Accepted Manuscript

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Please cite this article as: Dalhem, K., Engblom, S., Stén, P., Österholm, P., Subsurface hydrochemical precision treatment of a coastal acid sulfate soil, *Applied Geochemistry* (2019), doi: https://doi.org/10.1016/j.apgeochem.2018.12.005.

Floating groundwater antenna

Targeting hydrologically active macropores through injection of calcium carbonate/hydroxide suspensions

Reducing the release of acidity and metals in discharge waters

Oxidised soil horison
(acid sulfate soil with sulfuric material)

Stored groundwater

Traditional subsurface drainage

pH > 6   pH ≤ 4

Plastic sheet
to prevent by-pass flow

Sulfidic-/ parent sediment
(acid sulfate soil with sulfidic material)

Subsurface hydrochemical precision treatment of a coastal acid sulfate soil

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ABSTRACT

Some of the most economically valued soils for agricultural use are naturally occurring sulfide rich sediments. However, formation of acid sulfate soils with sulfuric materials (pH $\leq$ 4) can occur when sulfidic materials are exposed to air, which can then result in mobilisation of large amounts of acid and metals into nearby water bodies. In this study, controlled drainage, subsurface irrigation and hydrochemical precision treatments are combined to reduce acidic discharges on a novel project field in western Finland. The PRECIKEM project field consists of nine identical hydrologically isolated 1 ha subfields. Each field had a drainage system consisting of three subsurface drainage pipes (c. 1.3 m deep), a collector pipe, and a control well enabling manual groundwater table management. Utilising such

drainage installations already common on farmlands, suspensions of fine-grained (d_{50} = 2.5 μm) calcium carbonate and/or calcium hydroxide were pumped in to control wells in order to be distributed in to subsoils with sulfuric materials via drainage networks with the aim to: (1) neutralise acidity, (2) inhibit microbially mediated sulfide oxidation and (3) immobilise metals. The discharge waters from the fields were monitored during the project period 2012–2016. As is typical for acid sulfate soils with sulfuric materials, the discharge waters from the reference fields (n = 3) that had been treated with water only, had very low pH values (≤ 4) and the acidity and concentrations of several metals were up to two magnitudes higher than the average in Finnish stream waters. Excavation of selected treated fields revealed the calcium carbonate to have formed a neutralising coating on the surfaces of hydrologically active macropores in the soil matrix near the subsurface drainage pipes. This effectively resulted in a long-term (1–4 years) situation of raised pH, lower acidity and lower concentrations of several acid sensitive metals, most prominently a significant decrease (> 90%) in Al concentrations. Fe concentrations in discharge waters were subsequently decreased as the predominance of Fe shifted toward the schwertmannite and iron oxides stability phases due to changes in pH/redox conditions. The methods presented in this work showed favourable steps toward environmentally sustainable agriculture and improving the chemical and ecological status of acid sulfate soil affected coastal waters.
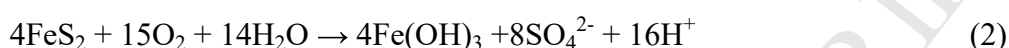
1. Introduction

Coastal acid sulfate soils (ASS) with sulfuric materials are among the nastiest soils in the world, mobilising large quantities of potentially toxic metals (e.g. Al, Cd, Co, Cu, Mn, Ni and Zn) into rivers and estuaries (Dent & Pons, 1995; Johnston, Morgan, & Burton, 2016; Nordmyr, Åström, & Peltola, 2008; Nystrand et al., 2012). Simultaneously they are some of the most economically valued soils due to their high organic content and extraordinary good soil structure, making them invaluable for agricultural use (Österholm et al., 2015). These naturally occurring sediments and acid sulfate soils with sulfidic materials, which are rich in sulfide minerals such as pyrite, cover over 17 million hectares of coastal regions in Asia, Africa, Australia, Europe, North America and Latin America (Andriesse & van Mensvoort, 2006; Fanning, Rabenhorst, & Fitzpatrick, 2017). In Finland these are typically fine-grained sediments deposited in the post-glacial boreal brackish water sedimentary environment of the Baltic Sea since the Littorina Sea stage (7600 BP). Due to post-glacial isostatic uplift extending the Littorina Sea shoreline up to 100 m above sea level (a.s.l.), this area today covers c. 50 100 km^2 of the coast of Finland (Beucher et al., 2015).

The parent material of a coastal ASS is often hypersulfidic (Isbell & National Committee on Soil and Terrain, 2016; Sullivan et al., 2010; IUSS Working Group WRB., 2015), i.e. will become severely acidic (incubation pH < 4) during oxidation, brackish water sediments, containing $\geq$ 100 mg kg^{-1} of sulfidic sulfur mostly as pyrite (FeS$_2$) and in form of highly metastable iron monosulfide (FeS$_{1.1}$) (Boman, Åström, & Fröjdö, 2008). The AS soil profile forms when these sediments are exposed to air due to groundwater table lowering, which begins a rapid oxidation of the sulfides. This produces sulfuric acid (reactions 1 and 2), which enhances the

3

chemical weathering of silicates, leading to the leaching of metals. Snow melts, spring and autumn floods then trigger the mobilisation of the leached metals as well as the produced acidity into surrounding waters (Åström & Björklund, 1997; Boman et al., 2010; Nordmyr et al., 2006).

$$4FeS + 9O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 4SO_4^{2-} + 8H^+ \qquad (1)$$

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8SO_4^{2-} + 16H^+ \qquad (2)$$

There is a growing concern for increased eutrophication and hypoxia in the Baltic Sea due to anthropogenic enrichment of nutrients and increased primary production and thus an increased pressure of legislation to improve the quality of our stream waters (Diaz & Rosenberg, 2008; HELCOM, 2014; Puttonen et al., 2014). The main culprit for coastal rivers not meeting EU standards of good chemical and ecological quality stems, however, not from nutrient loads, but from the enhanced oxidation and weathering of AS soils with sulfuric material that increases the mobilisation of acidity and metals (Åström & Björklund, 1995; Toivonen, Österholm, & Fröjdö, 2013).

Projects focusing on mitigating the problems have been attempted with various results (Åström et al., 2007; Bärlund et al., 2005). By combining controlled drainage and subsurface irrigation, the groundwater table can be kept at a preferred level, low enough for agricultural use, but high enough that the underlying parent sediments with hypersulfidic material are not affected by oxidation. However, it is not certain this has any significant short-term effect (Österholm et al., 2015). The PRECIKEM (Chemical precision treatment of acid sulfate soils to prevent the formation of acid) and PRECIKEM II (Precision chemical treatment of acid sulfate soils for the

4

protection of waters in environmentally sustainable agriculture) projects are unique in treating the exposed oxidation zone directly through subsurface chemical precision treatments to inhibit the microbial population, minimising the oxidation and most importantly, neutralising the acidity (Wu et al., 2015). Whereas from an agricultural point of view the technique of topsoil liming is enough to raise the pH and making the AS topsoil a perfect environment for cultivation (Åström et al., 2007), the method does not hinder the microbial aided oxidation and subsequent acidity production, nor does it neutralise the acidic discharge water or affect the mobilisation of elements.

The goal of this study is to saturate the exposed surfaces of the hydrologically active macropores directly using precision treatments with fine-grained alkaline calcium carbonate and/or hydroxide suspensions through subsurface irrigation, thus enabling an acidity neutralising effect, which would raise the soil pH and hinder the mobilisation of pH sensitive elements. The hypotheses are that: (1) the quality of discharge waters will be significantly improved in chemically treated subfields, (2) the effects of the chemical treatments will be seen instantly and observed for several years, and that (3) the pyrite oxidising acidophilic bacteria will be de-activated, leading to a decrease in sulfate and known ASS leached elements. The impact of this study will be the presentation of viable methods for improving the chemical and ecological status of rivers in a coastal ASS land system.

2. Material and methods

2.1. Study site

The Risöfladan experimental area (63°2.76′N, 21°42.5′E) is located in Vaasa in Ostrobothnia, western Finland (Fig. 1). The area is part of a polder drained for agricultural use by embankment and pumping since the 1950's (Bärlund et al., 2005; Boman, Åström, & Fröjdö, 2008; Joukainen & Yli-Halla, 2003; Wu et al., 2013). As the polder is currently about 0.5 m below current sea level, it is continuously drained by pumping excess water into the nearby Laihianjoki River (506 km^2 catchment area, 30% arable land) which flows into the Södra Stadsfjärden estuary and ultimately into the Gulf of Bothnia (Roos & Åström, 2005). The parent sediment is a hypersulfidic (0.74–1.1% sulfidic S) silty clay loam, which has been deposited in brackish water since the last glaciation (Nordmyr et al., 2006). Due to the oxidation of the iron sulfide bearing sediments with hypersulfidic material and subsequent production of sulfuric acid, the formation of an active coastal AS soil profile with sulfuric material has since been established, its physicochemical characteristics extensively detailed in previous studies (e.g. Bärlund et al., 2005; Boman, Åström, & Fröjdö, 2008; Nordmyr et al., 2006; Wu et al., 2013). Additional field observations are available in Supplementary Material S1. In brief, the profile consists of an organic rich plough layer with pH ranging between 4.1–7.7 (due to surface liming), ASS with sulfuric material (pH c. 4) from a depth of c. 0.4 m to 1.3 m, followed by a transition zone where pH rapidly rises with depth to where the underlying parent ASS with sulfidic material (pH 6.5–7.5) begins (c. 1.7 m).

Figure 1: Study site located on the western coast of Finland with the former Littorina sea extent shaded. Schematic of experimental area consisting of nine subfields located besides the Laihianjoki River.

6

2.1.1. Climate

The area has a cold, temperate climate with a median annual temperature of 3.6 °C, with five months (November to March) of below 0 degrees (Fig. 2). The median annual precipitation is 542 mm with August receiving the highest amount of rainfall, with median precipitation of 60 mm and 50-year maximum of 200 mm. Snow melts and ground thawing coupled with spring rains leads to increased runoff in April–May and heavy rains in August–October leading to autumn peak flows. Regional interpolated (10 x 10 km grid) weather data is available from Vaasa Airport weather station, which is only 3 km from the study area (Finnish Meteorological Institute, 2017).

Figure 2: Interpolated monthly precipitation (as deviation from 50 year median) and monthly median temperature for experimental area (data from nearby Vaasa airport weather monitoring station) during project period 2012–2016. Daily water level for Laihianjoki River (m.a.s.l.) from Karkmo monitoring station (c. 8 km upriver) and groundwater tables for PRECIKEM reference fields (ground surface approximately at -0.5 m.a.s.l.).

