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Department of Soil and Environment

Water flow and solute transport through a frozen clay soil

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Abstract

Freezing and thawing of soil affect water flow in the vadose zone for instance by altering soil structure or ice blocking parts of the pore system. Changes in soil hydraulic properties impact solute transport and therefore the risk that pesticides and other agrochemicals are transported towards groundwater. In models currently used for pesticide registration freezing of soil is not accounted for, even though some substances –especially those applied in autumn– may persist throughout the winter. The objective of this study was to quantify the effect of soil freezing on pesticide leaching for a Swedish clayey topsoil. The herbicides clomazone, propyzamide and diflufenican and the non-reactive tracer bromide were applied to undisturbed soil columns (20 cm high, 12.5 cm diameter), which were frozen to -2 °C and exposed to simulated rain. Three repetitions of the freezing-irrigation cycle were performed. Pesticide and bromide concentrations were measured in the effluent and compared to the results of non-frozen columns. X-ray tomography was used to visualise and quantify the macropore structure. Most concentrations of the least mobile pesticide (diflufenican) were below the limit of quantification. Relative leaching of pesticides was between 0.15 % and 2.67 % of the applied amount for clomazone and between 0.10 % and 1.67 % for propyzamide. Considering all three irrigation events no significant difference was found between frozen and non-frozen soil columns regarding pesticide transport. However, relative leaching in percent of the applied amount as well as concentrations of clomazone and propyzamide were significantly higher in the non-frozen columns during the second irrigation event. The non-reactive tracer showed the same trend, with the difference that the major part of the transport appeared already during the first irrigation event, showing significantly higher amounts of bromide transported in the non-frozen columns. A possible explanation is that soil freezing created fine voids and therefore increased diffusion into soil aggregates and reduced preferential transport.

Keywords: Pesticides, Freezing, Thawing, Leaching, Soil

Popular Science Summary

In modern agriculture pesticides are used to control weeds and pests. Those substances can be transported through the soil towards groundwater or via drainage tiles into surface waters, where they may affect ecosystems. The transport in the soil takes place in the soil pore system and depends on soil and substance properties, as well as the amount of water which is percolating downwards. Models are commonly used to assess the risk for ground- and surface water related to pesticide application. Those models are not accounting for freezing and thawing of soil water, even though big parts of the soils in the temperate zones are subject to seasonal freezing and thawing.

Soil freezing influences a number of processes in the soil. For instance, freeze-thaw cycles have been shown to change the soil structure resulting in the formation of cracks. Such features change the water flow paths and transport patterns in the soil. However, ice might also block parts of the soil pore space and therefore decrease infiltration into the soil.

Laboratory experiments were conducted to quantify differences in pesticide transport and water flow between frozen and non-frozen soil. In addition, bromide was used as a non-reactive tracer for solute transport, since in contrast to pesticides bromide does not adsorb to soil particles.

Water flow was delayed in frozen soil when the soil had a certain water content, which can be explained by ice blocking parts of the pore system. This resulted in ponding on the soil surface. The results indicate that solute transport through soil might be reduced by soil freezing, since the amount of bromide transported was larger in the non-frozen soil. No significant difference in the total amounts of pesticides transported were found, but pesticide leaching occurred later in the experiments in the frozen soil.

To be able to explain the results it would be necessary to assess changes in the soil structure during the experiment. This could be done by comparing X-ray images of soil columns before and after freezing and thawing cycles.

Contents

1. Introduction

Around 50 % of the land in the northern hemisphere is subject to seasonal freezing (Zhang et al., 2003). Freezing and thawing of soil affect structural properties as well as chemical and biological processes in the vadose zone, which influence infiltration, runoff and erosion (Hayashi, 2013; Zhang et al., 2003). Due to climate change higher temperatures – especially in the northern zone – as well as a change in precipitation patterns are expected (Kjellström et al., 2011). Climate models for Sweden project changed freeze-thaw cycles, shortened periods of persistent snowpack (Mellander, Lofvenius and Laudon, 2007) and increased winter precipitation (Kjellström et al., 2011), which may lead to substantial consequences for the hydrological cycle and soil hydrological processes including transport processes of potentially harmful substances through soil (Xu, 2000). Improving quantification of freezing-induced dynamics of water flow and solute transport in soil is therefore crucial to better predict the impacts of a changing climate on ground- and surface water quality (Ireson et al., 2013).

