MAR site, Virttaankangas, in southwestern Finland.

Biological processes favour the lighter ^{12}C isotope, which is enriched in organic material (Deines, 1980; Schiff et al., 1997; Vogel, 2012). As DOC is decomposed, it forms inorganic carbon compounds, such as carbonic acid, bicarbonate, carbonate and carbon dioxide (Lindroos et al., 2002; Grünheid et al., 2005; Kortelainen and Karhu, 2006; Kolehmainen et al., 2009). Together these compounds are referred to as dissolved inorganic carbon (DIC). The decomposition process can be monitored by monitoring the isotopic composition of DIC (Kortelainen and Karhu, 2006; Niinikoski et al., 2016). DIC formed from carbonate dissolution or equilibration with atmospheric CO_2 has a distinctly heavier isotopic composition than organic carbon. Therefore, as DOC is decomposed to form DIC, it adds lighter carbon into the DIC pool. This change in the

isotopic composition of DIC can be monitored as an indicator of decomposition of DOC. In this study these compositional changes, as well as other chemical and microbial parameters were used to determine, if PACl treatment is harmful for the MAR process. The effect of residence times was taken into account by doing experiments with varying durations.

2. Geological background

The Virttaankangas esker is a part of the glaciofluvial Säkylänharju-Virttaankangas complex, located in southwestern Finland (Fig. 1). It formed during the late Weichselian and early Holocene deglaciation. The formation is a meltwater deposit between two sublobes of the retreating Baltic Sea ice-lobe (Punkari, 1980; Kujansuu et al., 1995; Mäkinen, 2001) and it can be divided into three units:

1. The lowermost part resulted from repeated deposition of subaqueous fans containing glaciofluvial sands and gravels (Artimo et al., 2003).
2. The intermediate part contains glaciofluvial sand and silt, and associated glaciolacustrine silt and clay deposits of proglacial water body (Artimo et al., 2003).
3. The uppermost 10–20 m of the complex are 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).

Calcite is present in units 1. and 2. The concentration is highest in the <0.2 mm fraction, 3.7–5 weight-%, which corresponds to 0.5–1.4 weight-% of the total sediment (Artimo et al., 2003). The $\delta^{13}\text{C}$ value of the calcite is $-4.8 \pm 0.5\%$ (Kortelainen et al., 2007). Calcite dissolution elevates the pH of natural groundwater to 8–9, with the potential to produce pH as high as 9.5 (Artimo et al., 2007; Kortelainen and Karhu, 2009). Sediment was collected from layers 2 and 3, from an area not affected by the MAR process, in the non-saturated zone.

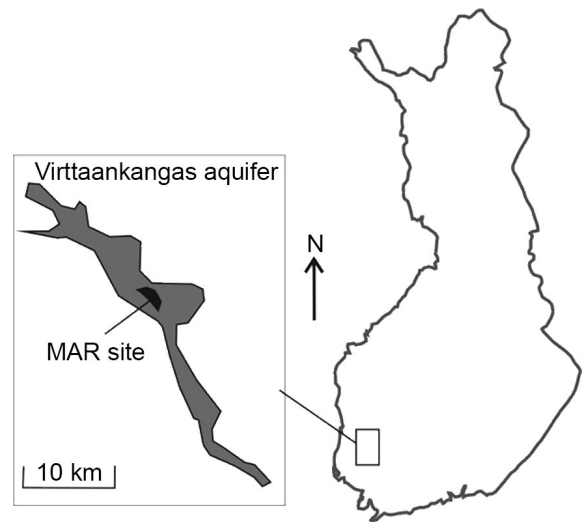


Figure 1. The location of the study area in south-western Finland.

The MAR facility at Virttaankangas was commissioned in 2010. The infiltrated water comes from the Kokemäenjoki River, located 30 km north from the site (Niinikoski et al. 2016). The infiltrated water volume varies according to demand, in the beginning of production it was 65.000 m³/day (Niinikoski et al. 2016). The mean residence time of the infiltrated water was estimated by Niinikoski et al. (2016) as varying between 15 and 40 weeks, while travelling distances vary between 300 and 700 m.