2.1.2. Experimental field

The PRECIKEM experimental field at Risöfladan is divided into nine identical 1 ha subfields, each with drainage systems consisting of three subsurface drainage pipes at c. 1.3 m depth, a collector pipe and a control well (Fig. 1). Subfields 1–4 and 9 are located on the northern side of the field, bordering the northern drainage ditch, and subfields 5–8 on the southern side, bordering the southern ditch. The

7

groundwater table can be manually raised by subsurface irrigation through the control well or lowered by lowering the drain level in the well, allowing natural flow into drainage ditches. Groundwater table management is enhanced by prevention of by-pass flow due to the subfields being hydrologically isolated by a plastic film inserted vertically at the edges of the fields from a depth of 0.4 m to 1.9 m, down into the structureless clayey parent material. The film hinders lateral by-pass flow of groundwater between the subfields and drainage ditches and helps to maintain the groundwater table during dry periods in tandem with subsurface irrigation. Subfield 2 (REF 2) is without a plastic film toward the northern end of the field, in order to provide information about the field's natural by-pass flow.

2.1.3. Groundwater monitoring

Each subfield has three groundwater pipes for sampling and monitoring. Simple poles attached to liquid level floaters allows for quick visual inspection of the groundwater table in each field (Österholm et al., 2015). Detailed monitoring is carried out using automatic water level and temperature loggers (Solinist Levelogger Junior Edge 3001) in groundwater pipes on each field and in both the northern and southern drainage ditches. A separate barometric pressure logger (Solinist Barologger Edge 3001) is placed above water level in a groundwater pipe on subfield 3. During chemical treatments and subsurface irrigation, water is pumped from the Laihianjoki River by a network of pipes that reaches all subfields. The flow of water during subsurface irrigation is controlled by a calibrated flow meter (GE Panametrics Model PT878). The hydrology of Laihianjoki River is monitored at an automatic station at Karkmo c. 8 km upriver.

2.2. Chemical treatments of subfields during 2011–2016

The first chemical treatments (Table 1) were carried out in July 2012 when subfields 3 and 5 were treated with a suspension of calcium carbonate ($CaCO_3$, Nordkalk C2, d50 2.5 μm, Nordkalk Corporation) (680/770 kg) and subfields 1 and 8 with suspensions of calcium hydroxide ($Ca(OH)_2$, Nordkalk SL 90T, slaked lime with a $Ca(OH)_2$ content of > 93% and with 96.3% of particle diameters < 90 μm, Nordkalk Corporation) (150/110 kg). In August 2013, the treatments with $Ca(OH)_2$ were repeated, now with a larger dose (380/360 kg), and subfields 6 and 9 were treated with a smaller dose (350/400 kg) of $CaCO_3$. Treatments for subfields 6 and 9 were repeated in August 2014 with similar concentration, but four time larger volume of water and amount of $CaCO_3$ (1640/1590 kg). The last treatments were done in August 2016, with subfields 1 and 8 receiving a large dose (660/820 kg) of $CaCO_3$. The results from this will, however, not be discussed in this paper, as data from only one sampling occasion is available for analysis. The treatment doses were adapted for full-scale field use on the basis of previous laboratory studies (Wu et al., 2015). The doses were varied during the study period in order to achieve a frame of reference on the minimum amounts needed to achieve a suitable long-term neutralisation capacity. With this in mind, enough water was needed in order to reach and saturate the hydrologically active macropores across the 1 ha subfields with the suspensions simultaneously being diluted enough to avoid flocculation and clogging of the subsurface drainage pipes.

Two of the subfields, REF 4 (N side) and REF 7 (S side), were used as reference fields during the course of the experiments. REF 2 was likewise a reference field, in the sense that it was left untreated and a plastic film did not hinder the by-pass flow of water. During the chemical treatments, equal amounts of river water were pumped

into the reference fields as the treatment fields, with volumes between 100–450 m^3 per field. The chemical treatments were carried out in the late summer (August) when the groundwater table was at its lowest, making the fields receivable to large amounts of water and suspension. Certain fields were manually drained by pumping down to a predetermined level in case the groundwater table was deemed too high.

Table 1: Summary of subsurface chemical precision treatments of PRECIKEM subfields during 2012–2016. Chemically treated subfields (1, 3, 5, 6, 8 & 9) have been treated with a suspension of river water (as volume of water in m^3) mixed with either $CaCO_3$ or $Ca(OH)_2$ (as mass of chemicals in kg), whilst reference fields (2, 4 & 7) have only been treated with river water.

2.3. Sampling and analyses

During the project period of 2012–2016 routine sampling procedures were carried out during the spring and autumn months. Summer and winter months were excluded from the sampling due to the extreme changes in hydrology during the dry summer periods and frozen winter periods. In order to obtain samples during representative flow conditions every season the sampling dates could sometimes vary with several weeks. A total of 288 water samples were taken from the control wells of all subfields and periodically from Laihianjoki River, with 225 samples used for analysis after exclusion of unrepresentative sampling conditions, such as extreme variations in temperature or hydrology.

2.3.1. pH, EC, ORP, acidity

The discharge water from each subfield was sampled by the following procedure: first, any stagnant water in the well was removed by pumping into the nearby ditch using a petrol pump (Honda WX 15), next, a battery-powered peristaltic pump (Eijkelkamp) was employed to pump fresh discharge water as it emerged into the control well directly through a YSI flow-through cell (Quatro Cable FlowCell, YSI Incorporated). During sampling the pH, electrical conductivity (EC), temperature and oxidation-reduction potential (ORP) were measured with a YSI Professional Plus multiparameter instrument (YSI Incorporated) connected to the associated flow-through cell. Unfiltered discharge water for acidity titrations and ion chromatography were pumped into 250 ml polyethylene bottles. These were stored at +4 °C until acidity measurements were conducted at room temperature in accordance with the Finnish standard method (SFS 3005) the same day or day after sampling.

2.3.2. Sulfur and metals

Subsamples were filtered (0.45 μm Membrane Filters, SARSTEDT AG & Co. KG) in the field into 50 ml polypropylene falcon tubes (SARSTEDT) and acidified (< 2 pH) with ultra-pure HNO_3 (Merck Suprapur) and stored at +4 ºC up to 3 months until multi-element analysis with ICP-OES and ICP-MS (Activation Laboratories Ltd., Canada). Sulfate (SO_4^{2-}) was analysed from filtered (0.45 μm) samples using ion chromatography (Dionex ICS-1100) and the results were used to verify $S:SO_4^{2-}$ ratio. Statistical analysis was done with nonparametric Spearman's rank correlation (r_s) with a significance level of 95% ($\alpha = 0.05$).

2.3.3. Fe(II)

Samples for Fe(II) were initially unfiltered but later during the project filtered (0.45 μm) directly into 50 ml bottles that had been prepared beforehand by the addition of a reagent mixture. In short, a reagent mixture containing 1,10-phenanthroline for colour reaction with Fe(II), glycine buffer for maintaining a pH of 2.5, and nitrilotriacetic acid (NTA) for the masking of Fe(III), was freshly prepared before each sampling trip. Fe(II) concentrations were measured according to Fadrus & Malý (1975). As sample was added in the field, Fe(II) formed a coloured complex with the 1,10-phenantroline while Fe(III) was complexed by the NTA. Thus, the balance between the species of the redox couple was stabilized. The absorbances at 510 nm of the samples plus reagent mixture were measured in the laboratory using a double beam Shimadzu UV-VIS 1601 spectrophotometer. In the reference position was a sample plus a reference reagent mixture containing only buffer and NTA (no colour reagent).

2.3.4. Eh-pH diagrams

Eh-pH predominance diagrams for Fe species were drawn using PhreePlot (http://www.phreeplot.org/). This software contains an embedded version 3 of the PHREEQC software (Parkhurst & Appelo, 2013). Equilibrium constants used were those provided in the wateq4f database, dated 2016-04-21, and supplied with the PhreePlot software. For schwertmannite the log K value of 18 was used for the solubility of the mean composition $Fe_8O_8(OH)_{4.8}(SO4)_{1.6} + 20.8H^+ \rightarrow 8Fe^{3+} + 1.6SO_4^{2-} + 12.84H_2O$ (Bigham et al., 1996). The temperature of the discharge waters (range of 2–9 °C during measurements) had to be considered when calculating the Eh values: Eh = E (measured ORP) + E (reference electrode vs SHE). The reference

12

electrode in the YSI probe is a Ag/AgCl (3.5 M KCl) electrode. Bates (1973) lists standard potentials for the Ag/AgCl (3.5 M KCl) electrode at different temperatures, and a linear fit to these values was used to calculate Eh values at the sample temperatures. As noted by Langmuir (1971), the 3.5 M KCl solution becomes saturated at temperatures below 7 °C. However, a similar calculation using values for the Ag/AgCl (saturated KCl) electrode yielded Eh values that differed by less than one millivolt from the ones used here for sample temperatures of less than 7 °C. The measured Eh-pH values for the different subfields are shown against a background of the predominance diagram calculated using median concentrations and temperatures for the reference fields. The partial pressure of CO_2 in the gas phase was not measured, but it has been shown to be very high in drained coastal acid sulfate soils with sulfuric materials (Jeffrey et al, 2015). For the purpose of constructing the diagram, it was estimated at 0.03 atm. The diagram is intended as a qualitative guidance only because of the estimates involved, as well as the uncertainties in and lack of thermodynamic information. The diagram is calculated for 4.3 °C, the median temperature of the groundwater from the reference fields. For an exothermic dissolution reaction the solubility will increase with decreasing temperature (Appelo & Postma, 2005), i.e. the predominance field will become narrower with decreasing temperatures. Therefore, e.g. jarosite will be stable only under very limited Eh-pH conditions in a Boreal climate.

2.3.5. Excavation and visual inspection of subfields

In August 2013 the insides of the drainage pipes were investigated with a fiberscopic camera (unpublished results), and in September 2014 the subfields were excavated near the subsurface drainage pipes for a visual inspection of the

hydrologically active macropores. The purpose of the investigations was to study if suspension residue remained in the subsurface drainage system and how far the suspension had spread into the fields. Images from the excavations are provided in the Supplementary Material S2.