Processes in Soil due to Freezing and Thawing

Freezing and thawing of soil water is influencing several processes, which are related to water flow and solute transport in soil. Soil water in the largest pores freezes first, since it is bound at higher pressure potential than the water in smaller pores. When temperatures decrease further, freezing proceeds towards water bound in successively smaller pores. Thus, thawing will occur at lower temperatures for water in the smaller pores and will then – with increasing temperatures – continue to water held in larger pores. Since natural soils contain a distribution of pore sizes, depending on the soil texture and structure, there will be water in form of ice as well as liquid water in soils with a temperature of a few degrees below 0 °C. (Johnsson and Lundin, 1991)

The decrease of liquid water content during freezing causes a drop in hydraulic conductivity. Watanabe and Flury (2008) developed a physically based model to describe water flow in frozen soil. They showed that the decrease in hydraulic conductivity during soil freezing is similar to that while drying non-frozen soil as long as the temperature is close to 0 °C. When comparing two soils with the same total water content (both water and ice) of which one is frozen and the other one is not, the non-frozen soil will have a higher hydraulic conductivity, since its liquid water content is higher. The liquid water content is the critical factor for determining the hydraulic conductivity (Watanabe and Osada, 2016).

Furthermore, decreasing liquid water content during soil freezing causes a redistribution of solutes by exclusion of ions from the ice grid and increasing solute concentrations in the remaining liquid water (Stähli and Stadler, 1997). Since the freezing proceeds from the large towards the small pores, higher concentrations of solutes in the smaller pores could be the result of this exclusion process.

Differences in the spatial temperature distribution during freezing lead to gradients in water potential in soil with lower pressure in the parts of lower temperatures and therefore lower liquid water content. This can cause a transport of water towards the freezing front and formation of ice lenses and frost heave (Gray and Granger, 1986; Kane and Stein, 1983). Together with the water, solutes can be transported towards the ice front and diffuse between frozen and non-frozen layers with different concentrations (Stähli and Stadler, 1997).

Freeze-thaw cycles have been shown to influence soil structure. The change of volume of water in the soil due to phase change from liquid to solid and the formation of ice-lenses are causing higher pressures within soil pores, which can result in crack formation. Those structures can have a big impact on the hydraulic conductivity of soils. Hotineanu et al. (2015) showed that macropores were created in two clay materials (bentonite and kaolinite) due to freezing and thawing of the material. The pore size distribution shifted from a predominance of very fine pores ($< 1\,\mu\text{m}$) towards meso- and macropores ($> 10\text{-}100\,\mu\text{m}$). Chamberlain, Iskandar and Hunsicker (1990) reported creation of microscopic voids and macroscopic cracks due to freezing and thawing of a silty clay soil. They linked those structural changes to a significant increase of hydraulic conductivity after the freeze-thaw treatment.

Infiltration into Frozen Soil

Snowmelt in spring is a very important process in the hydrological cycle in the northern zone as a large part of the winter precipitation can be stored in the snow cover and be released within a short time period. The soil is often frozen during the time of snowmelt. Therefore, the infiltration capacity of the soil is limited, which affects the partitioning of meltwater between surface runoff and groundwater recharge.

Several studies have shown that soil water content and the proportion of ice-filled pores are of great importance for soil infiltrability. In a laboratory study about infiltration into frozen soil columns Moghadas et al. (2016) concluded that the soil water content was the critical factor affecting the time required to reach steady percolation. In soils with higher total water content more ice is blocking parts of infiltration paths and needs to melt before attainment of steady percolation. In a field study Kane and Stein (1983) showed that the infiltration rate into frozen soils was inversely proportional to the total water content and was controlled by the ice content near the surface.

Water flow in soil pores with a diameter larger than 0.3-0.5 mm is called macropore flow or preferential flow (Jarvis, 2007). Rapid flow of water in macropores leads to lateral non-equilibrium conditions, since only parts of the soil are conducting the water and large parts of the soil matrix are bypassed (Kördel, Egli and Klein, 2008). Models not accounting for preferential flow tend to underestimate vertical transport, since they assume that lateral dispersion of solutes in soil is fast compared to vertical convective transport (Jarvis, 2007).