3. Methods

3.1. Building the columns

Black PEH plastic was chosen for the construction of the columns, because, in order to simulate conditions in the esker, light was not allowed to penetrate them. The plastic was tested with pure water to see if it would release carbon into the water, which would interfere with the experiment. The test tube was filled with distilled water, sealed at both ends and allowed to react for three days. After this the water was drained out and the isotopic composition of the DIC it might contain measured.

Table 1. The different columns and their contents.

Column	A	B	C	D
Water type	PAC-treated	river water	PAC-treated	river water
Sediment type	calcite	calcite	no calcite	no calcite

The test on the column material showed that there was no measurable DIC leaching from the PEH plastic.

After the experiment four columns were built using pipe made of the same PEH plastic. The columns were 200 cm high and the diameter was 20 cm. At the bottom an approximately 25 cm layer of gravel was placed to facilitate the water flow from the tap placed at 20 cm height. On top of the gravel a metallic sieve was placed, before placing in the sediments. Water was introduced with a hose from the top of the column.

Two of the columns were filled with Virttaankangas sediment containing calcite (A and B, Table 1), and two with the littoral sands from unit 3 known to be calcite free (C and D in Table 1). One column with each type of sediment was filled with untreated river water from the Kokemäenjoki River (B and D in Table 1), and the remaining two with the PACl treated water (A and C in Table 1). The water was allowed to react for a period of time before draining the columns and analysing the water, after which the columns were filled again, and the time period increased. With each filling the ingoing water was also analysed for the same parameters. The columns were placed in room temperature. Altogether eight sets of experiments were made, in the first ones the water was run straight through the columns (0 days), and in the following ones it was allowed to stand for 1, 2, 4, 8, 16, 32 and 64 days.

3.2. Chemical and isotopic analyses

Isotopic composition of DIC, alkalinity, pH, DOC contents, dissolved oxygen (DO) and main ions sodium, potassium, magnesium, fluoride, chloride, nitrate, sulphate and phosphate were analysed, and temperature was measured. The DOC contents as

well as DO and pH were measured in the field using an YSI water quality meter equipped with 6562 Rapid Pulse Sensor (dissolved oxygen, precision ± 0.2 mg/L, DOC, precision ± 1 mg/L) and pH 6561 sensor (± 0.2). Other parameters were measured at the University of Helsinki, in the Department of Geosciences and Geography. The contents of the main ions were analysed from the samples from 0 residence time to 16 days residence time by Tandem Metrohm Mic12 ion chromatograph (IC). The detection limits for fluoride (F), chloride (Cl) and sulphate (SO_4) were 0.05 mg/L, for nitrate (NO_3) 0.1 mg/L, and for sodium (Na), potassium (K), calcium (Ca) and magnesium (Mg) 0.08 mg/L. The precision of these analyses was 10%.

Both sediment types were also tested for carbonate. 2 kg of both sediments were first dried and burned in 700°C overnight, in order to remove any organic compound present in the sediment. After burning the <1 mm fraction was separated from the samples by sieving. These samples were analysed for carbon by using a CNS Vario Elementar Micro Cube analyser, the precision of which was 10%.

The isotopic composition of DIC was analysed by Isotope-ratio mass spectrometry (IRMS), using a Thermo Finnigan Delta Advantage mass spectrometer, together with laboratory standards, which have been calibrated against an international standard (NBS19). The accuracy for the analysis was 0.1‰. The 5 ml samples were injected through 0.8/0.2 μm Supor membrane syringe filters into helium filled Exetainer tubes, which contained eight drops of 85% phosphoric acid. The standards were prepared using the same procedure and both were allowed 24 hours to stand in room temperature before analysis.

3.3. Microbial analysis

Samples for cell number and viability analysis were collected from untreated river water and from PACl-treated water. Water samples (500 ml each) were collected into sterile glass bottles (Schott) and kept cool prior to analysis, in order to minimize biological changes that might take place during transport. Untreated water was visibly brownish and contained some solids. PACl-treated water was clear.