3. Results

3.1. General hydrology

The groundwater table in the experimental area follows the same general trend as the water level in Laihianjoki River (Fig. 2), measured at Karkmo monitoring station. The mean water level at the monitoring station was 3.34 m a.s.l. (N60), with annual mean low (2.86 m) and annual mean high (4.80 m). The mean volumetric flow rate in the river is 3.3 m^3 s^{-1} with highest mean flows (up to 31.0 m^3 s^{-1}) during spring and autumn melt/rain seasons (Raitalampi et al., 2016). Due to different weather conditions, the groundwater fluctuated between 1 m and 1.5 m below soil surface, occasionally down to the un-oxidised parent sediment. The groundwater table was also lowered due to manual drainage of fields before subsurface irrigation and associated chemical treatments and was constantly 10–20 cm lower on the northern side (REF 4) of the field. In REF 2, the only field with no plastic film installed to prevent by-pass flow, the groundwater table was slightly higher than REF 4.

3.1.1. Water quality in reference fields

The quality of the discharge water from the reference fields is extreme and representative for coastal farmland ASS (Fig. 3), with acidity and element concentrations in the order of one magnitude higher than Laihianjoki River and up to

14

two magnitudes higher than the median of Finnish stream waters (Lahermo et al., 1996). Differences between reference fields were relatively small and smaller than seasonal variations (Table 2). EC as well as total concentrations of S and Al were slightly higher during spring whilst Cu, Ni, Zn, Pb and U concentrations were higher during autumn. Subfield differences are most likely due to the heterogeneity of the hydrologically active sulfuric material, however, the median concentrations tended to be somewhat higher in the northern subfield. This may be related to the somewhat lower groundwater table on the northern side, causing more oxidising conditions. pH was stable at c. 3.9, seldom rising above 4, whilst the pH in Laihianjoki River fluctuated between 4.5–6.5. EC varied between 1300–2100 μS cm^{-1}, nearly six times higher than Laihianjoki River and two magnitudes higher than the median for stream waters in Finland.

Figure 3: Quality of discharge waters from PRECIKEM reference fields in comparison with nearby Laihianjoki River and the average Finnish stream waters (Lahermo et al., 1996). Bars indicating min–max range for reference fields and Laihianjoki River.

Table 2: Median of the median and median range (min and max) values for spring and autumn for discharge waters from PRECIKEM reference fields compared with median values for Laihianjoki River and the average Finnish stream waters (Lahermo et al., 1996).

Ion chromatography verifies that the majority of S is derived from SO_4^{2-} (Spearman correlation, r_s: 0.94), and there is a marked rise of EC with increasing S

15

concentration (r_s: 0.93). Acidity is high (> 4 mmol L^{-1}) as well as S concentrations (> 200 mg L^{-1}). The subsequent leaching and mobilisation of metals from the sulfuric material is also apparent as Al (> 20 mg L^{-1}), Mn (> 3.9 mg L^{-1}), Zn (> 620 μg L^{-1}), Li (> 200 μg L^{-1}), Ni (> 250 μg L^{-1}), Co (> 140 μg L^{-1}), Cu (> 13.9 μg L^{-1}) and Cd (> 2.2 μg L^{-1}) are up to one and two magnitudes higher than in Laihianjoki River and the average national stream waters, and correlate well with increasing S concentration (r_s: 0.92–0.43). ORP fluctuates between 250–450 mV but does not indicate seasonal variety or subfield dependent variations.

By comparison with national stream waters, Fe concentration is only slightly higher (+0.5 mg L^{-1}) with a larger median variation in concentration during spring than autumn. Fe occurs mainly as ferrous iron (Fe(II)). The Fe(II) determinations correlate (r_s: 0.99 (filtered) – 0.93 (unfiltered)) with the total Fe concentrations measured by ICP-OES. This is consistent with the PHREEQC model that forms the basis for the predominance diagrams in Fig. 4. A prediction using the model and recorded ORP and pH values indicates that the iron species in solution would be predominantly Fe(II), and that available Fe(III) occurs mainly in the form of jarosite and schwertmannite. Jarosite has been visually confirmed at the Risöfladan experimental area (Joukainen & Yli-Halla, 2003), and experimentally in an XRD analysis (Wu et al., 2015).

Figure 4: Measured Eh-pH values for the discharge waters from the reference fields and subfields treated with $CaCO_3$ and $Ca(OH)_2$ are shown in an experimental Eh-pH predominance diagram for Fe species calculated with untreated reference field values.

3.2. Treatments with CaCO₃

The effects of $CaCO_3$ could for all treatments immediately be observed as a marked increase in pH in the discharge water (Fig. 5 & 6), however, only the large dose in fields 3 and 5 had a long-term effect, with pH still well above the reference (+0.4 pH units) four years after application. In fields 6 and 9 treated with the smaller dose and later replenished, the pH dropped faster, though remaining well above the reference (+0.6 pH units) two years after. Similar trends are observed for acidity and concentrations of pH sensitive elements. Acidity is nearly halved compared to the reference fields and stayed under 2.5 mmol L^{-1} until the following autumn when it started to approach near reference values (4.0 mmol L^{-1}). With the smaller dose and replenishment, the acidity drops about one third and continues to be c. 0.5 mmol L^{-1} lower than the reference. As pH rises and ORP decreases due to the treatments, the Eh-pH diagram indicates that the predominance of Fe species is shifted toward the phases dominated by schwertmannite and amorphous iron oxides (Fig. 4). This is consistent with the fact that Fe concentrations are lowered, while Fe(II) still remaining the main species in solution.

Figure 5: 2012–2016 overview of discharge water quality in subfields 3 and 5 treated with $CaCO_3$ with comparison to untreated reference fields (subfields 4 and 7). Cd is shown as an example of chalcophilic elements.

Figure 6: 2012–2016 overview of discharge water quality in subfields 6 and 9 treated with $CaCO_3$ with comparison to untreated reference fields (subfields 7 and 4). Cd is shown as an example of chalcophilic elements.

The effects of the pH rise can most clearly be observed in the marked drop of aluminium concentrations in all the treated subfields. With the large treatment dose aluminium concentrations dropped with c. 95% to c. 1 mg L^{-1} and increased to reference values two and a half years later. The smaller dose with replenishment resulted in a c. 90% decrease to c. 3 mg L^{-1} and concentrations were still slightly lower in the end of the study period two years after treatment. Cu follows the same general trend as Al, though, with far smaller changes in concentration.

Only a minor decrease in concentration if any was detected for chalcophile elements (Cd, Co, Mn, Ni, Pb and Zn) immediately after treatment. Of these elements, Cd concentrations decreased most noticeably in subfields 6 and 9 following the replenishment dose (Fig. 5 & 6), but the effect lasted only during the autumn. Sulfur concentrations remained unaffected by the CaCO$_3$ treatments. Seasonal highs and lows are most likely explained by hydrology and the field heterogeneity. Ca concentrations are highly elevated (+100%) directly after the treatments and in the case of the large dose treatments on subfields 3 and 5, respectively, Ca is still c. 20% elevated two years later, while Ca was only slightly elevated in the following spring after the low dose treatment. This was also the case after the replenishment in fields 6 and 9. The Ca fluxes were, however, minor as compared to the amounts injected into the field during treatment.

3.3. Treatments with Ca(OH)$_2$

The first treatments of 110 and 150 kg Ca(OH)$_2$ only raised the pH to 4.5 which started to drop already during the following autumn (Fig. 7). The larger dose raised the pH to c. 6 (occasional peak values up to 11) but dropped down to approximately pH 4.5 one year later. The treatments had corresponding effects on acidity, lowering

it only slightly with the small dose and significantly (< 1 mmol L^{-1}) with the large dose, with values returning to normal the following year. The concentration of Fe decreased after both treatments, and similar to the fields treated with $CaCO_3$, the predominance of Fe species shifted toward the phase dominated by schwertmannite and amorphous iron oxides with Fe(II) being the only species in solution (Fig. 4). This was clearer with the larger dose treatment, as the smaller dose only shifted the predominance field slightly.

Figure 7: 2012–2016 overview of discharge water quality in subfields 1 and 8 treated with $Ca(OH)_2$ with comparison to untreated reference fields (subfields 4 and 7). Cd is shown as an example of chalcophilic elements.

Aluminium behaviour was similar to that after the $CaCO_3$ treatment. There was a remarkable decrease (99%) in concentration immediately after the large dose treatment and a slight decrease after the smaller dose. The effects, however, were not long lasting, with concentrations back to normal values already one year later. Cu, Zn, Cd, Pb, Co, Mn and Ni follow the same trend corresponding to the large pH raise (represented by Cd in Fig. 7), with a noticeable drop in concentration immediately after the treatment. Ca concentrations were clearly elevated after the low/large dose treatments (20/120%) but were only c. 15% higher than those in the reference fields one and a half years later. Again, the fluxes of Ca were minor as compared to the amount of Ca injected as $Ca(OH)_2$ into the field.

19

4. Discussion

Before and during the project period pH values remained below 4 in the reference fields and concentrations of potentially toxic metals were 3–50 times higher than in nearby Laihianjoki River. Consequently, the subsurface irrigation with water from river Laihianjoki did not raise element concentrations in the discharge from the fields, and since the amount is insignificant compared to the annual discharge potential dilution effects were minor. Moreover, since subsurface irrigation was conducted on all fields, potential effects would also have been similar for all fields. Groundwater tables in the fields imitate the flow conditions of river Laihianjoki and are climate driven, as heavy precipitation raises the water level and warm sunny days increase evapotranspiration, which efficiently lowers the groundwater table. Seasonal in-field variations indicate that there are some minor inherited hydrological soil heterogeneities, which also may cause some differences in the oxidation depth and element mobilisation.

The groundwater table was marginally lower on the northern side of the study area during summertime since the ground is slightly slanted towards SW. This may also cause an increased oxidation depth. The oxidation and subsequent production of acidity and leaching of elements would also explain the slightly higher concentrations in the northern reference field. There was noticeably lower element concentrations and conductivity in REF 2 than REF 4 indicating that there is free flow of water between the field and the northern ditch and vice-versa, which would decrease the oxidation depth during high water levels in the ditch. Drainage during discharge events would be restricted to the subsurface drainage pipes and control wells in REF 4 and the plastic film would prohibit by-pass flow between the field and the northern ditch during high water events. The lack of a hydrologically

isolating film would typically allow free drainage of groundwater to a nearby ditch, but as the research area is situated beneath the average sea level, the water table in the nearby ditches can be higher than that in the field allowing instead infill of water from the ditch into the field.

All treatments had a neutralising effect on the discharge water from the fields, as was observed by a significant increase in pH and decrease in acidity in the autumns following the treatments. The large dose of $CaCO_3$ had the most promising long-term effect, followed by the small dose and refill and lastly the large dose of $Ca(OH)_2$. Though the refill with $CaCO_3$ in subfields 6 and 9 was over twice the amount as the large dose in fields 3 and 5, the larger amount of water possibly distributed the $CaCO_3$ over a larger area from the drainage pipes, thus diluting its effects. On the other hand, the small dose of $Ca(OH)_2$ was not enough to neutralise the acidic discharge to any considerable degree.

