Design, construction and monitoring of pilot systems to evaluate the effect of freeze-thaw cycles on pollutant retention in wetlands

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Abstract:

Substantial knowledge is available on purification processes occurring in treatment wetlands. However, there is still a lack of understanding regarding pollutant removal under winter conditions in cold climate regions, especially with respect to the effect of freeze-thaw cycles. Due the complexity of soil freeze/thaw processes and the variety of factors affecting pollutant removal, pilot systems can be seen as powerful tools offering a rare opportunity to observe processes that have a significant impact on year-round purification. This paper describes the design, construction, monitoring and operation of two replicate pilot peat-based wetlands subjected to two simulated freeze-thaw cycles. Undisturbed peat soil and treated process water samples were collected from a full-scale treatment wetland operating at a mining site in Northern Finland. In general, the design approach and monitoring methodology developed were successful and the pilot wetlands functioned well. Fluctuations in removal efficiency of target compounds due to freezing and thawing conditions were observed. Overall, removal of sulphate and arsenic decreased during frost periods, while removal of antimony increased. Monitoring data from the full-scale treatment wetland were used to assess the representativeness of the results obtained. Comparisons of seasonal variations in pollutant concentrations in outflow samples from the full-scale wetland and those measured in the pilot wetlands revealed similar fluctuations in removal efficiency during frost and frost-free periods, suggesting that the pilot wetlands simulated the real system rather well. Carefully designed pilot systems can thus be valuable tools for assessing the effect of harsh winter conditions on wetland processes and operation.

Keywords: natural wetlands, mining water, metals, nitrogen, arctic conditions

1. Introduction

In general, wetlands are well-suited for purification of water from diffuse sources, as they retard the flow of water and provide a large filtration network with many adsorptive surfaces on plant roots or soil particles where nutrients, suspended solids (SS) and other harmful elements (e.g. metals and humic substances) can be retained (Kadlec and Wallace, 2009; Vymazal, 2011; Heikkinen et al., 2018; Kujala et al., 2019; Khan et al., 2019a). Treatment wetlands can be established in natural areas (making use of natural soil, vegetation etc.) or can be constructed as completely separate, purpose-built systems. In the Northern hemisphere, more than 50% of the exposed land surface is regularly influenced by seasonal soil frost (Zhang et al., 2004). Soil freezing is known to limit and control ecosystem functions (Sulkava and Huhta, 2003; Cleavitt et al., 2008), nutrient availability (Edwards and Cresser, 1992), soil texture (Kadivar and Manahiloh, 2019) and processes such as nutrient leaching (e.g. Fitzhugh et al., 2003) and gas fluxes (Groffman et al., 2006). These are key issues to be considered when wetlands are used for water purification in cold climate regions. Northern wetlands can experience repeated freeze-thaw cycles (lasting from days to months) every winter. Short freeze-thaw cycles occur frequently in the beginning of winter, as cold night temperatures lead to freezing of upper soil layers, while warmer day temperatures lead to thawing. On the other hand, soil can be frozen for several months during the middle of winter if an insulating snow cover is thin or absent.

Soil frost and other winter-related conditions can have a significant effect on the pollutant retention efficiency of wetlands. For example, soil frost can change flow pathways within wetlands (Postila et al., 2015b) and reduce hydraulic retention time significantly (Ronkanen and Kløve, 2007; Heikkinen et al., 2018). Physical-chemical processes (adsorption, retention of particles etc.), which are strongly dependent on contact between water and soil particles and on residence time of water, can decline, affecting pollutant removal. In addition, low temperatures have a direct impact on microbe-driven processes (e.g. nitrification, denitrification, sulphate (SO_4^{2-}) reduction) by decreasing process rates, thus leading to reduced removal efficiencies (Smid and Beauchamp, 1976; Knoblauch and Jørgensen, 1999; Kadlec and Reddy, 2001; Stein et al., 2007; Tourna et al., 2008; Postila 2015a). Although substantial knowledge is available on wetland processes, the overall effect of cold climate conditions on water purification efficiency is not entirely clear. For example, there is still a lack of understanding regarding pollutant removal (e.g. nitrogen, metals, SO_4^{2-}) under winter conditions, especially for organic soils, and the effect of freeze-thaw cycles. As wetlands (and similar systems such as buffer zones etc.) are extensively used in cold climate regions for pollution control at e.g. mining sites, peat extraction sites and urban areas (Heikkinen et al., 2018; Kujala et al., 2019), there is a clear need for knowledge and technological advances as regards identifying and understanding the effect of freeze-thaw cycles on pollutant retention processes.

The overall aims of this study were to extend available knowledge on the effect of freeze-thaw cycles on pollutant retention in wetlands and to develop technological and methodological solutions for monitoring soil frost and thawing processes in these systems. The novelty of this work lies in the use of pilot wetland systems designed to simulate real freeze-thaw conditions in a controlled environment. Due the complexity of soil freeze/thaw processes and the variety of factors affecting pollutant removal in wetlands, pilot systems can be seen as powerful tools offering a rare opportunity to observe processes that have a significant impact on year-round purification.

The design, implementation and operation of two pilot wetlands submitted to fully-controlled freeze and thaw cycles was studied. The objectives were i) to create freezing and thawing environments that replicated real conditions as accurately as possible and ii) to monitor parameters that can be used in combination to identify possible pollutant retention processes. The main research questions addressed were: Is it possible to construct a cost-effective pilot wetland system where freeze-thaw cycles can be simulated in a way that satisfactorily replicates real conditions? Do observations made in a pilot wetland system match observations made in a full-scale treatment peatland?

2. Design and construction of pilot systems

This study was conducted a part of a project seeking ways to minimise the environmental impacts of the mining industry in high-latitude regions (Min-North, Interreg Nord). Therefore the pilot systems were tested for purification of mining water and peat was selected as the medium in the pilot wetlands. Peat is a type of organic soil abundant in boreal regions and peatlands are widely used as buffer zones receiving mining-affected waters prior to discharge to recipient water bodies such as lakes or rivers.