Van der Kamp, Hayashi and Gallén (2003) demonstrated that macropores were of high importance for infiltration into frozen soils. They observed that soils in the grasslands in the Canadian prairie region were able to absorb most or all of the snowmelt, while significant surface runoff occurred in cultivated fields. They ascribed their findings to the well-developed macropore networks of the grassland soils. This approach was validated by a dye tracer study visualising the pathways of water infiltrated into frozen soil columns. The results showed that the applied solution infiltrated and percolated mainly along macropores and that dispersion into the soil matrix was minimal (Stadler et al., 2000). Earlier, Johnsson and Lundin (1991) had pointed out the importance of including fast infiltration rates through large ice-free pores of frozen soils into models simulating the fate of snowmelt. They found that infiltration and tile-drainage started long before the soil had thawed and before infiltration was predicted to occur by model simulations not accounting for macropore flow.

Transport of Pesticides

Agrochemicals like pesticides or nutrients can be transported through the vadose zone to groundwater or via drainage tiles, surface runoff and erosion into surface waters, where they may affect ecosystems (Flury, 1996). Rapid percolation of meltwater through partially frozen soil might lead to a transport of pesticides and nutrients along preferential flow ways bypassing the soil matrix contributing to increased leaching to ground- and surface waters. The European Union has set the threshold value for pesticide residues in drinking water to $0.1\,\mu g\,L^{-1}$. This limit is also used in risk assessment regarding groundwater contamination. The risk that a certain pesticide is transported towards ground- and surface waters is commonly analysed based on solubility in water, sorption and degradation characteristics of the substance. Properties of the soil and soil solution, as well as weather patterns and application time, also influence the pesticide behavior (Flury, 1996) and are included when assessing the risks of pesticides to the aquatic environment in the European Union (Campbell et al., 1998).

Preferential water flow in macropores can lead to high leaching losses of pesticides and has been found to be a dominant transport process at some sites (Ulén et al., 2014). Generally, the highest concentrations of pesticides in surface- and groundwater are found during the growing season (Frank, Clegg and Patni, 1991; Riise et al., 2004; Sharratt, Sander and Tierney, 2003). In some studies pesticides were also detected in spring prior to field application. In the corn belt, a region of the United States that is intensively used for agriculture, herbicides were detected in most of the river systems during spring flow (Thurman et al., 1991). Riise et al. (2004) showed that propiconazole was stored in the soil during winter in Norway and reappeared in the runoff water in March during the melting period. They also found a peak in bentazone concentration in the leachate at the same time. In a study performed in eastern Sweden Ulén et al. (2014) found autumn applied glyphosate in drainage water in connection with snowmelt after a cold winter. Similar observations were reported by Frank, Clegg and Patni (1991), who found residues of metolachor reappearing in the tile drain water in spring at a study site in Canada.

Overall, only a few studies have investigated the impact of frozen or partially frozen soils on pesticide leaching, even though it has been emphasized that improvement of existing models in regard to winter-related processes like soil freezing and thawing is of great importance for risk assessment of pesticides in the northern zone (Stenrød et al., 2016).

Aim

This study was performed to quantify the differences in pesticide transport between frozen and non-frozen soil from a Swedish agricultural topsoil with clayey soil texture. To do so, column leaching experiments were conducted under unsaturated conditions. The pesticides used in this study were clomazone, propyzamide and diflufenican, which present a range of different mobilities in soil. Pesticide transport is discussed in relation to differences in water flow, in macropore structure and in the transport of the non-reactive tracer bromide. The hypothesis was that transport of pesticides would be larger in frozen soil where mesopores were blocked by ice leading to increased transport in soil macropores due to limited lateral infiltration.

2. Material and Methods

2.1. Soil Properties, Soil Sampling and Sample Preparation

The soil samples used in this study were taken at Ultuna Egendom (59° 49´N 17° 39´E), which is about five kilometers south of Uppsala (middle Sweden).