Due to the strong pH and redox driven solubility of Fe (Virtanen, Simojoki, & Yli-Halla, 2010), and the heterogeneity of the hydrologically active soil layer and groundwater table fluctuations, all subfields have somewhat large differences in Fe concentration, as well as higher and more variable concentrations during spring than autumn months. There is a clear seasonal trend with high concentrations of Fe(II) in spring. Prolonged reducing conditions are created in the autumn as the soil becomes wet because soil ventilation is limited in the winter due to ground frost and snow cover. Such conditions are expected to mobilise iron as Fe(II) and would be the most likely explanation for the larger fluxes of Fe(II) in the spring after the thaw. On the contrary, oxidising conditions are created during the dry summer seasons leading to precipitation of Fe(III) in the soil. According to Wu et al. (2013) summer seasons allow microbial activity as soil temperatures reach 14 °C but biotic oxidation is

21

likely inhibited in winter seasons due to ground frost. Iron species in the discharge waters were dominated by Fe(II) as indicated by both the Eh-pH predominance calculations as well as the Fe_{tot}/Fe(II) correlations. Mosley et al. (2014) describes a similar predominance of Fe(II) in solution for acidic groundwater in acid sulfate soils with sulfuric material. As pH is raised after the chemical treatments, the stability of Fe is shifted towards the schwertmannite and amorphous iron oxide phases and consequently the total concentration of Fe is lowered, as Fe(III) is precipitated on soil surfaces. As the environmental effect of the chemical treatments are declining the pH drops, which leads to schwertmannite dissolving, leading to more Fe(II) in solution with the predominance of Fe shifting back towards the more stable jarosite/Fe(II) field. This is also in agreement with previously conducted laboratory scale column leaching experiments where the jarosite/schwertmannite dissolution/precipitation equilibrium was observed under similar chemical treatment conditions (Wu et al., 2015).

The most prominent effect of the subsurface chemical treatment is the marked decrease in aluminium concentration in the discharge water. This was expected because the solubility of Al is strongly pH dependent and raising the soil pH leads to the hydrolysis and precipitation of Al hydroxides. This result is important because soluble Al in acid water is most likely the biggest short-term threat for aquatic life affected by ASS, leading to reoccurring events of fish mortality (Hudd, 2000). As the pH in stream waters drops below 5, soluble Al^{3+} is mobilised and can precipitate on the gills of fish, ultimately suffocating them. Although aluminium hydrolysis produces H^+, the net effect is negligible as witnessed by the raise in pH after the treatments. After the initial $CaCO_3$ treatments in 2012 of subfields 3 and 5 the pH was raised to 6 and is still well above 4 in 2017, five years later. The drop in Al

levels was, however, not as long-lived. The larger dose showed positive results with nearly 50% less aluminium one year later, but the smaller dosage of $CaCO_3$ was only effective until the first spring floods the following year. pH also dropped considerably faster in fields 6 and 9, though still remaining well above the reference (+0.6 pH-units) two years later. Assuming that all aluminium, in the order of 20 mg L^{-1} occurs as free Al^{3+} and hydrolyses completely, c. 2 mmol L^{-1} H^+ would be produced in the complete hydrolysis of aluminium. In theory, two moles of H^+ are neutralised per one mole of $CaCO_3$, i.e. 1 mmol L^{-1} $CaCO_3$ would be required to neutralise the aluminium acidity (immobilising Al), releasing c. 40 mg L^{-1} Ca. There was a significant increase in Ca concentrations after the treatments corresponding with a decrease in acidity in the same order of magnitude.

Fiberscope investigations of the drainage pipes revealed only a thin layer of $CaCO_3$ in the bottom of the pipes, indicating that nearly all suspension had spread into the soil. This was also evident when comparing the amounts injected into the fields and the Ca concentrations in the discharge water after the treatments (Österholm et al., 2014). Several fields were excavated two years after the initial treatments to confirm that the $CaCO_3$ suspension had adhered to the surfaces of macropores in the hydrologically active soil layer thus affecting the pH of the discharge water for a long period after the treatments. The suspension had, however, not reached far into the field, only a few meters from the subsurface drainage pipes. As evident for the decrease in pH dependent elements, this is sufficient to improve the quality of the discharge water from the treated subfields. Continued sampling and measurements will reveal how long the positive effects of the treatments will persist.

After excavation of the fields treated with calcium hydroxide it was evident that it did not have the same desired properties as the calcium carbonate suspension, as it

did not adequately flow through and saturate the hydrologically active macropores in the sulfuric material. Already during pumping of the suspension there were difficulties caused by clogging of the drainage system, and the fiberscope investigations revealed the bottom of the subsurface drainage pipes were covered in a white slurry. Since calcium hydroxide is a very strong base, a rapid rise in pH was expected, and the extreme pH values after the treatments were likely caused by much of the $Ca(OH)_2$ slurry returning to the control well during discharge events. Although similar physicochemical properties (e.g. high pH, low Al, acidity, ORP, Fe) were observed for the $Ca(OH)_2$ as the $CaCO_3$ treatments, it is likely that the effects were a direct result from the extreme neutralisation capacity of the retained $Ca(OH)_2$ slurry in the drainage pipes. Once the slurry was flushed out after the autumn and spring discharge events, values returned to normal. $Ca(OH)_2$ is also more soluble and will likely be consumed at a faster rate than $CaCO_3$, thus minimising any long-term effects.

Some pH dependent elements, such as Cu, behave similarly to Al and decrease in concentration for a certain time after the chemical treatments. Other elements typically associated with ASS leaching (Cd, Ni, Co, Zn, Mn) did not exhibit similar behaviour and were only moderately or not at all affected by the rise in pH, as they are not as strongly pH dependent as Al. As there is an enormous reserve of leached elements in the soil pore-water, the short-term treatments are not enough to diminish the concentrations, although a portion may be coprecipitated with aluminium and iron hydroxides as they are precipitated due to solubility changes at a higher pH (Burton et al., 2008). There were no signs of a decreased sulfide oxidation as S values were similar to that of the reference fields during the course of the experiments. Although, as most of the field remained unaffected by the chemical

24

treatments because the suspensions only reached a few meters from the subsurface drainage pipes, a decrease in sulfate concentration in the treated area would be masked by the pore-water concentration from the untreated portion of the field. It is therefore possible that treatments have chemically de-activated the acidophilic bacteria that mediate pyrite oxidation in the area closest to the subsurface drainage pipes.

The mitigation method presented here requires a nearby source of water for the subsurface irrigation and a previously installed controlled drainage system. If this infrastructure already exists, all that is needed is the addition of fine-grained $CaCO_3$ to the subsurface irrigation water. Based on the results from this study, a c. 8 g L^{-1}, < 1 ton ha^{-1}, suspension applied every couple of years could maintain a neutralisation effect and minimise metal discharges from agricultural AS-soils as the treatment affects in a positive way the acid-producing soil horizon at drainage depth. The neutralisation agents used in this study are several times more expensive than conventional agricultural lime but on the other hand expected to be much more effective due to their fine grain size and solubility. Moreover, the doses applied are in the order of one magnitude smaller than that of conventional surface liming and in the order of two magnitudes smaller than the theoretical neutralisation demand for the bulk soil. Nevertheless, unlike with conventional surface liming, positive effects on crop growth are expected to be smaller or non-existent (still requiring surface liming) and the treatment is more laborious. Consequently, to be adopted by the farming community as a whole, subsidies are required. Considering the lack of effective treatment methods for reducing acidic discharges from agricultural AS-soils this should be considered in agri-environment measures.

5. Conclusions

As evident of previous studies, mitigating acid sulfate soils with sulfuric material (pH < 4) by controlled drainage and surface liming is not enough to reduce the mobilisation of acid and metal rich discharge water (Åström et al., 2007). It was shown in this study that subsurface chemical treatments (injection of chemicals through subsurface irrigation) increased pH and decreased acidity and concentrations of several acid sensitive metals, particularly aluminium, soon after treatment. It is challenging to find treatment substances that are mobile and/or have a particle size small enough to be widely spread into the subsoil pore system. Fine-grained $CaCO_3$ (median grain size 2.5 µm) used in this study was successful in targeting the hydrologically active macropores and forming a buffering coating for the acidic groundwater a few meters from the subsurface drainage pipes. Effects of these treatments were seen up to four years after treatment, with the immediate effects being a neutralisation of the acidic discharge waters and > 90% decrease in Al concentrations. The pH and redox conditions in the treated subfields were positively effected as indicated by the Eh-pH predominance of Fe shifting from jarosite toward the schwertmannite and iron oxides stability phases and the overall decrease of total Fe concentrations. Suspensions of $Ca(OH)_2$ were, on the contrary, poorly spread in the subsoil but, during a short-term, still effective in neutralising the acidic discharge water.

Although a large area of the fields remained seemingly unaffected by the chemical treatments and it wasn't possible to judge if the microbial aided oxidation had been impeded by the chemical treatments, the methods and results presented in this study are an important step towards mitigation practices that can lead to improving the chemical and ecological status of stream waters affected by discharge from coastal

acid sulfate soils with sulfuric materials. With the aid of agri-environmental subsidies the method of precision chemical treatment using subsurface irrigation could be combined with conventional surface liming for more environmentally sound farming practices.