Mining-affected water and undisturbed peatland soil samples from a full-scale treatment wetland purifying treated excess mining process water since 2010 in Northern Finland were used in pilot wetland construction and operation (two replicate units). Long-term monitoring data and data on operating parameters (e.g. water residence time, average frost depth) from the same site were used as the basis for the pilot design. In addition, climate data from the study site location were used to define the freeze-thaw conditions simulated.

2.1 Dimensioning parameters, soil sampling and stabilisation procedure

2.1.1 Pilot wetland sizing

The actual dimensions of the peat samples collected from the treatment wetland were based on practical factors that were critical for the sampling procedure. Samples were taken in the beginning of May 2017 during the frost period (i.e. when surface peat layers were frozen) to avoid collapse of the peat sample at the time of sampling. Due to the nature of the wetland soil and its position in the landscape, motorised machinery/vehicles could not be used to assist in sampling. Thus the procedure used was manual, simple and cost-effective. Readily available plastic boxes (moving boxes) were selected as sample containers, which allowed for sample dimensions of 50 cm x 38 cm x 30 cm (length x width x height) or 0.057 m^3 volume. This container size was selected to achieve a reasonable weight and allow manual transportation of the samples from the wetland. Prior to sampling, snow was removed from the selected sampling area in the wetland and a power saw was used to cut the frozen soil samples. Soil was excavated around the actual samples to allow insertion of straps used to lift the samples from the ground and lower them into the moving boxes. The samples were collected from an area of the treatment wetland that does not receive a high hydraulic load, in order to avoid soil samples being affected by possible accumulation of heavy metals that could lead to a high risk of pollutant leaching, as reported for the treatment peatland (Palmer et al., 2015; Khan et al. 2019a).

2.1.2 Residence time and frost depth selection

Hydraulic residence time in the pilot wetlands was selected based on the known residence time of the treatment wetland from which the peat material was taken, as this is a critical hydraulic parameter controlling purification processes in treatment wetlands. According to available data for the full-scale treatment wetland, residence time (T_r) typically varies from 25 to 30 days. A mean inflow rate (Q_i) of 2 L d^{-1} to the pilot wetlands was selected. Mean peat porosity (n) measured at the peat sampling site was 0.9 (0.88-0.92) and thus the mean water volume ($V_{water} = n*V$) in the pilot wetlands was 0.051 m^3. Using Eq. 1, mean residence time in the pilot wetlands was determined to be 25.7 days, which was within the range observed in the full-scale treatment peatland (frost-free period).

$$Q_i = \frac{V_{water}}{T_r} \qquad (1)$$

The frost depth to be achieved in the pilot wetlands was based on the sample size (depth = 30 cm) and on frost depth data for the treatment wetland from which the peat material was taken. The target frost depth was set between 10 and 13 cm, as this would allow for continuous water flow underneath the frozen peat and result in a measurable effect (at least in terms of flow regime) of freezing conditions. The freezing process was considered to begin when the temperature dropped below 0°C. During frost conditions, the active water flow volume was reduced, which affected the residence time. In determination of water residence time in the pilot wetlands during frost conditions, the properties of the frozen and frost-free peat layers were taken into consideration. Water volume (V_{water}) during frost conditions was calculated using a frost-free porosity of 0.9 for the layer of non-frozen peat and 20% of that value (i.e. 0.18) for the top frozen layer. A water content of 20% of total porosity was selected for the frozen layer based on studies conducted by Mustamo et al. (2019). In order to evaluate real hydraulic conditions in the pilot wetlands, well-known tracer tests were performed under both frost-free and frost conditions (see section 2.2.7).

2.1.3 Stabilization phase

Peat samples were transported to the laboratory at the University of Oulu along with about 700 L of mining-affected water (collected from the inflow to the treatment wetland). Soil samples and mining-affected water were stored in a refrigerator (5°C) prior to the start of the stabilisation phase. The plastic boxes were fitted with quartz sand (particle size 2-3 mm) compartments at the beginning and end of their longitudinal profile (width = 32 cm, length = 4 cm, height = 30 cm) and with inflow and outflow pipes (Fig. 1). Mining-affected water was introduced to the individual pilot wetlands at a rate of 2 L d^{-1}. Electric conductivity (EC) sensors (HOBO-logger) were installed in the outflow pipes for continuous monitoring. Inflow and outflow water samples were collected at 2- to 4-week intervals and analysed for a number of contaminant concentrations (e.g. arsenic (As), antimony (Sb), dissolved organic carbon (DOC) etc.). The stabilisation phase lasted around six months (May-November 2017), although stable contaminant concentrations were observed in the outflow of both pilot wetlands after about four months (data not presented).

2.1.4 Preliminary freezing tests and selection of system temperature

Preliminary freezing experiments were conducted using disturbed natural peat soil samples of the same volume, placed inside the same type of plastic boxes as were used for the actual pilot wetlands. Different refrigeration set-ups were tested and copper refrigerant tubes attached to a refrigeration unit (Lauda RK 20) were selected. Freezing was conducted from the top down and the sides of the pilot wetlands were insulated with mineral wool, to simulate *in situ* conditions as closely as possible. The refrigerant tubes were placed a couple of cm from the soil surface, in a typical configuration with bends and parallel lines. Suitable freezing temperatures were identified from trial freeze/thaw cycles. For clear, progressive frost development, an initial temperature of -20°C was found to be suitable. This was then gradually adjusted as the frost proceeded downwards from the soil surface, to keep the maximum frost depth at around 13 cm.