The soil is a heavy clay soil classified as a Eutric Cambisol (Löfkvist, 2005) formed from postglacial clay, which overlies glacial clay (Andersson and Wiklert, 1959). Soil texture, organic matter content and particle density of the top soil were determined by the soil laboratory at the Department of Soil & Environment (SLU) for five columns after the experiment had been performed. The results are presented in table 2.1. The crop was wheat sown in September 2015. Crop residues in the soil indicated a ploughing depth of about 20 cm.

Table 2.1.: Soil properties.

Property	Value
Texture class[1]	Clay
Clay	55 %
Silt	33 %
Sand	12 %
Organic matter	4 %
Particle density	2.6 g cm^{-3}

[1] Soil texture classification USDA.

Twelve undisturbed soil columns (20 cm high, 12.5 cm diameter) were sampled from the topsoil on the 14th of April 2016 using a tractor-mounted hydraulic system which pressed plastic pipes into the soil. Then the soil columns were dug out by hand. The plastic pipes were filled with soil to approximately 18 cm height to allow for ponding during irrigation. The bottom parts of the soil columns were carefully prepared with a knife to preserve the structure. Small irregularities were filled up with moist sand to get an even surface. Each bottom was then covered with a piece of polyamide cloths (mesh size 50 µm) that was fixed using an elastic band. The columns were put on a sand bed for four days to adjust the water pressure to -30 cm to make sure that all continuous macropores were air-filled at the beginning of the experiment. During this treatment all columns gained weight.

To monitor the temperature of the soil in the columns assigned to the frozen treatment group (see chapter 2.2) two thermistors (Campbell Scientific 107, In Situ Instrument AB, Ockelbo, Sweden) per column were installed at a depth of 6 cm and 12 cm from the soil surface. The temperature was logged every 15 minutes. The results were used to ensure that the soil was frozen when starting the irrigation experiment. To better mimic field conditions, allow for top-down freezing of the soil columns and delay warm up during irrigation all columns were insulated with a 4.5 cm thick layer of glass wool. All samples were stored at +2 °C until the start of the experiment.

2.2. X-ray Tomography

The high-resolution industrial X-ray scanner (GE Phoenix v/tome/x m) at the Department of Soil & Environment (SLU) was used to visualize and quantify the soil macropore networks of the columns. The scanner has a 240 kV X-ray tube, a tungsten target (beryllium window) and a GE 16” flat panel detector. The spatial resolution of the reconstructed 3-D images was 115 µm. The actual resolutions was estimated to be the double pixel size and therefore 230 µm.

Parameters characterizing the macropore networks were calculated from the images. The first was macroporosity which is the pore volume divided by the total volume of the soil. The specific surface area of the macropore networks was calculated by dividing the pore surface area by the total volume of the sample. In addition, the mean macropore thickness and the fractal dimension of the macropore system were determined. The macropore thickness is calculated for each pore voxel and is given as the diameter of the largest sphere fitting into the pore while containing the voxel. The fractal dimension indicates how equally the macropores are distributed over the whole soil volume. A small number for the fractal dimension means that the pore volume is concentrated in one or a few big macropores, whereas a large number implies a more even distribution of macropores throughout the whole volume. The results are presented in table 2.2. Figure 2.1 shows some example images.

The X-ray scanning and image analyses were not carried out within this master's project. More detailed information about X-ray computed tomography and image processing and analyses is provided by Larsbo et al. (2013).