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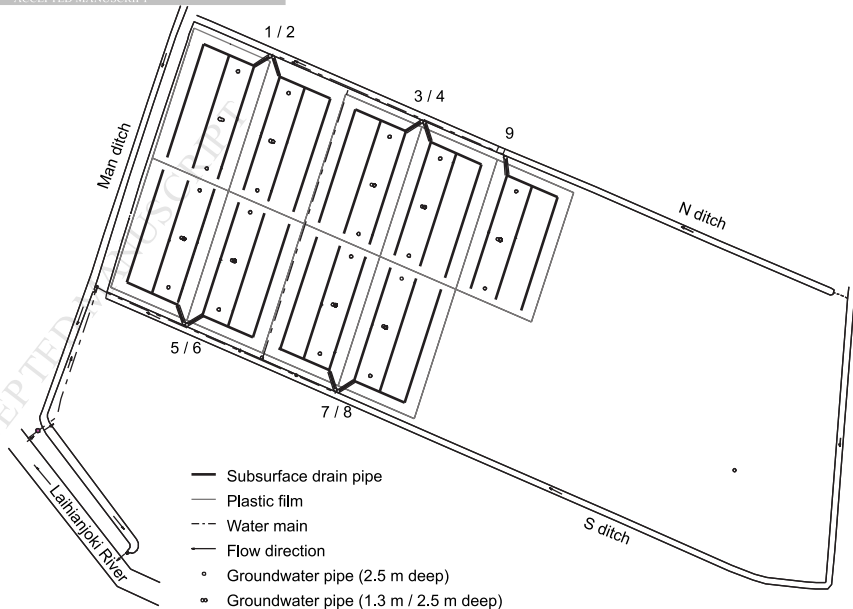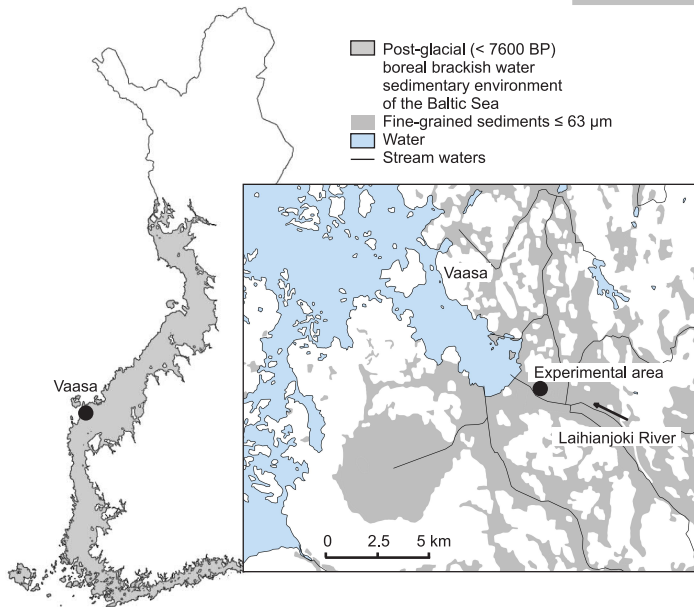
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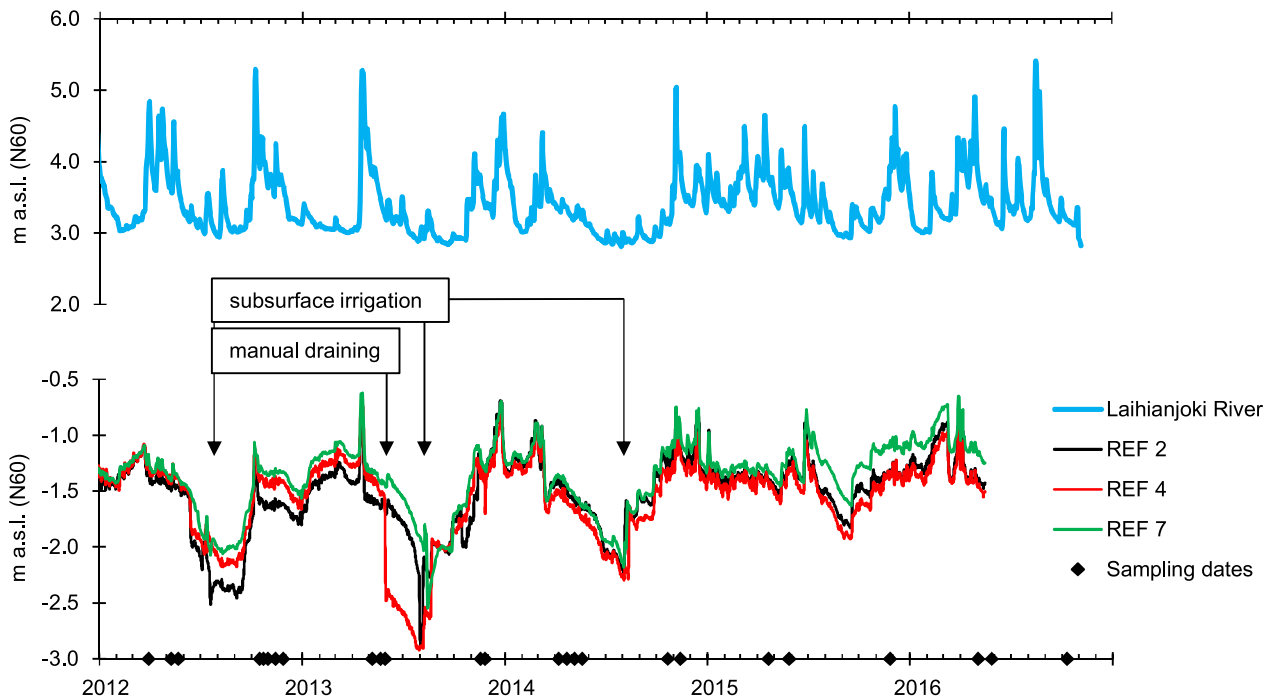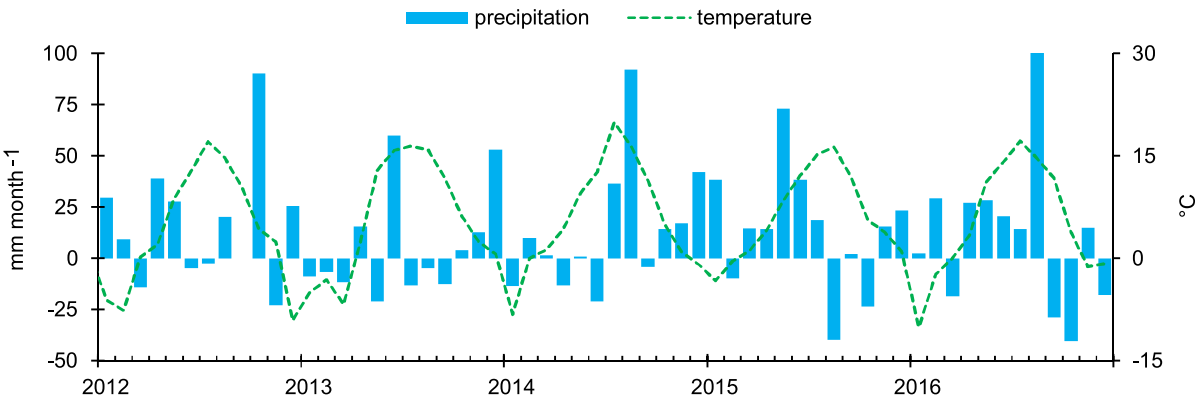
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Field	kg *	2012 treatment	m³ **	kg *	2013 treatment	m³ **	kg *	2014 treatment	m³ **	2015 untreated	kg *	2016 treatment	m³ **
1	150	Ca(OH)$_2$	99	380	Ca(OH)$_2$	129					660	CaCO$_3$	130
2		H$_2$O	92		H$_2$O	137		H$_2$O	459			H$_2$O	130
3	680	CaCO$_3$	109										
4		H$_2$O	122		H$_2$O	174		H$_2$O	476			H$_2$O	131
5	770	CaCO$_3$	107										
6				350	CaCO$_3$	126	1640	CaCO$_3$	461				
7		H$_2$O	108		H$_2$O	140		H$_2$O	434			H$_2$O	134
8	110	Ca(OH)$_2$	100	360	Ca(OH)$_2$	116					820	CaCO$_3$	134
9				400	CaCO$_3$	127	1590	CaCO$_3$	427				

* mass of chemicals, ** volume of river water

		REF 2			REF 4			REF 7			Laihianjoki River	Stream waters
		median	min	max	median	min	max	median	min	max	median	median
N60	spring	-1.5	-1.7	-1.3	-1.5	-1.6	-1.4	-1.4	-1.5	-1.2	-	-
m	autumn	-1.4	-1.6	-1.1	-1.4	-1.5	-1.2	-1.2	-1.3	-1.0		
temp	spring	4.1	3.4	4.3	3.8	3.3	4.1	3.8	3.4	4.1	11.8	-
°C	autumn	7.9	7.5	8.3	7.6	7.2	8.2	7.7	7.2	8.2		
pH	spring	3.9	3.8	4.0	3.9	3.8	4.1	3.9	3.8	4.0	5.0	5.9
	autumn	3.8	3.7	3.9	3.9	3.8	4.0	3.9	3.8	4.4		
ORP	spring	389	304	433	382	367	425	382	368	426	297	-
mV	autumn	387	315	413	383	286	412	381	311	412		
EC	spring	1665	1442	1849	1739	1570	2074	1806	1411	1946	200	44
μS cm^{-1}	autumn	1687	1325	1943	1702	1454	1924	1706	1314	1853		
acidity	spring	4.04	3.93	4.72	4.59	3.89	4.94	4.46	3.92	4.86	0.51	-
mmol L^{-1}	autumn	5.04	4.37	5.34	4.57	4.32	5.13	4.21	3.68	5.61		
S	spring	207	167	229	217	180	264	217	161	235	29.0	2.4
mg L^{-1}	autumn	204	151	262	197	166	241	210	140	225		
Fe	spring	0.96	0.57	1.61	1.46	0.79	2.40	2.08	1.01	2.49	0.65	0.68
mg L^{-1}	autumn	1.05	0.83	1.33	1.15	0.74	1.66	1.11	0.86	1.70		
Al	spring	21.2	18.4	27.9	23.7	20.8	27.7	22.7	20.4	29.0	1.85	0.095
mg L^{-1}	autumn	23.4	16.6	30.3	22.2	19.1	24.3	21.4	16.4	29.5		
Ca	spring	83.5	70.3	89.4	81.8	74.2	101.0	75.0	59.5	83.1	17.1	4.06
mg L^{-1}	autumn	91.5	68.4	98.9	85.6	72.4	97.7	83.6	59.5	89.8		
Mn	spring	3.95	2.90	4.10	4.64	3.35	6.10	4.43	3.08	4.54	0.62	0.029
mg L^{-1}	autumn	3.43	2.52	4.85	3.90	3.06	4.87	3.99	2.63	4.18		
Co	spring	131	109	164	155	131	189	137	118	158	18	0.17
μg L^{-1}	autumn	143	104	165	153	131	164	144	110	186		
Cu	spring	12.5	11.0	13.5	13.5	12.0	15.5	13.0	13.0	16.0	7.2	0.64
μg L^{-1}	autumn	15.0	12.0	18.0	16.0	13.0	17.0	16.5	13.0	19.5		
Ni	spring	224	199	253	251	229	291	226	213	267	45	0.52
μg L^{-1}	autumn	251	198	291	258	233	284	251	203	295		
Zn	spring	583	527	646	684	646	847	605	553	655	75	3.6
μg L^{-1}	autumn	626	517	699	720	656	759	620	533	715		
Li	spring	179	149	216	225	176	245	228	165	236	32	1.02
μg L^{-1}	autumn	207	150	275	195	172	273	213	165	239		
Cd	spring	1.80	1.39	2.13	2.32	2.17	2.85	2.06	1.75	2.22	0.25	< 0.02
μg L^{-1}	autumn	2.21	1.81	2.60	2.74	2.21	2.85	2.28	2.05	2.47		
Pb	spring	0.88	0.17	1.13	0.77	0.58	0.83	0.53	0.41	0.87	0.10	0.23
μg L^{-1}	autumn	0.88	0.01	1.49	0.94	0.01	1.14	0.64	0.01	1.14		
U	spring	1.00	0.81	1.34	1.09	0.96	1.47	1.36	0.98	1.76	0.23	0.073
μg L^{-1}	autumn	1.55	1.02	1.88	1.47	1.10	1.88	1.69	1.02	2.17		