2.2 Monitoring and final set-up

2.2.1 Sensors and their placement

Temperature sensors (in-house built thermocouples attached to a logger) were installed at the soil surface and at 2, 5, 10, 13, 15, 17 and 25 cm depth, longitudinally at 10 cm from the inlet and 10 cm from the outlet of the pilot wetlands. These were used to monitor frost depth. The freezing process was considered to have started when the temperature dropped below 0°C. Redox potential sensors (Ecotech GmbH, platinum redox electrode with Ag/AgCl reference electrode, art. no. 461) and pH sensors (Ecotech GmbH, glass pH electrode with Ag/AgCl reference electrode, art. no. 465) were installed in the centre of the pilot wetlands at 10 and 20 cm depth. Electric conductivity (EC) sensors (HOBO-logger) were installed at the outflow pipes for continuous monitoring (Fig. 1, Fig. S1 (scale-drawing) in Supplementary Material).

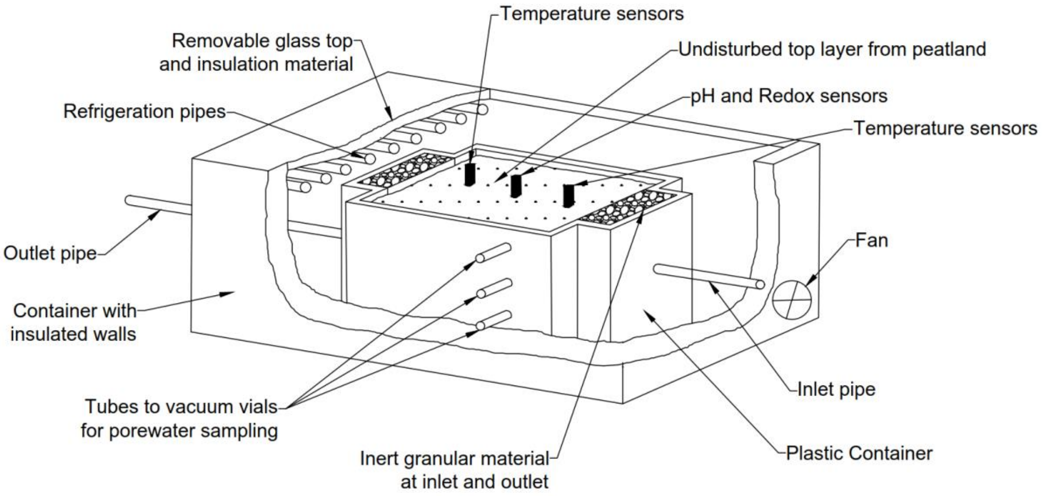

Figure 1 – Schematic drawing of pilot wetland showing the different compartments and placement of sensors, inflow and outflow pipes, porewater sampling tubes and refrigeration units.

2.2.2 Porewater collection

Porewater samplers were installed at three depths in the pilot wetlands while they were still in the unfrozen state. Rhizon samplers (Rhizosphere Research Products, The Netherlands) are thin tubes made of a hydrophilic porous polymer that acts as a microfiltration membrane. The samplers function by sucking porewater from soils and sediments due to a negative pressure created by attaching them to an evacuated tube or a syringe. For installation in the pilot wetlands, holes were drilled into the side of the plastic containers (8 cm from inlet) at three different depths (5, 15 and 25 cm). Rhizon flex samplers (pore size 0.15 µm, filter length 5 cm, tube length 30 cm) were covered with an outer perforated tube and inserted horizontally into the peat soil though the drilled holes (Fig. S1 in Supplementary Material).

Porewater sampling was conducted daily at all depths until the frost depth reached the layer in which the sampler was installed, leading to freezing of the porewater. That sampler was then passed over until the layer thawed again, but samples were still taken from unfrozen lower layers. Porewater samples were taken by attaching evacuated 12-

mL Exetainer® vials (Labco, UK) to the Rhizon samplers and waiting until a sufficient amount of porewater had been collected (3-5 mL). The use of evacuated vials prevented oxidation of sensitive chemical species. Samples were transferred from the vials to cryotubes using a syringe, frozen immediately in liquid nitrogen and stored at -20°C prior to analysis. In cases where the compounds of interest are not sensitive to oxygen, samples can be taken with a syringe and do not have to be kept frozen. The porewater samples were analysed for arsenic speciation (data not presented). However, porewater can be analysed for any compound of interest such as metals, total organic carbon (TOC), nitrogen compounds or sulphate.

2.2.3 Gas flux sampling

Measuring fluxes of gases such as nitrous oxide (N_2O), methane (CH_4), carbon dioxide (CO_2), volatile organic compounds and hydrogen sulphide (H_2S) can give valuable information on the processes occurring in the soil. Gas fluxes from the pilot wetlands were measured with the static chamber method, which has been widely used to measure emissions from soils (Robertson et al., 2000; Maljanen et al., 2001). Measurements were conducted twice during the frost-free period, once directly after the onset of freezing conditions, once (first freeze-thaw cycle)/twice (second cycle) while the peat was completely frozen and once during thawing. A high-density polyethylene (HDPE) chamber (55 cm x 35 cm x 12 cm) was fitted with an airtight seal to the pilot wetlands for the period of flux measurement (Fig. S2 in Supplementary Material). As the surface area of the pilot wetland was covered completely by the chamber, the combined fluxes from the whole pilot wetland were assessed. Gas samples (~30 mL) were taken from the chamber headspace with a polypropylene syringe 5, 10, 15, 20, and 25 min after positioning of the chamber. These samples were immediately transferred to evacuate 12-mL Exetainer® vials (Labco, UK). In the present analysis we focused on CO_2 fluxes, as CO_2 production can be used as an indicator of general microbial activity in the soil. The CO_2 concentration in gas samples in the vials was determined using a gas chromatograph (Agilent 6890N, Agilent Technologies, USA) equipped with an autosampler (Gilson, USA) and thermal conductivity detector. Compressed air containing 398 µL/L CO_2 was used for calibration. Gas flux rates were calculated from the linear increase in chamber headspace concentration over time (e.g. Liikanen et al., 2006).