Microbial cells of the water samples were fluorescence-stained with LIVE/DEAD *BacLight* Bacterial Viability Kit (Thermo Fisher Scientific, MA, USA) according to manufacturer's instructions. Shortly, 15 μ l of fluorescent dye was mixed with 50 ml of sample water. Mix was incubated in room temperature, protected from light for 15 min. Stained samples were concentrated on black 0.2 μ m pore-size polycarbonate membrane filters (IsoporeTM Membrane filters, 0.2 μ m GTBP, Millipore, Danvers, MA, USA) with a Millipore 1225 Sampling Manifold (Millipore, Danvers, MA, USA) using low vacuum suction. The filters were examined under UV light and an epifluorescence microscope at 100 \times magnification. Cells were counted in the field of view at 20 randomly chosen locations on the filter. The number of cells in the samples was calculated, on the basis of magnification factor, filtered sample volume, and the active surface area of the filter and the area of the imaging device. Cells with intact cell membranes emitting green fluorescence were considered alive. Red cells were considered nonviable as the cell membranes of these were damaged and were not able to remove the red dye from the interior of the cell.

3.4. Calculation

The isotopic composition of water is viewed with δ values, which are calculated from isotope ratios (the heavier isotope against the lighter one):

$$\delta_{\text{sample}} = R_{\text{sample}} / R_{\text{std}} - 1 \quad [1]$$

Where R_{sample} is the isotope ratio in the sample and R_{std} is the same isotope ratio in a standard. For carbon the standard used here is Vienna PeeDee Belemnite (VPDB) (Dansgaard, 1964; Coplen, 2011).

Mass balance is used to calculate fractions (f and $1-f$) of two components (A and B) in a mix:

$$f \times \delta_A + (1-f) \times \delta_B = \delta_{\text{mix}} \quad [2]$$

Saturation indices and DIC contents were calculated using the PHREEQC geochemical modelling program (Parkhurst and Appelo, 2013).

4. Results and discussion

The results of the analyses and modelling are given in Table 2 and in the electronic appendix A.

4.1. Carbon contents

The amount of carbon in the calcite-free sediment was 0.14 weight-% and 0.93 weight-% in the calcite containing sediment. The fraction of remaining DOC relative to that in input water decreased with increased residence time (Fig. 2), as did the $\delta^{13}\text{C}_{\text{DIC}}$ values (Fig. 3), whereas the calculated contents of DIC increased (Fig. 4). These are clear indicators of DOC decomposition in the columns (Kortelainen and Karhu, 2006; Niinikoski et al., 2016). The change in DIC isotopic composition (Fig. 3) mirrors the changes perceived in MAR facilities, with a steep decline in $\delta^{13}\text{C}_{\text{DIC}}$ values taking place early on and afterwards levelling down (Kortelainen and Karhu, 2006; Niinikoski et al., 2016). Similar trends, although less pronounced can be seen in the changes in DOC and DIC contents (Figs. 2 and 4).

The longest monitored time period was approximately two months, which is significantly shorter than the mean residence times of artificially recharged water in the aquifer at Virttaankangas (Niinikoski et al., 2016). According to the isotopic composition of DIC, there is no difference between the amount of DOC decomposition between the

Table 2. Selected analysis and modelling results (all results can be found in the appendix).