Post-glacial (< 7600 BP) boreal brackish water sedimentary environment of the Baltic Sea
Fine-grained sediments ≤ 63 µm
Water
Stream waters

Vaasa

Vaasa

Experimental area

Laihianjoki River

0   2.5   5 km

Man ditch

1 / 2

3 / 4

9

N ditch

5 / 6

7 / 8

S ditch

Laihianjoki River

Subsurface drain pipe
Plastic film
Water main
Flow direction
Groundwater pipe (2.5 m deep)
Groundwater pipe (1.3 m / 2.5 m deep)

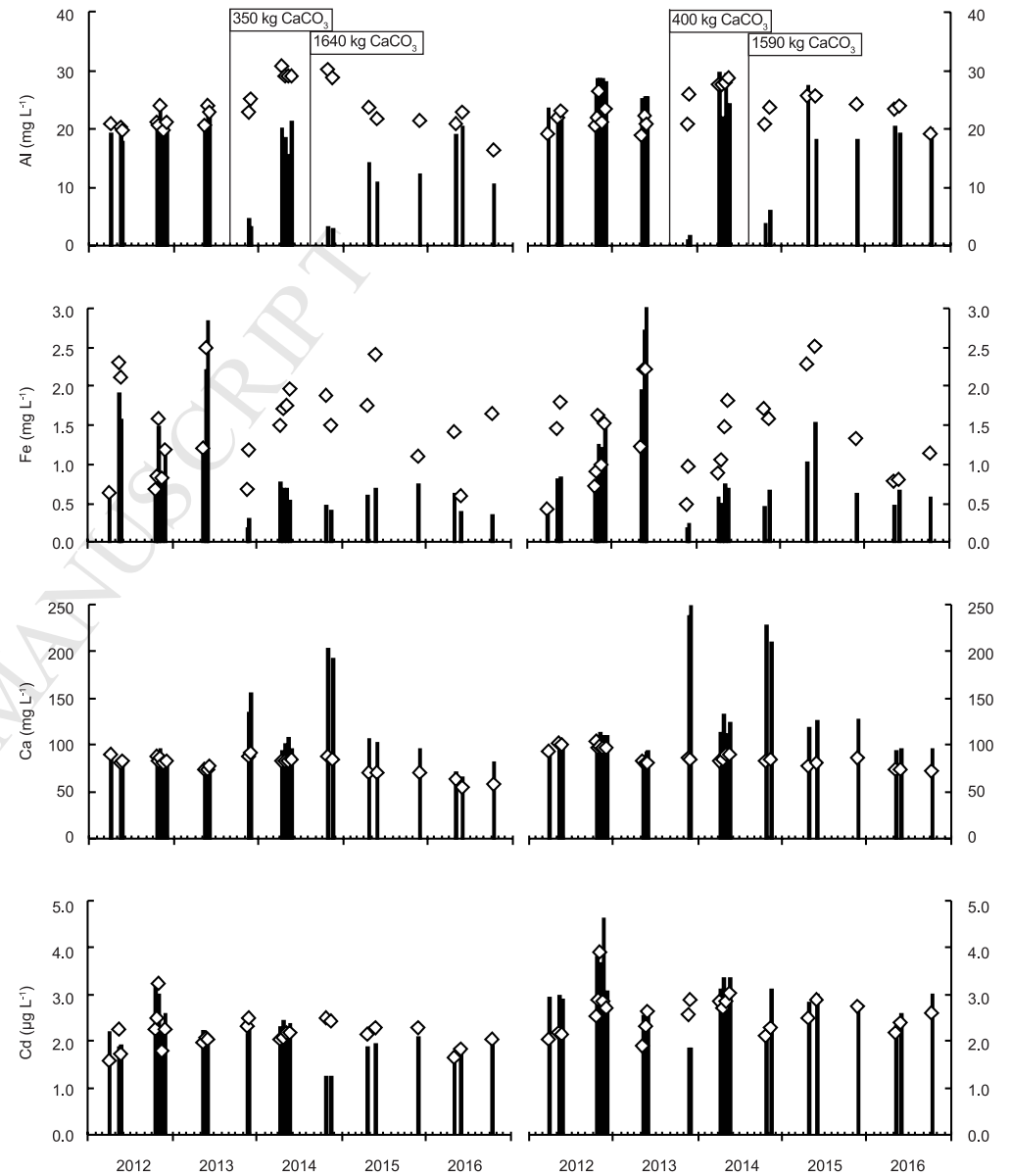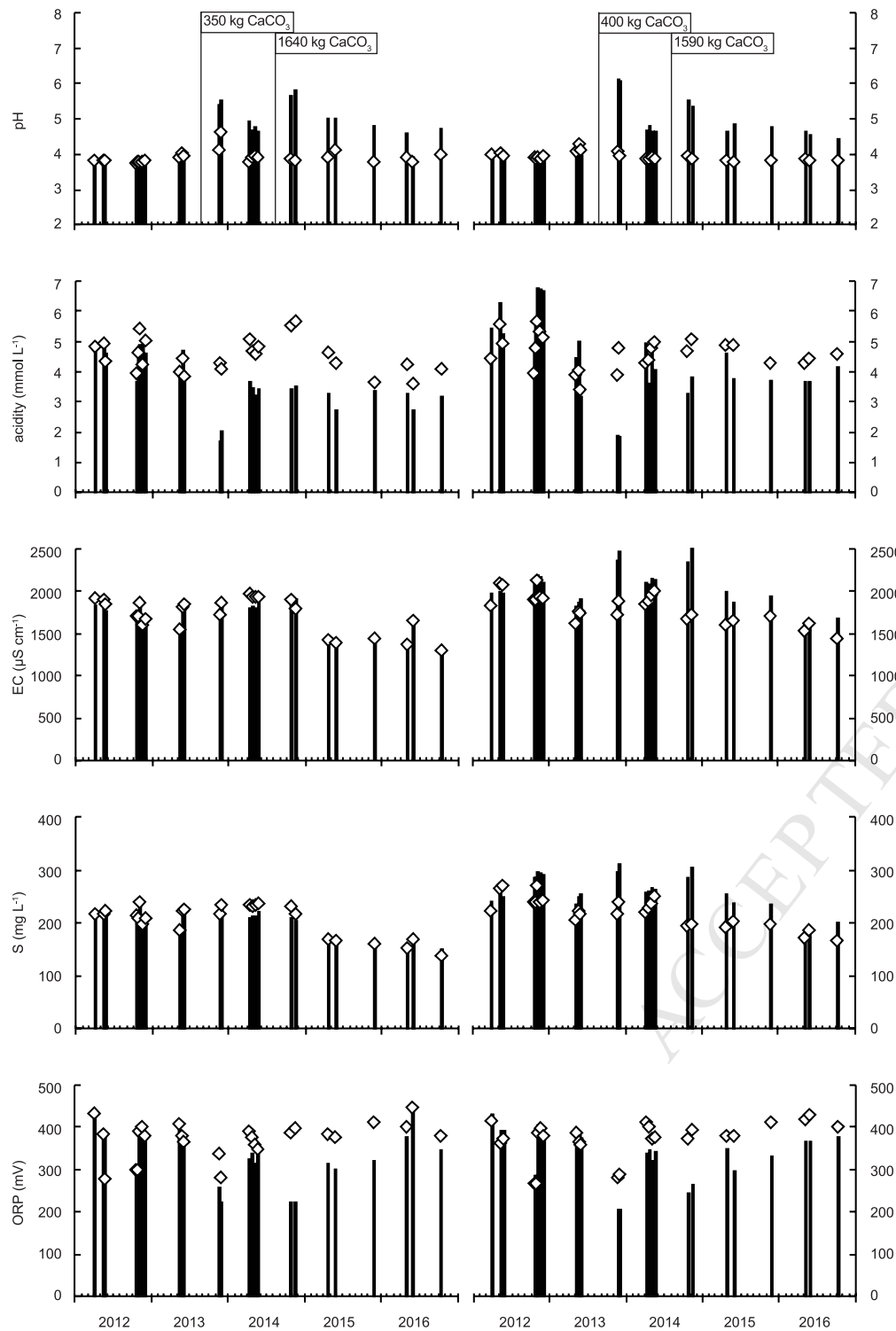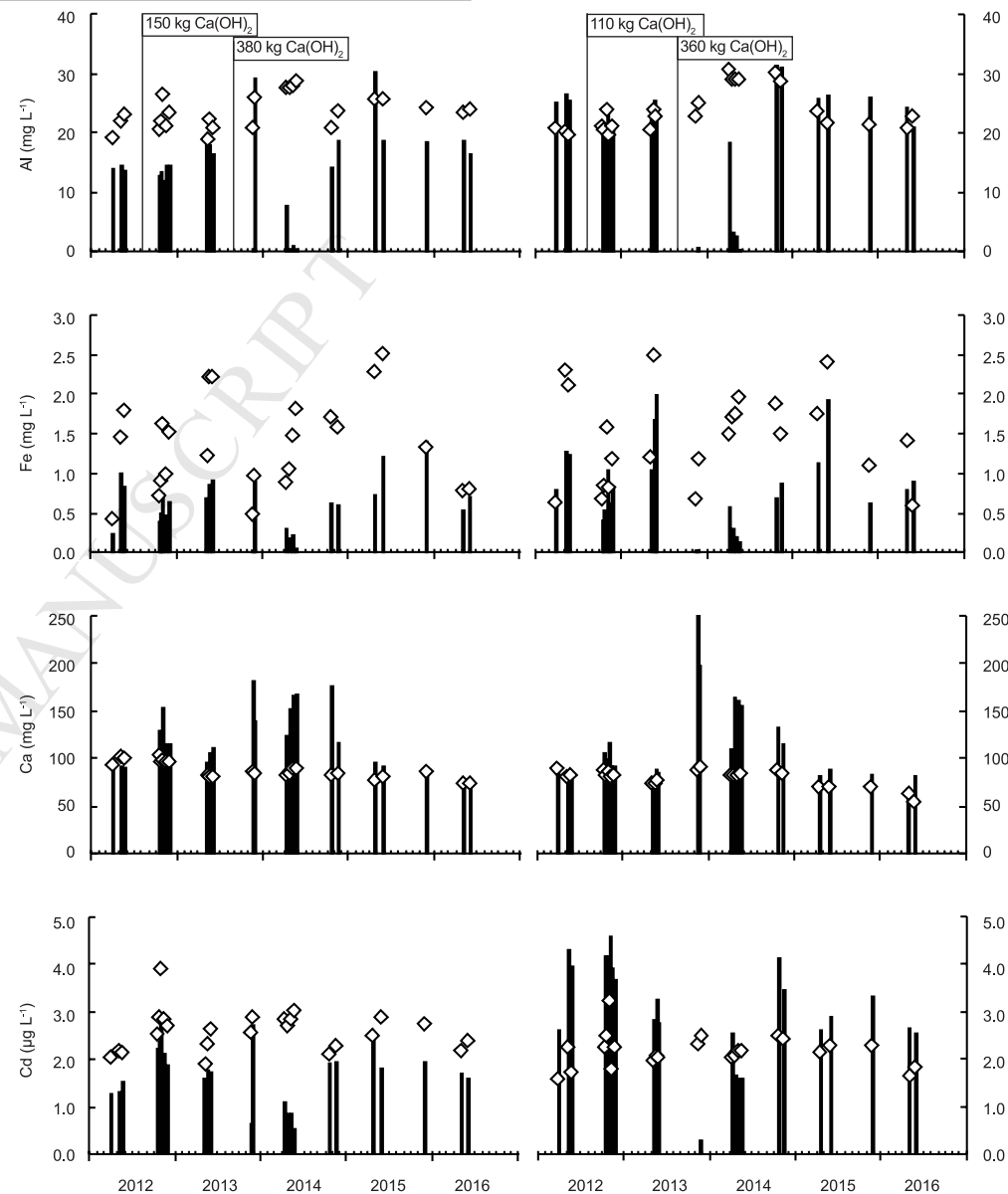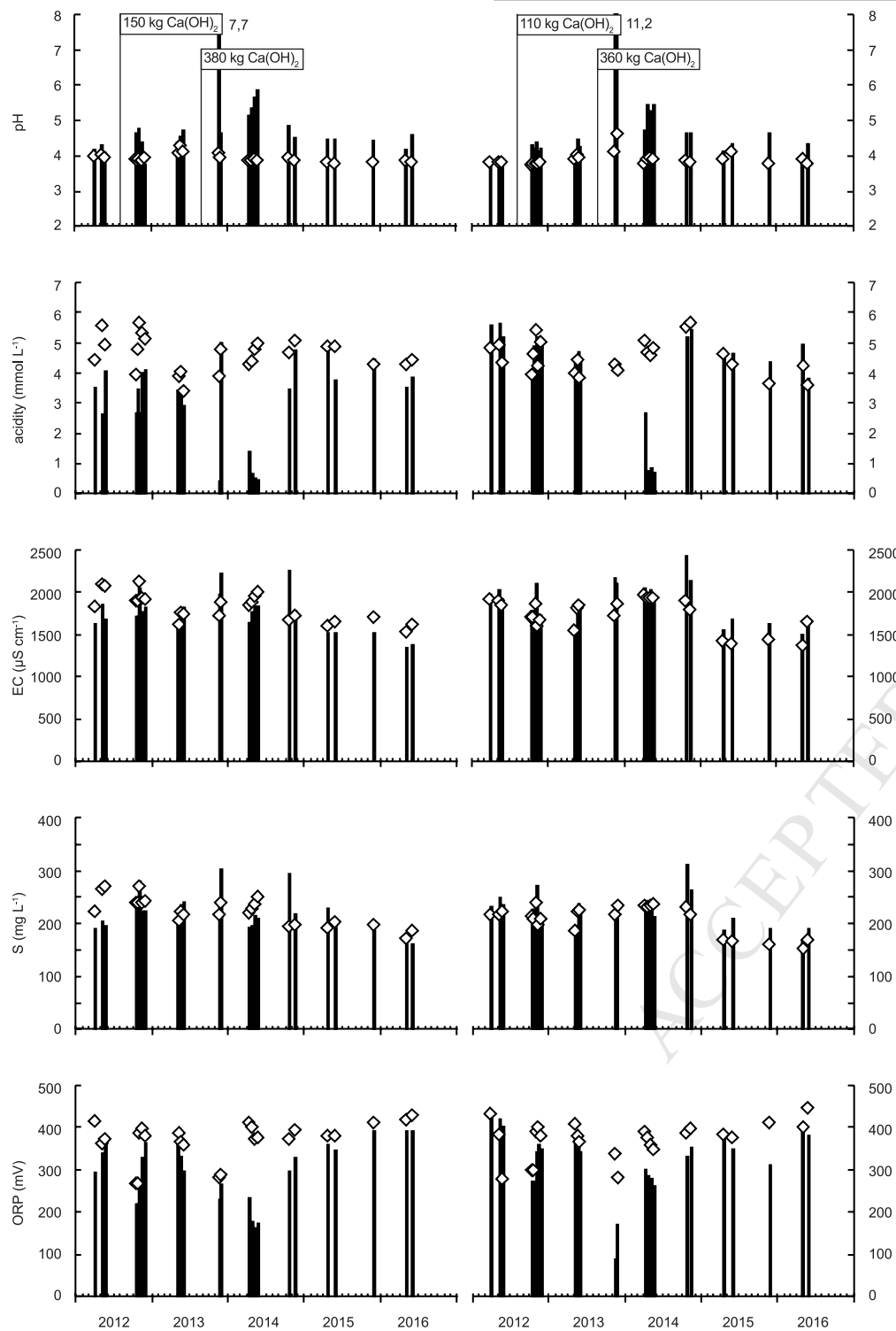Reference fields — CaCO₃-treated fields — Ca(OH)₂-treated fields