2.2.4 Pilot wetland insulation and final set-up

The pilot wetlands were placed inside climate control units that were identical in size (80 cm x 60 cm x 50 cm (length x width x height)) and were insulated in the same way. However, the unit which housed pilot wetland 1 was a pre-existing metal box and the unit which housed pilot wetland 2 was purpose-built from acrylic and polyurethane sheets and wood. To prevent freezing from the sides of the peat, the space between the wetland boxes and the walls of the host climate control unit was filled with mineral wool and fibreglass material packed between polyurethane sheets for easy application and removal. Sections of inflow and outflow pipes located inside the climate control units were also insulated to prevent freezing. In addition, insulation material was placed on the surface of the inflow and outflow compartments of the pilot wetlands to prevent freezing and blocking of inflow and outflow pipes. Thus, only the surface of the peat material was exposed to the freezing coil, which was placed about 1 cm above the soil surface. As the temperature was set to minus degrees Celsius, an ice layer formed around the coil. Insulation material (mineral wool and fibreglass packs) was also placed on top of the freezing coil (Fig. 2, Fig. S3 in Supplementary Material).

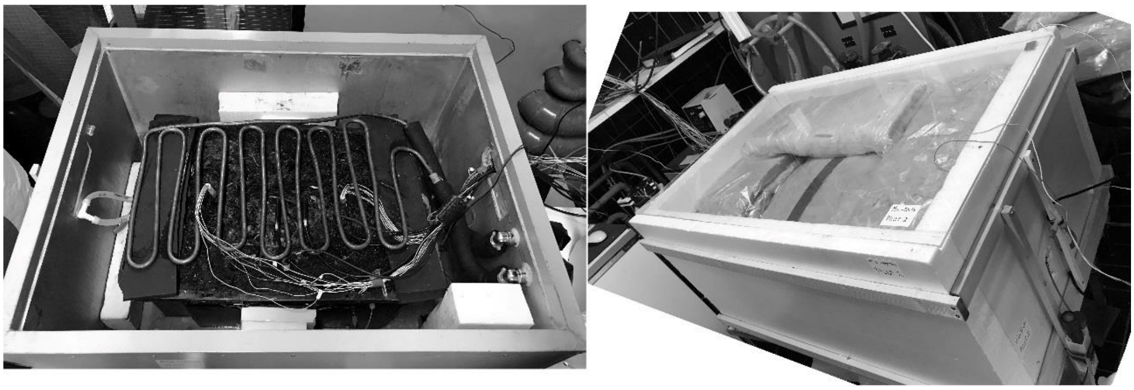

Figure 2 - Climate control units. Left: Position of the freezing coil and (right) the final set-up of the units covered with insulation material (Photos: Elisangela Heiderscheidt).

2.2.5 Freezing/thawing cycles

Two freeze-thaw cycles were applied to both pilot wetlands. The first cycle lasted five weeks (Dec. 2017-Jan. 2018), while the second cycle lasted about seven weeks (Feb. 2018-Mar. 2018). The frozen period was considered to begin when the temperature dropped below 0°C in the 10-13 cm soil layer. Although very similar conditions were applied to both pilot wetlands, freezing and thawing of the peat progressed at slightly different rates (Table 1).

Table 1 – Duration of different phases of freezing and thawing in pilot wetlands 1 and 2 during the first and second freeze-thaw cycles

First cycle	Freezing (weeks)	Frozen (weeks)	Thawing (weeks)	Frost-free (weeks)
Pilot 1	1	2	1	1
Pilot 2	1.5	1.5	1	1
Second cycle	**Freezing (weeks)**	**Frozen (weeks)**	**Thawing (weeks)**	**Frost free (weeks)**
Pilot 1	1	4	1	1
Pilot 2	1.5	4.5	1	1

During the first freeze-thaw cycle, as frost developed, it caused expansion of the top layers of the wetland soil, exerting inwards pressure on the lower portion of the plastic boxes holding the soil. This caused a crack to appear at the bottom of the box in pilot wetland 1. The leak was identified and the crack was mended with multi-purpose glue and a rubber-like material. The data gathered during this period were not used in the assessment of pilot wetland 1.

2.2.6 Water feeding and sampling

Inflow water (container) was kept in a refrigerator (5°C) and pumped to the pilot wetlands at an inflow rate of between 1 and 2 L d^{-1} (frozen/frost-free). Inflow (Table S1 in Supplementary Material) and outflow water samples were collected twice per week (once in holiday periods). The samples were divided into two sub-samples, one of which was filtered (syringe filtration, GF 0.45 µm) while the other was not. Filtered and unfiltered samples were sent to accredited laboratories for analysis of dissolved and total concentrations of pollutants (e.g. SO_4^{2-}, As, Sb etc.) using SFS-EN ISO methods.

Inflow water quality varied between the two freeze/thaw cycles as it represented different sampling periods at the full-scale treatment wetland inlet. The collected samples contained typical contaminant concentrations found in the inflow of the full-scale treatment wetland according to monitoring data for 2017 and 2018 (Fig. 3, Table S1).