Type	Res. Time	Alk	DIC	pH	Ca	F	Cl	NO ₃	DOC	O ₂	δ ¹³ C	SI _{CaCO3}	SI _{CaF2}
	Days	mmol/L			mg/L						%oVPDB		
RW	0	0,26	0,29	7,3	6,71	0,15	4,44	0,87	7,6	8,1	-9,53	-2,00	-3,49
RW	0	0,26	0,30	7,1	8,15	0,14	4,35	0,97	8,6	8,65	-9,22	-2,12	-3,47
RW	0	0,28	0,31	7,3	7,05	0,16	4,53	1,24	7,5	9,7	-9,22	-1,95	-3,41
RW	0	0,28	0,31	7,3	7,10	0,16	4,67	1,17	6,5	10,1	-9,02	-1,95	-3,41
RW	0	0,28	0,30	7,4	7,34	0,14	4,78	1,47	9,3	11,11	-7,80	-1,83	-3,52
RW	0	0,26	0,29	7,2	6,77	0,15	4,48	3,40	7,5	8,81	-9,66	-2,10	-3,49
PAC	0	0,12	0,20	6,5	6,89	0,09	11,92	1,03	3,6	9,29	-8,84	-3,12	-3,92
PAC	0	0,12	0,17	6,7	6,78	0,06	8,76	0,72	4,0	9,37	-9,59	-2,92	-4,27
PAC	0	0,12	0,20	6,5	6,87	0,10	11,88	1,06	3,4	9,53	-9,47	-3,12	-3,83
PAC	0	0,14	0,22	6,6	7,08	0,10	12,19	1,15	2,0	11,2	-8,55	-2,95	-3,82
PAC	0	0,14	0,19	6,8	7,23	0,07	12,37	1,27	4,4	11,89	-7,64	-2,74	-4,12
A	1	0,10	0,17	6,5	8,39	0,04	11,96	0,74	3,8	8,62	-12,88	-3,11	-4,54
A	2	0,12	0,17	6,7	8,18	0,03	11,92	0,54	3,7	9,23	-13,31	-2,85	-4,80
A	4	0,11	0,17	6,6	9,63	0,04	11,92	0,39	3,5	9,06	-13,91	-2,92	-4,48
A	8	0,14	0,20	6,7	8,25	0,04	11,89	0,49	2,3	8,94	-15,71	-2,78	-4,55
A	16	0,11	0,17	6,6	8,28	0,03	12,06	0,97	2,7	8,54	-16,36	-2,98	-4,79
A	32	0,15	0,20	6,8	9,07	0,02	12,20	1,26	3,0	9,72	-17,71	-2,61	-5,11
B	1	0,17	0,23	6,8	6,03	0,05	4,47	0,84	5,5	8,51	-11,80	-2,72	-4,48
B	2	0,15	0,20	6,8	6,26	0,05	4,48	0,40	4,8	8,68	-12,75	-2,76	-4,46
B	4	0,17	0,26	6,6	6,54	0,05	4,45	0,43	5,4	8,53	-14,61	-2,89	-4,44
B	8	0,20	0,27	6,8	6,92	0,04	4,52	0,53	2,5	8,77	-16,44	-2,59	-4,62
B	16	0,23	0,29	6,9	7,33	0,04	4,54	0,90	3,2	8,73	-17,25	-2,41	-4,59
B	32	0,28	0,31	7,3	8,32	0,03	4,65	1,14	5,0	8,64	-18,88	-1,87	-4,79
C	1	0,06	0,13	6,3	6,71	0,03	11,99	0,62	2,7	8,85	-12,07	-3,63	-4,88
C	2	0,06	0,13	6,3	6,91	0,03	11,92	0,52	2,7	9,57	-11,77	-3,62	-4,87
C	4	0,06	0,14	6,2	6,81	0,03	11,96	0,39	2,2	9,44	-12,25	-3,72	-4,88
C	8	0,07	0,13	6,4	6,67	0,03	11,90	-0,01	2,6	8,86	-17,50	-3,46	-4,88
C	16	0,08	0,15	6,4	6,82	0,03	12,06	0,43	1,7	9,76	-18,71	-3,40	-4,88
C	32	0,10	0,15	6,6	7,41	0,01	12,21	0,62	3,1	9,9	-18,05	-3,07	-5,80
D	1	0,28	0,52	6,4	4,45	0,03	4,48	0,92	2,7	8,52	-10,66	-3,04	-5,06
D	2	0,08	0,14	6,5	4,43	0,03	4,49	0,90	4,0	8,71	-10,65	-3,48	-5,05
D	4	0,09	0,17	6,4	5,71	0,04	4,48	0,60	2,4	8,93	-12,01	-3,42	-4,70
D	8	0,15	0,22	6,7	5,22	0,04	4,49	0,89	4,9	9,22	-13,77	-2,94	-4,74
D	16	0,17	0,23	6,8	5,61	0,04	4,55	1,28	5,1	8,92	-16,04	-2,76	-4,71
D	32	0,19	0,24	6,9	6,08	0,02	4,64	1,60	4,9	9,09	-17,61	-2,57	-5,28