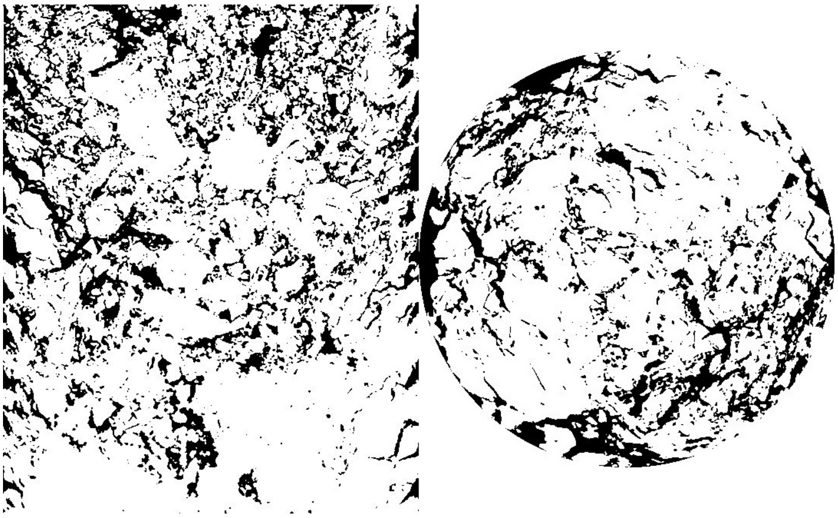

Figure 2.1.: Example 2D slices from X-ray scans, left: vertical slice (20 cm x 12.5 cm), right: horizontal slice (Ø 12.5 cm).

Table 2.2.: Measures of the macropore network. Mean values and standard deviations (in parenthesis).

Measure	Unit	Frozen columns	Non-frozen columns
Macroporosity	–	0.17 (0.05)	0.15 (0.01)
Specific macropore surface area	$mm^2\,mm^{-3}$	0.03 (0.01)	0.026 (0.003)
Mean macropore thickness	mm	1.91 (1.07)	1.66 (0.27)
Fractal dimension	–	2.64 (0.07)	2.63 (0.03)

Visual assessment of the images and preliminary results of the image analyses were used to sort out two columns that showed some disturbance due to the sampling procedure, in form of a large gap between column wall and soil and a larger stone at the bottom of the column. The remaining 10 columns were ranked by their macroporosity and grouped into pairs of similar macroporosity. One column of each pair was then randomly assigned to the frozen treatment group. This procedure was used to minimize differences in macropore network characteristics between the treatments. Using a two-tailed Student's t-test with a significance level of 0.05 no significant difference between the two treatment groups regarding the measures of the macropore system could be observed.

2.3. Chemicals

Analytical standards of the used pesticides clomazone, propyzamide and diflufenican were purchased from Dr. Ehrenstorfer GmbH, Augsburg, Germany. The three herbicides were chosen since they are authorized for use in Sweden, can be applied in autumn and represent a range of adsorption distribution coefficients and solubility in water, properties which are important for pesticide mobility in soil. Table 2.3 shows the pesticide properties according to the Pesticide Properties Database (Lewis et al., 2016).

Table 2.3.: Properties of the included pesticides (Lewis et al., 2016), applied doses of pesticides and bromide.

Substance	Applied dose (kg ha^{-1})	Solubility in water (mg L^{-1})	Koc[1] (cm^3 g^{-1})	DT50 lab[3] (days)
Clomazone	0.12	1102	287[2]	89
Propyzamide	0.5	9	840	47
Diflufenican	0.15	0.05	1996[2]	142
Bromide	50	–	–	–

[1] Organic carbon sorption distribution coefficient.
[2] Freundlich adsorption coefficients (Kfoc).
[3] Degradation half-life at 20°C.

Clomazone, propyzamide and diflufenican were dissolved in methanol and evenly applied to the soil surface using a pipette (5 ml solution per column) before the first freezing of the columns. The used pesticide doses (see table 2.3) are according to recommendations for Sweden for clomazone and propyzamide. Twice the recommended dose for diflufenican was used because of its relatively high limit of quantification of 0.05 µg L^{-1} and strong sorption to organic matter.

Potassium bromide (KBr; purity 99.5 %) was used as a non-reactive tracer and was purchased from Merck KGaA, Darmstadt, Germany. It was applied dissolved in 5 ml deionized water per column directly before the first irrigation event.

2.4. Experimental Set-up

After the application of the pesticides five columns (group “frozen”) were frozen at -2°C and the other five columns were stored at +2°C (group “non-frozen”). The columns were considered frozen when a temperature of -1.5°C or lower throughout the soil was reached. The first freezing took 21 days. The freezing went much faster after the first irrigation, so that the second and third irrigation could take place after ten days and nine days of freezing, respectively.