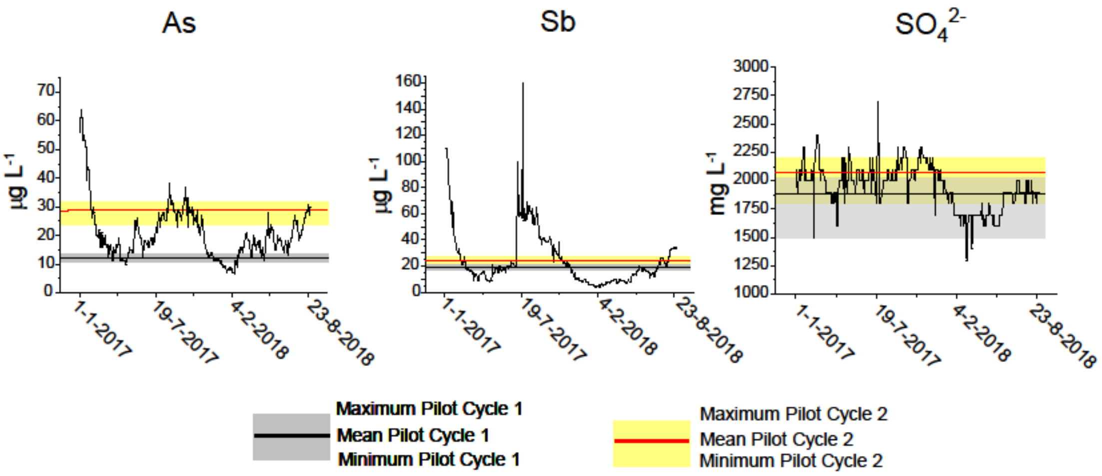

Figure 3 - Inflow water concentrations of arsenic (As), antimony (Sb) and sulphate (SO4^{2-}) over time in the full-scale treatment wetland and quality of samples used during pilot experiments.

2.2.7 Tracer tests for water residence time determination

Nominal water residence time (T_r) in the pilot wetlands was estimated based on the water volume (V_{water}) of soil samples and the inflow rate (Q_i) using Eq. (1). In order to determine the hydraulic conditions during pilot experiments, an additional freeze/thaw cycle was conducted and conventional tracer tests were performed. Water residence time, for both frost-free and frozen conditions, was determined using the conservative tracer method with sodium chloride (NaCl) (described in detail e.g. in Postila et al., 2015b). A solution was made by diluting 254 g of NaCl in 750 mL mining-affected water. The solution was then fed to the pilot wetlands (inflow period ~8.5 h) and EC was measured continuously in outflow water (once per hour). Outflow tracer concentration was determined using linear regression analysis between NaCl concentration and the resulting EC response. The water residence time in the pilot wetlands was calculated based on the tracer response curve and the first moment method (Kadlec and Wallace, 2009).

During tracer tests, inflow rate to the pilot wetlands was 2 L d^{-1} during the first 72 days from the time of tracer addition but was then decreased to on average 1.5 L d^{-1} and 1.6 L d^{-1} for pilot wetland 1 and 2, respectively (frost-free condition). Mean inflow rate in the tracer test under frozen conditions was 1.7 L d^{-1} for both pilot wetlands. Normalised residence time response curves were plotted so that hydraulic conditions in the pilot wetlands could be compared in frost-free and frozen conditions. The outflow tracer concentrations were normalised based on estimated initial concentration and time was normalised based on flow-weighted time (e.g. Werner and Kadlec, 1996).

3. Pilot wetland operation and purification results

3.1 Overall functioning of pilot wetlands and monitoring equipment

Two freeze/thaw cycles were applied to both pilot wetlands. Freezing of wetland peat material was carried out slowly, to mimic real conditions and avoid damage to the peat and holding containers. For example, during the first cycle, it took around 10 days for soil at 10 cm depth to reach -0°C (temperature at 2 cm depth was -3°C). Peat soils have been found to freeze at temperatures lower than -2°C and may not be fully frozen even at -5°C (Konovalov and Roman, 1973; Smerdon and Mendoza, 2010). Thus, in the pilot experiments, for temperatures higher than -5°C partly frozen conditions can be assumed, which represent conditions commonly found in real treatment wetlands.

Most sensors performed as expected and data were recorded throughout the tests. The redox potential measured at 10 cm depth drastically increased following the onset of soil frost (Fig. 4). This sudden increase in redox potential was most likely due to i) pore water space around the sensor becoming smaller and its water quality changing during frozen periods and ii) increased diffusion of oxygen into the soil through cracks and channels formed by frost action (Fig. 4). The placement of the temperature sensors allowed for good monitoring of frost depth, while the data gathered by the pH, redox (20 cm) and EC sensors provided useful information regarding the processes occurring (Fig. 4). The methodology and equipment used for porewater and gas sampling proved to be sufficient, as samples were extracted and analysed without incident.

In future studies, additional sensors could be used to improve understanding of processes within the wetland soil. For example, oxygen sensors at different depths might give further insights on the reasons for the redox potential increase and help identify the oxic/anoxic interphase in different stages of freeze-thaw cycles. Moreover, additional porewater samplers (at more depths or at different distances from the inlet) could be used to assess e.g. the transformation of certain compounds with depth and/or distance travelled within the pilot wetland.