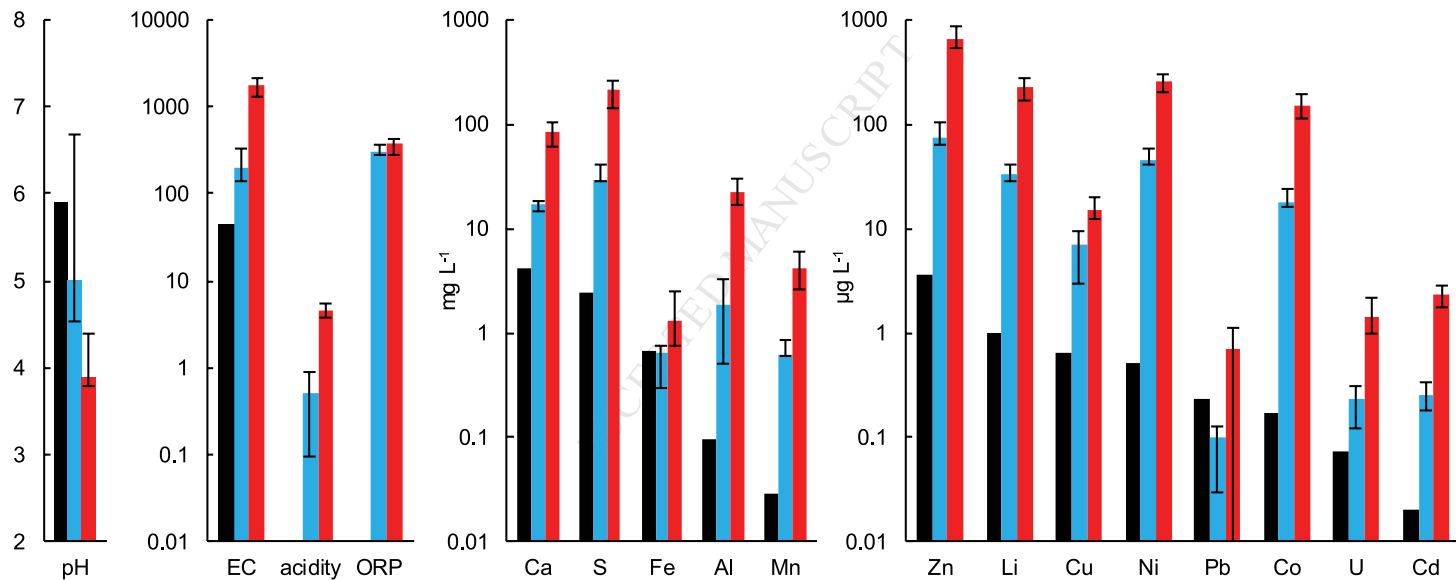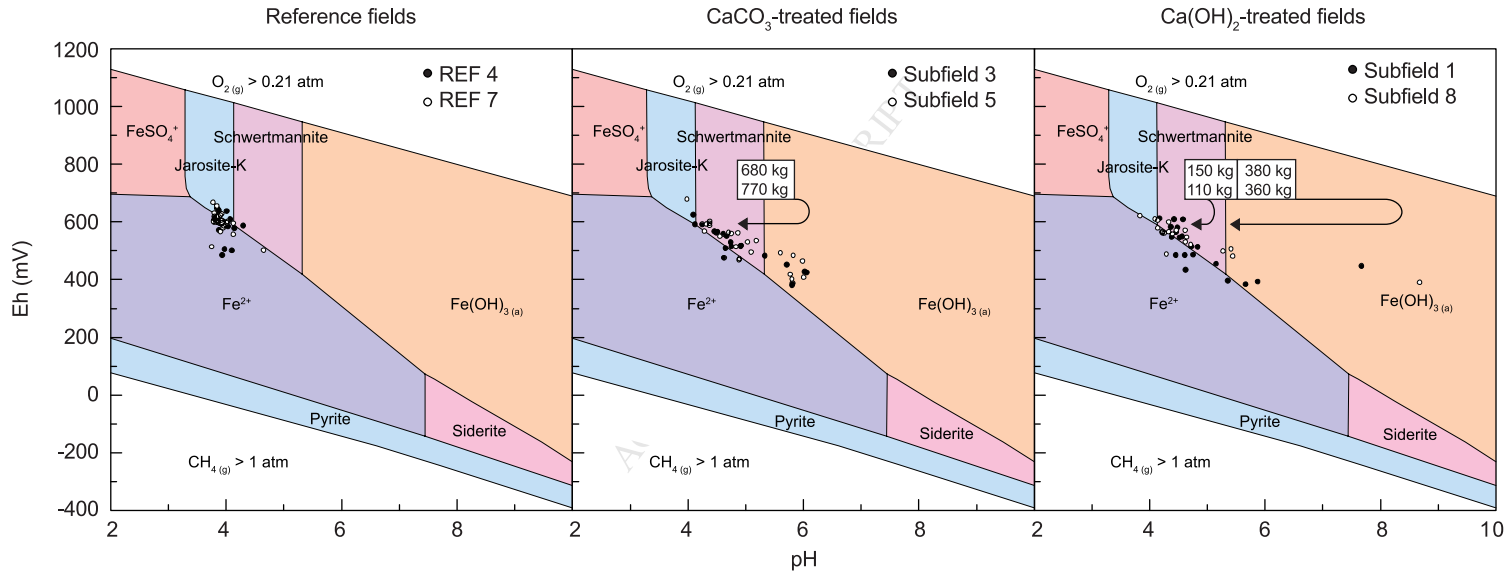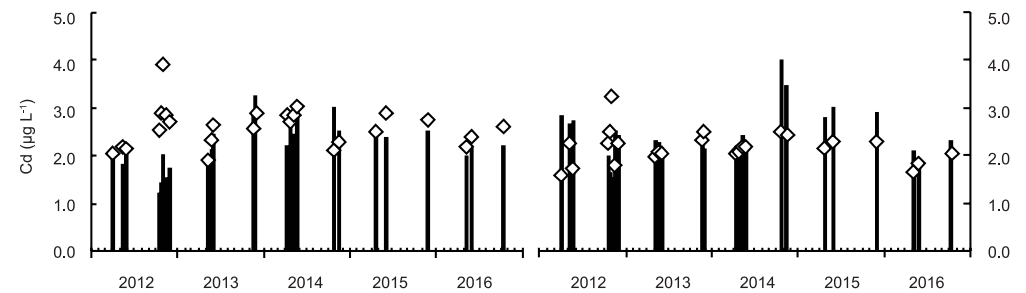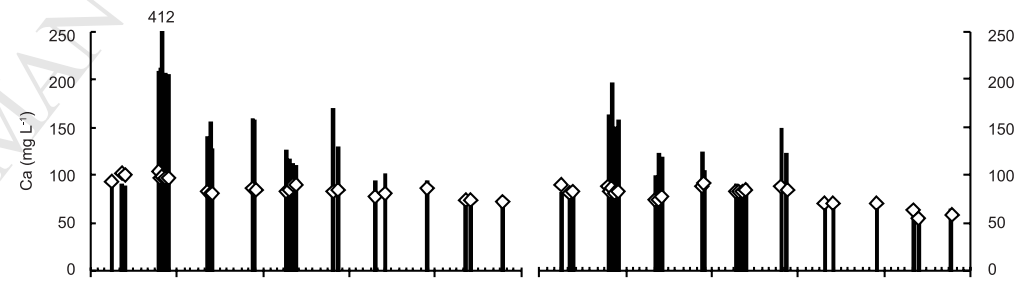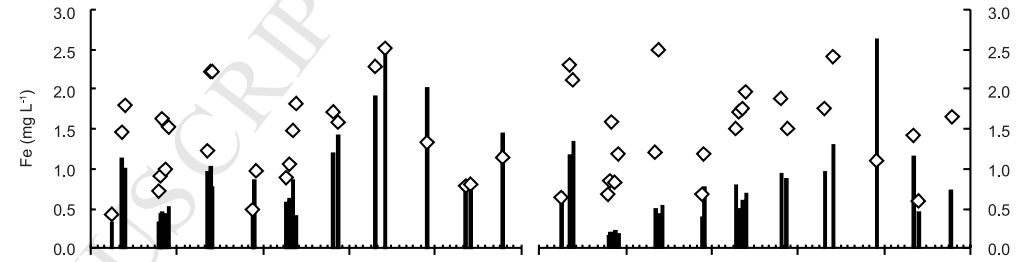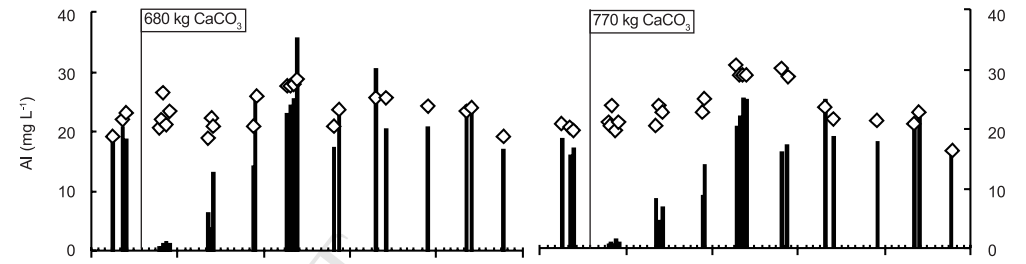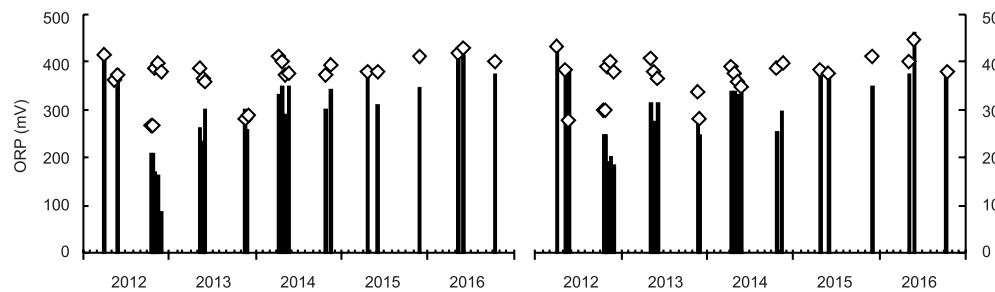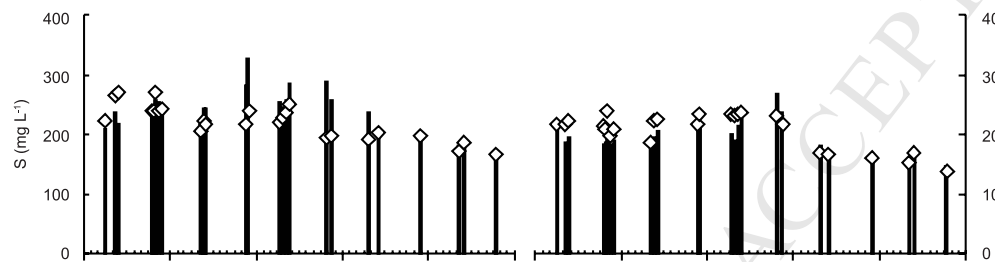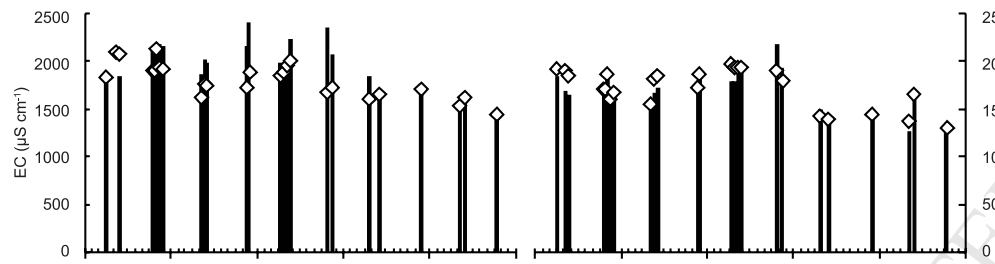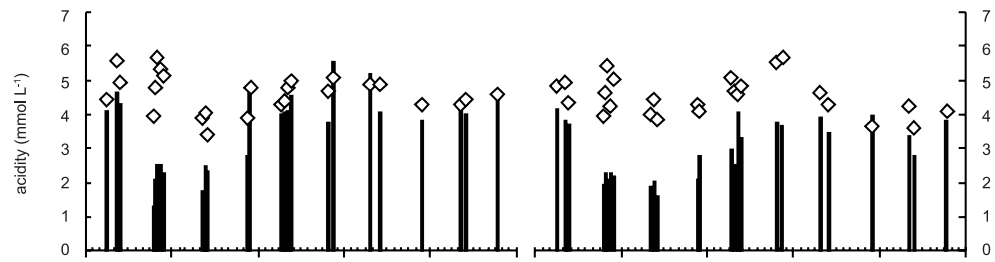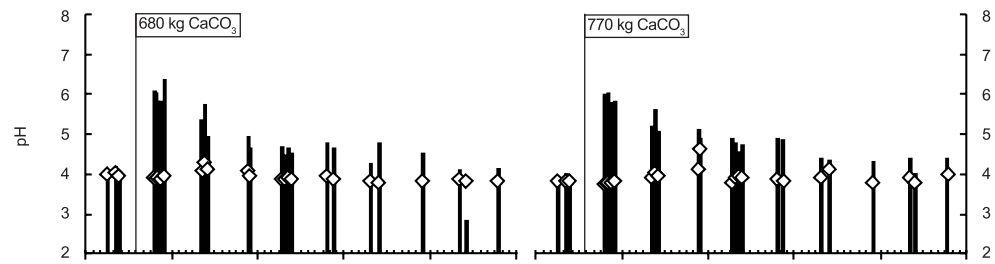
| subfield treated with large dose of $CaCO_3$

◇ reference values
(REF 4 for subfield 3, REF 7 for subfield 5)

SUBFIELD 6   SUBFIELD 9   ACCEPTED MANUSCRIPT   SUBFIELD 6   SUBFIELD 9

| subfield treated with small dose and refill of CaCO₃

◇ reference values
(REF 7 for subfield 6, REF 4 for subfield 9)

SUBFIELD 1 | SUBFIELD 8 | ACCEPTED MANUSCRIPT | SUBFIELD 1 | SUBFIELD 8

150 kg Ca(OH)₂ 7,7
380 kg Ca(OH)₂
110 kg Ca(OH)₂ 11,2
360 kg Ca(OH)₂

| subfield treated with small dose and refill of Ca(OH)₂

◇ reference values
(REF 4 for subfield 1, REF 7 for subfield 8)

Highlights

- Long-term neutralisation capacity with fine-grained $CaCO_3$ precision treatment

- Significant increase in discharge water pH

- Significant drop in Al concentrations

- Decrease in Fe due to changes in pH and redox conditions