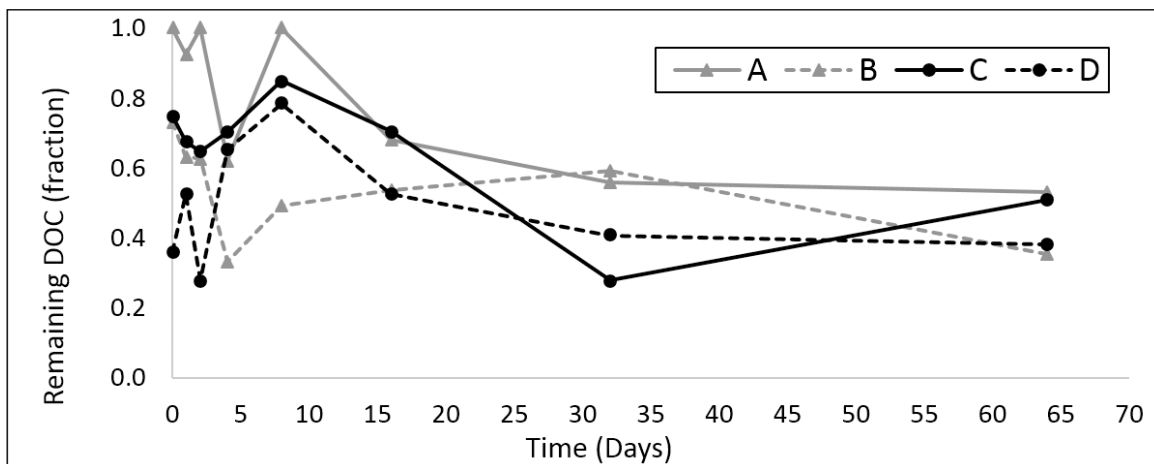


Figure 2. The fraction of dissolved organic carbon (DOC) still remaining in the water as a function of 0-64 days residence time. (A: PACI-treated water with calcite, B: No PACI, with calcite, C: PACI-treated water, no calcite, and D: No PACI and no calcite.)

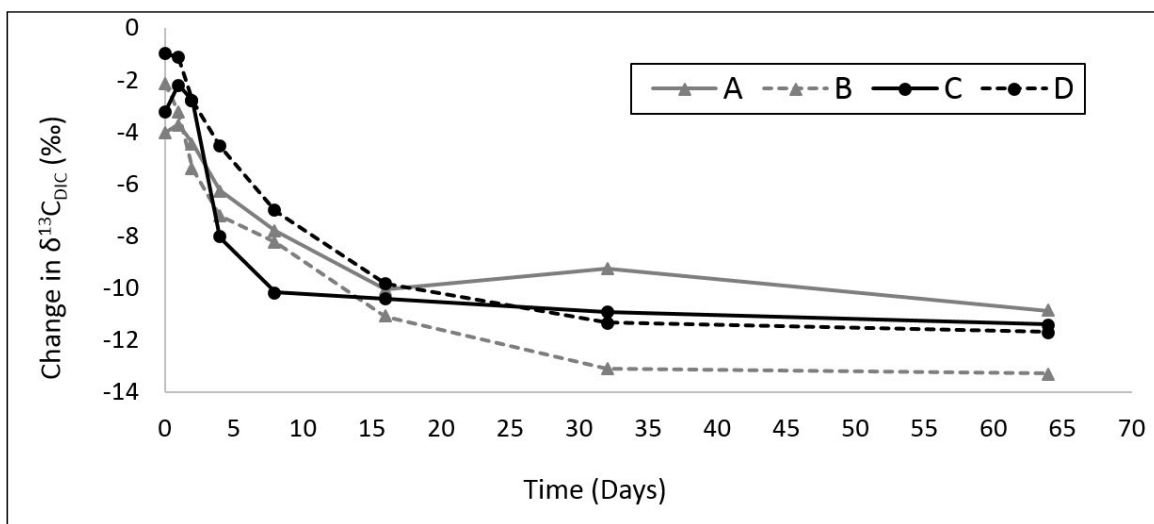


Figure 3. The change in the isotopic composition of dissolved inorganic carbon (DIC) in columns A-D as a function of 0-64 days residence time. (A: PACI-treated water with calcite, B: No PACI, with calcite, C: PACI-treated water, no calcite, and D: No PACI and no calcite.)