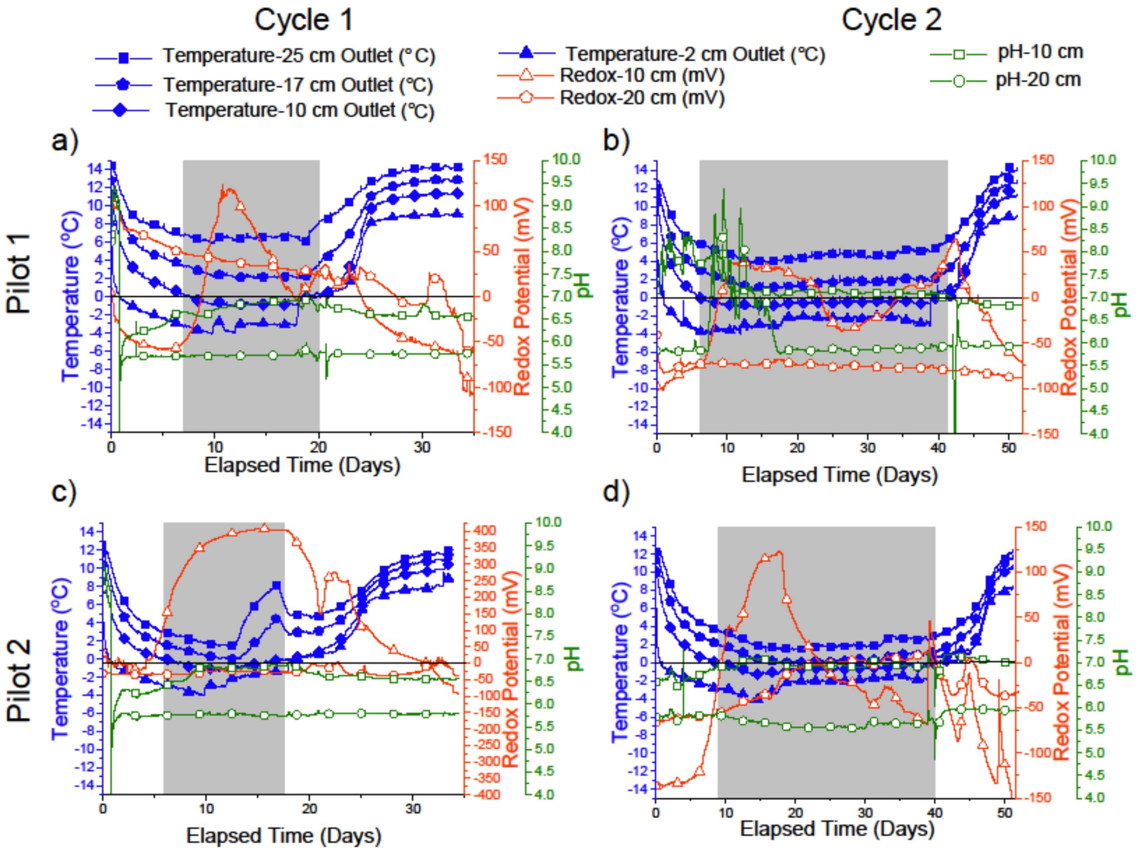

Figure 4 - Temperature (2, 10, 17 and 25 cm depth), redox and pH (10 and 20 cm depth) measured 10 cm from the outlet of the pilot wetlands during (left) the first freeze-thaw cycle and (right) the second freeze-thaw cycle. The shaded area indicates the frost period, when the temperature at 10 cm soil depth remained at or below 0°C.

3.2 Hydraulic conditions

Based on the results of the tracer experiments, theoretically estimated water residence time for frost-free conditions (Eq. 1) was 25.7 days for an inflow rate of 2 L d^{-1}. During tracer experiments, the actual inflow rate to pilot wetland 1 was 1.5 L d^{-1} and to pilot 2 was 1.6 L d^{-1}, leading to theoretical residence times of 34 and 32 d, respectively. Based on tracer (NaCl) break-through curves, mean water residence time in the pilot wetlands was much longer, 84 d (yield of tracer 71%) and 43 d (yield of tracer 30%) for pilot wetland 1 and 2, respectively. This difference in measured mean residence time can be due to different flow pathways within the peat, as also suggested by the five separate peaks observed in the normalised residence time distribution curve for pilot wetland 1 (Fig. 5). The last peak occurred at around 193 days after tracer addition.

During frost period tracer tests, an inflow rate of 1.7 L d^{-1} was maintained and theoretical residence time (Eq. 1) was 20 d. Mean water residence time based on the tracer break-through curve was determined only for pilot wetland 1 and was found to be 14 d. Fewer peaks were observed in the normalised residence time distribution curve (Fig. 5). However, rather low yield of tracer (26%) was achieved, which can partly explain the difference between the theoretical and tracer-based estimated mean residence time. The lower yield of tracer observed in the test carried out during frozen compared with frost-free conditions may be due to infiltration and retention of water (and thus NaCl) into the frozen layer of soil (Iwata and Hirota, 2005). Generally, mean residence time was shorter during frost than frost-free conditions, reflecting the fact that larger peat surface area and longer reaction times are available during frost-free periods.

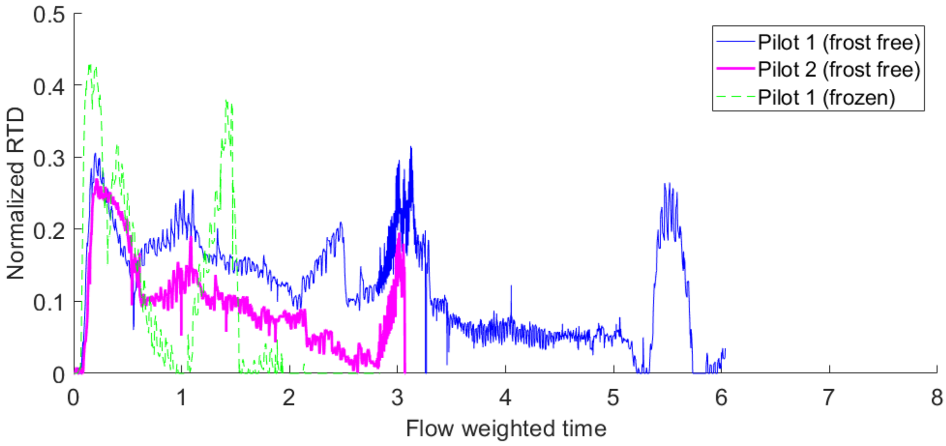

Figure 5 – Normalised tracer breakthrough curves for pilot wetlands 1 and 2. Outflow tracer concentrations were normalised based on estimated initial concentration and time was normalised based on flow-weighted time.

3.3 Effect of freezing and thawing on pollutant removal efficiency

Variations in pollutant concentrations in outflow samples collected from the two replicate pilot wetland systems displayed similar patterns. Thus, the removal of targeted contaminants achieved in the two systems was comparable and the two pilot units can be considered good replicates. Changes in purification efficiency due to freezing and thawing conditions occurred, with higher/lower removal observed under different conditions for different pollutants (Fig. 6). Monitoring data from the full-scale treatment wetland were used to assess the representativeness of the results obtained (Fig. 7). However, as sampling intervals and length of freeze/thaw cycles were much longer in the full-scale system, straight comparisons between pollutant concentrations in samples from the full-scale and pilot wetlands was not considered a viable approach. Thus a general comparison was made focusing on seasonal variations in pollutant concentrations and removal efficiency. Similar patterns in removal efficiency fluctuations during frost and frost-free periods were observed in the pilot wetlands (especially for the second freeze-thaw cycle) and in the real wetland purifying the same type of water (Fig. 7), with the exception of a few specific compounds. Based on this general comparison, it was concluded that the pilot wetlands simulated the full-scale system rather well.