32 and 64 day residence times, which implies that residence times longer than one month are not required for adequate DOC decomposition.

The average starting concentration for DOC in PACI-treated water was 3.5 mg/L, and in non-treated river water 8 mg/L. In the end the DOC concentrations were 2.5 mg/L and 4 mg/L, respectively. For pre-treated water this amounted to a 30% decrease in DOC contents,

and for non-pre-treated water the decrease was 50%. These numbers are within the spectrum found in other studies on DOC decomposition in MAR (Vartiainen et al., 1987; Sundlöf and Kronqvist, 1992; Hatva, 1996; Grünheid et al., 2005; Kortelainen and Karhu, 2006; Niinikoski et al., 2016). Due to the relatively high imprecision of the DOC analysis (± 1 mg/L) compared to the perceived concentration changes, there is a large

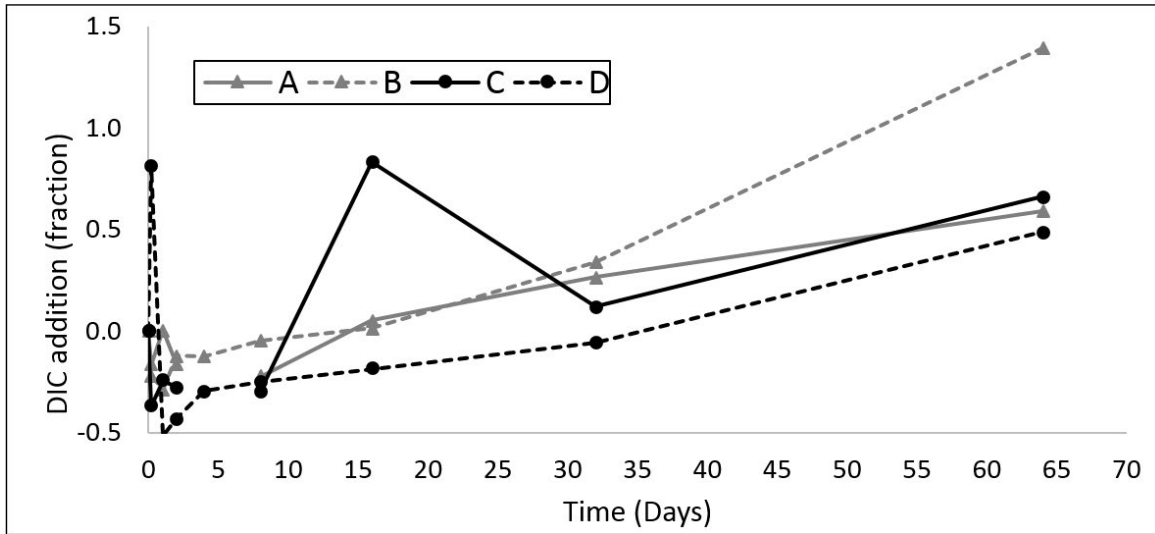


Figure 4. The addition in DIC as a function of residence time in columns A-D, as calculated by PHREEQC. (A: PACl-treated water with calcite, B: No PACl, with calcite, C: PACl-treated water, no calcite, and D: No PACl and no calcite.)

inaccuracy involved with these calculations. The isotopic composition of DIC and Equation 2 give approximately 60% as the amount of DIC which originates in DOC decomposition in the two-month residence time samples. There are no differences between the two water types.

4.2. Changes in chemical composition

The concentration of phosphate was below the detection limit in all samples. The largest chemical difference between the PACl-treated and the river water is chloride concentration, which is between 11.9 and 12.4 mg/L in PACl-treated water and the water in columns A and C, and in river water and in columns B and D it is between 4.4 and 4.8 mg/L (Table 2). The higher chloride contents of PACl-treated water and columns A and C reflects the added PACl, and does not play a part in the reactions taking place in the columns.

The contents of nitrate, oxygen and fluoride decrease in all columns. The average concentration of nitrate in the PACl-treated water was 1.1 mg/L, compared to 1.5 mg/L in the non-treated river water (Table 2). The concentration decreases in all

columns, reaching zero in one of the experiments in Column C (PACl-treated water with non-calcite bearing sand). Therefore it is possible, that PACl that the removal of NO_3 from water can create a limiting factor in the functionality of MAR processes.

The decreasing contents of fluoride can be explained by either fluorite (CaF_2) precipitation, or by microbial activity using fluoride as a nutrient (Marquis et al. 2003; Mukherjee et al., 2017). However, all the samples are undersaturated with fluorite, which makes precipitation unlikely (Table 2). Both dissolved oxygen and fluoride concentrations decrease with increasing residence time (Figs. 5 and 6). DO exhibits a steadier decline (Fig. 5), whereas F decreases more rapidly in the beginning, and the decline in concentration levels out with increasing residence time (Fig 6). If these changes are the result of microbial activity taking place, the processes removing fluoride would be significantly faster than the processes removing dissolved oxygen.

None of the samples are saturated with calcite, the $\text{SI}_{\text{CaCO}_3}$ being approximately -3 in all of them. This is a clear difference compared to the natural conditions at Virttaankangas, where the natural

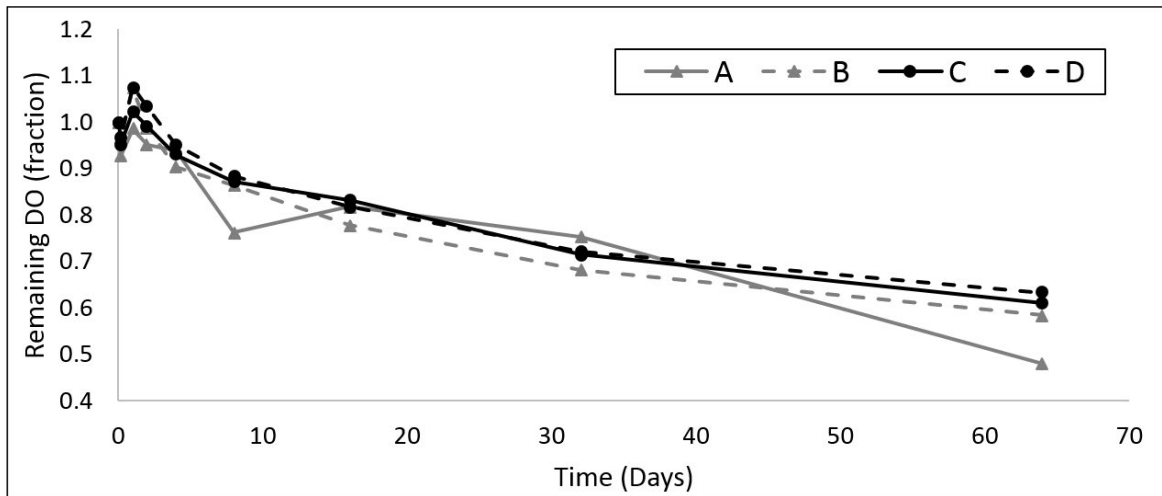


Figure 5. The decrease in dissolved oxygen (DO) contents with increasing residence time in columns A-D, in samples with 0-64 days residence time. (A: PACI-treated water with calcite, B: No PACI, with calcite, C: PACI-treated water, no calcite, and D: No PACI and no calcite.)