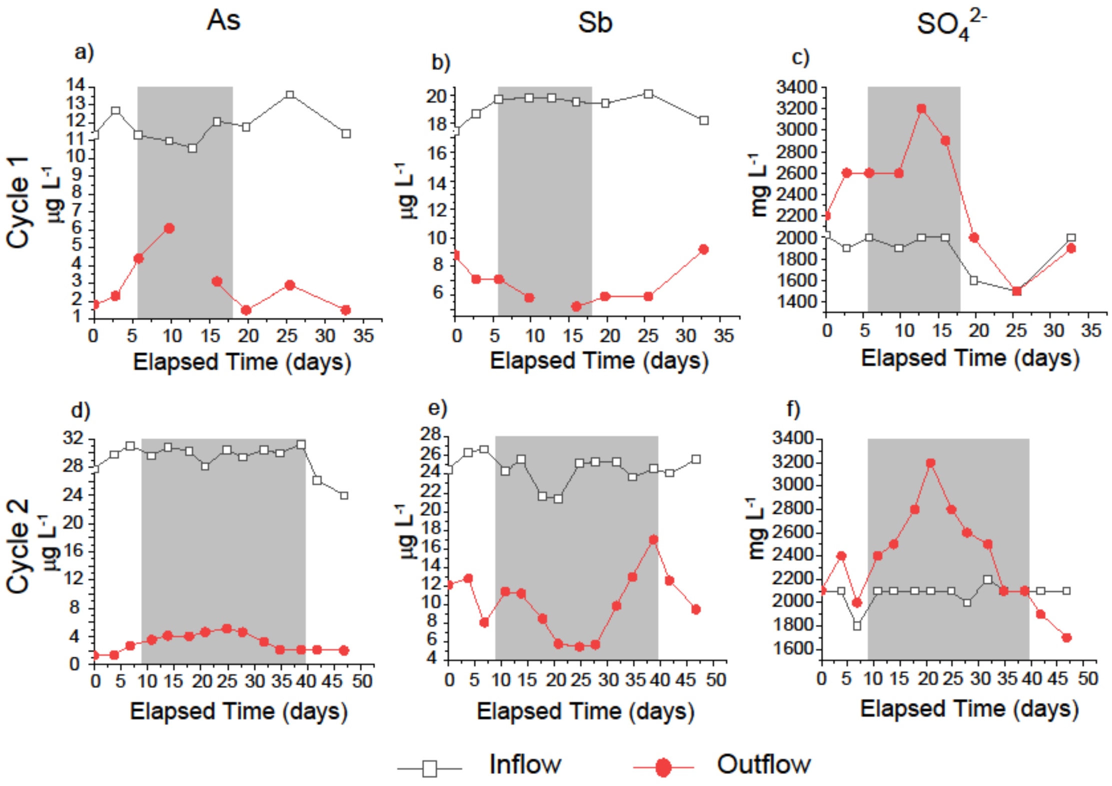

Figure 6 – Mean concentrations of arsenic (As), antimony (Sb) and sulphate (SO_4^{2-}) over time in inflow and outflow from pilot wetland 2 during (upper diagrams) the first freeze-thaw and (lower diagrams) the second freeze-thaw cycle. The shaded area indicates the frost period, when temperature at 10 cm soil depth remained below 0 °C.

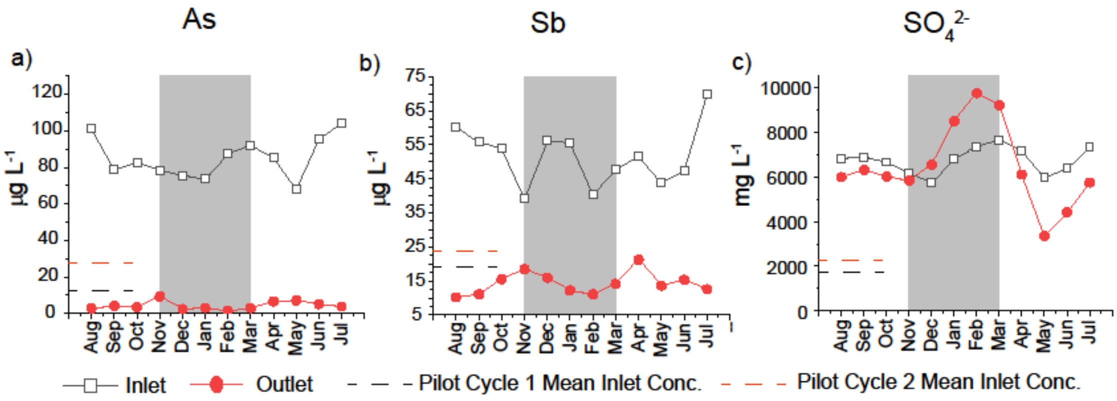

Figure 7 - Mean concentrations of arsenic (As), antimony (Sb) and sulphate (SO_4^{2-}) over time in inlet and outlet samples collected from a full-scale treatment wetland in Northern Finland. Data are grouped by months and represent water samples collected and analysed in the period 2010-2017.

Regarding the purification efficiency achieved in the pilot wetlands, it can be stated that soil frost formation and other winter-related conditions lowered the biological process-based removal of some pollutants (e.g. SO_4^{2-}) (Fig. 6). Carbon dioxide emissions decreased with decreasing temperature in the pilot wetlands, indicating reduced overall biological activity (Fig. 8). However, CO_2 emissions were detected even when the upper layers of the wetland soil was frozen (Fig. 8), indicating i) ongoing biological activity at low temperatures and ii) existence of pores and channels in the frozen layers through which gases can leave the system. As expected, flow conditions (such as residence time of water and active water volume) changed with the development of soil frost, leading to shorter residence time and smaller peat surface area available for pollutant retention processes. These changes had a direct effect on pollutant removal (Fig. 6), as processes such as sorption, biodegradation and precipitation are dependent on contact time and media surface area, and on temperature, redox conditions and oxygen availability (Schimel and Clein, 1996; Wang et al., 2017).