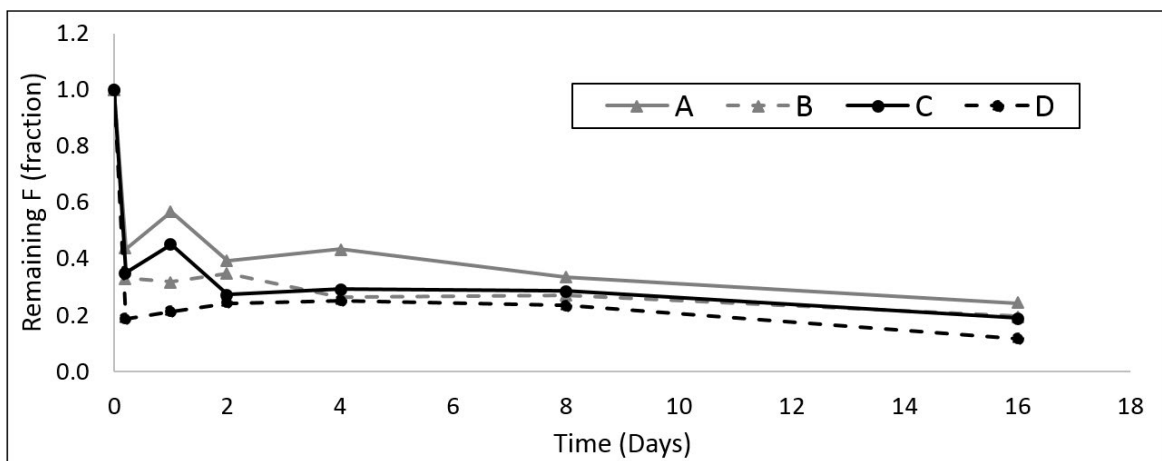


Figure 6. The decrease in fluoride (F) contents with increasing residence time in columns A-D, in samples with 0-16 days residence time. (A: PACI-treated water with calcite, B: No PACI, with calcite, C: PACI-treated water, no calcite, and D: No PACI and no calcite.)

groundwaters, excepting shallow perched waters, are saturated with calcite (Kortelainen and Karhu, 2009). As a result of calcite dissolution, the pH of the groundwater has reached values as high as 9 (Kortelainen and Karhu, 2009). The pH in all of the columns remained close to neutral (Table 2). The carbon contents of the sediment in columns B and D were higher than in the sediment in columns A and C, corresponding to the expected carbonate contents in these columns. However, the SI_{CaCO_3}

remained relatively constant in all columns, which implies that there was little or no calcite dissolution (Table 2). Calcite is relatively slow to dissolve in neutral pH conditions. In natural conditions, mildly acidic rain water is infiltrated into the esker, where it travels through a layer of soil. In addition, the acidity of soil water in natural conditions is increased by humic acid, further enhancing calcite dissolution.

Table 3. Microbial cell numbers per ml of water in untreated river water, and PACl-treated water.

Water type	Live	Dead	Total
River water	65500	13500	79000
PACl-treated water	58000	36000	94000

4.3. Microbial activity

The treatment of the water with aluminium chloride has a diminishing effect to the amount of living cells in the water (Table 3). Approximately 20% fewer cells were alive (functional) in the water after the pre-treatment, therefore it is possible that PACl treatment has an effect on the microbial community in the sediments of the esker. Microbial communities are found to be sensitive to environmental disturbance and changes in community composition may alter ecosystem process rates. However, novel community could be functionally alike to the original and thus, no significant change in ecosystem functioning might not occur (Allison and Martiny, 2008). Therefore, the biological capacity of the surviving microbial community to remove DOC from water cannot be deduced with this analysis.

5. Conclusions

There was DOC reduction due to decomposition perceived in all of the columns. A decrease in the contents of DOC was observed in all experimental columns, irrespective of the sediment type or the water pre-treatment. Changes in the DOC contents and the $\delta^{13}\text{C}_{\text{DIC}}$ values as well as the decrease in the number of viable cells in the PACl-treated water were some indications that the DOC decomposition process might not work

quite as efficiently in the PACl-treated water. The concentration of DOC decreased by 30% in the pre-treated water, as opposed to 50% in untreated water, and the microbial community in PACl-treated water had fewer viable cells than in the non-treated water. This difference was however countered by the lower starting concentration of DOC in the PACl-treated water, which resulted in lower ending concentration. One month was a long enough time to reach the lowest concentrations, after which the results did not improve further. The isotopic composition of DIC proved that DOC reduction was indeed due to decomposition, and differences in the DOC decomposition effects were minimal between the two types of water. It can be deduced from this study, that the PACl-treatment does not reduce the efficiency of MAR.

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Supplementary Data

Electronic Appendix A for this article is available via Bulletin of the Geological Society of Finland web page.

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