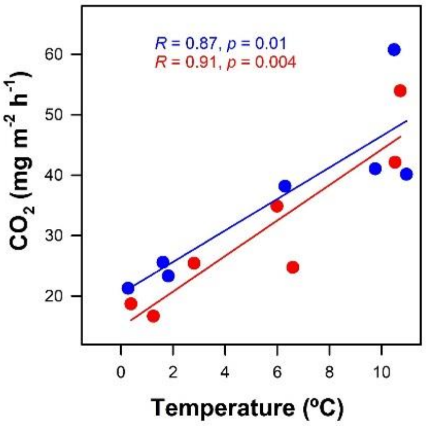

Figure 8 - Effect of peat temperature on carbon dioxide (CO_2) emissions from pilot wetlands. The average temperature for all layers (i.e. from all temperature sensors) was used. (A good correlation was also observed between CO_2 emissions and the temperature in individual peat layers; see Table S2 in Supplementary Material.)

Removal of arsenic decreased in the beginning of the frost periods (Fig. 6a and 6d) and then gradually increased again to pre-frost levels. The decrease was more abrupt in the shorter first freeze-thaw cycle than in the second cycle. Overall, redox conditions remained mildly reducing (between -150 and +125 mV) during both freeze/thaw cycles (Fig. 4). However, a spike was observed in redox potential at 10 cm depth in the beginning of the frost period in both pilot wetlands during both cycles. This spike was stronger (> +400 mV) and persisted for a longer time in pilot wetland 2 during the first freeze-thaw cycle. The pH varied from around neutral in the surface layers (at 10 cm depth) to slightly acidic (pH 5.5-6) in the deeper layers (at 20 cm depth). In the inflow, arsenic was mainly in the form of arsenate (i.e. in an oxidised state; data not shown). Under the pH and redox conditions observed in the pilot wetlands, arsenate can be reduced to arsenite by microbial activity (Kujala et al., in review). Indeed, mainly arsenite (along with methylated As species) was detected in the outflow (data not shown). Direct binding of arsenite via sulfhydryl groups to natural organic matter (NOM) has been identified as a major arsenic sequestration mechanism under reducing conditions in wetlands (Hoffmann et al., 2012; Langner et al., 2012; Besold et al., 2018), and might also be responsible for arsenic removal in the pilot wetlands.

The removal of antimony, on the other hand, increased in the beginning of the freezing period and then gradually declined (Fig. 6b and 6e). Field data for the full-scale treatment wetland did not indicate a significant difference in outlet antimony concentrations between summer and winter months (Fig. 7b). However, it should be noted that the dilution effect of spring snowmelt and rainfall on outlet antimony concentrations reported for full-scale wetlands (Khan et al., 2019b) was not replicated in this study. Under anoxic conditions and mildly acidic pH, antimony has been shown to be sequestered by carboxyl/phenol and thiol groups in peat NOM (Besold et al., 2019). Other processes for antimony removal in wetlands include adsorption (e.g. on iron (Fe) and manganese (Mn) oxides) and precipitation (e.g. with sulphide) (Bennett et al., 2017). Exactly how frost period affected these processes to enhance antimony removal in this study is unclear.

The differences in removal of arsenic and antimony (Fig. 6) indicate that the pilot systems effectively replicated the diverse biogeochemical processes and pollutant competition/interactions of the full-scale mining water treatment wetland, as seen in Fig. 7. However, there were some differences between the pilot wetland and field measurements, due to various reasons. Freezing of the top layer can result in surface flow in the full-scale wetland, but was not present in the pilot wetlands. Another important difference between the full-scale and pilot wetlands is the degree of contaminant accumulation in the peat. In the full-scale wetland, gradual contaminant accumulation has been detected in peat samples collected from within preferential flow areas (Khan et al. 2019b). Note that the undisturbed soil samples used in the pilot wetlands were not collected from these preferential flow area. Recent outflow samples collected from the full-scale wetland actually show re-mobilisation of some of these accumulated contaminants (Khan et al. 2019b).

4. Conclusions

Two replicate pilot wetlands were constructed using peat material from a full-scale treatment wetland and submitted to two fully controlled freeze-thaw cycles. The pilot systems were simple and constructed with low-cost materials, and were thus cost-effective. The freeze-thaw cycles satisfactorily replicated real conditions. The parameters monitored (temperature, EC, pH and redox) enabled extrapolation/comparison of the results obtained to seasonal variations observed in the full-scale treatment wetland. In addition, the parameters monitored within the wetland soil, combined with measurements of gas flux and analysis of porewater samples, provided critical clarifications regarding the processes taking place and overall process conditions. Based on the results obtained, the following conclusions can be drawn:

- The design approach and monitoring methodology developed were successful and the pilot wetlands functioned well.
- There were changes in purification efficiency due to freeze and thawing conditions in the pilot wetlands, with higher/lower removal observed in different conditions for different pollutants. Overall, soil frost formation and other winter-related conditions lowered the removal of some pollutants, for example those based on biological processes (e.g. sulphate).
- Flow conditions (such as residence time of water and active water volume) changed with the development of soil frost, leading to shorter water residence time and smaller peat surface area available for pollutant retention processes.
- Removal of arsenic and sulphate decreased during frost periods in the pilot wetlands, while removal of antimony slightly increased.
- Similar patterns in removal efficiency fluctuations during frost and frost-free periods were observed in the pilot wetlands and in the full-scale peatland-based treatment wetland. It can thus be concluded that the pilot wetlands simulated the full-scale system rather well.

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