An indoor sprinkler system with space for ten soil columns was used to perform the irrigation. A detailed description of the rain simulator was provided by Liu et al. (2012). The columns were set up so that the bottom sides were exposed to atmospheric pressure. Rainfall was simulated with an average intensity of 5 mm h^{-1} for 4 h from nozzles located 80 cm above the center of each column. Therefore, approximately 20 mm of artificial rain were applied per irrigation round. The standard deviation between nozzles was 0.5 mm h^{-1}. There were no significant differences in irrigation intensities between the treatment groups.

The artificial rainwater used for irrigation had pH 5 and contained 0.58 mg NaCl L^{-1}, 0.70 mg $(NH_4)_2SO_4$ L^{-1}, 0.50 mg $NaNO_3$ L^{-1} and 0.57 mg $CaCl_2$ L^{-1}, which is similar to the composition of natural rainwater (Löv, personal communication, June 2016). For practical reasons the irrigation water had a temperature of 20 °C.

The water drained from the columns was collected in plastic bottles, which were exchanged by new bottles after approximately 20 ml of leachate had been collected. The last sample was taken in the morning the day after performing the irrigation. After the last sample was taken the columns were again frozen to -2°C (group “frozen”) or stored at +2°C (group “non-frozen”) until the next irrigation event. In total three repetitions of the freezing-irrigation cycle were performed.

Between 4 and 10 samples per column and irrigation event were collected. Depending on the total amount collected for one column during each irrigation event, 30 % to 50 % of the collected leachate were transferred to a glass bottle to get one volumetric grab sample per column and irrigation event for determination of pesticide concentrations. Thus, 30 samples were analysed for the three applied pesticides. Bromide concentrations were measured for all 247 samples separately. The pesticide samples were stored at -18°C, the bromide samples at +2°C before the analyses. All columns were weighed before the first irrigation event and after the last samples were collected.

2.5. Laboratory Analyses

Pesticide concentrations in the leachate were determined using a multiresidue analyses method according to Jansson and Kreuger (2010). The method is using an online solid-phase extraction coupled with HPLC/MS/MS referred to as OMK 57 (Jansson and Kreuger, 2010; Loos, 2012). Using this method the limit of detection (LOD) is 0.001 µg L^{-1} for clomazone as well as propyzamide and 0.005 µg L^{-1} for diflufenican, while the limit of quantification (LOQ) is 0.002 µg L^{-1} for clomazone and propyzamide and 0.05 µg L^{-1} for diflufenican. The analyses were done by the Organic Risk Pollutants Laboratory at the Department of Aquatic Sciences and Assessment (SLU).

Bromide concentrations were first measured using ion chromatography (IC). Due to problems with the ion chromatograph, the measurements were repeated using inductively coupled plasma mass spectrometry (ICP-MS). The measurements could not be repeated for three of the samples, since there was not enough sample left after the ion chromatography. The bromide analyses were done by the Inorganic Analyses Laboratory at the Department of Biology (Lund University).

2.6. Statistics

To compare the two treatment groups ("frozen" and "non-frozen") regarding the amounts of pesticides and bromide leached, the leached mass was calculated from the measured concentrations and effluent volumes. To enable comparisons between different substances leaching was normalized to the applied amounts. The Shapiro-Wilks test was used to test for normality of the datasets. Due to outliers, most of the datasets were not normally distributed and therefore the Wilcoxon test was used to test for significant differences between frozen and non-frozen columns. In case of normally distributed data Welch's variation of the t-test, which corrects for unequal variances, was used to test for significant differences between the treatment groups. The level of significance was set to $p = 0.05$.

The same tests were used to test, if the amount of drainage in each irrigation round and over the whole experiment was different between the treatments.

Statistical analyses and graphical presentation were carried out using the statistical software R version 3.0.2 (R Core Team, 2013). Data management and creation of data tables were done in LibreOffice version 4.2.8.2.

3. Results

3.1. Macropore Thickness

The two treatment groups did not differ significantly in any of the parameters characterizing the macropore networks (see section 2.2). However, figure 3.1 shows that column number f 5 (group “frozen”) had twice to three times as high mean macropore thickness as the other columns. The high mean macropore thickness of column number f 5 might have been caused by distortion of the soil structure during sampling.

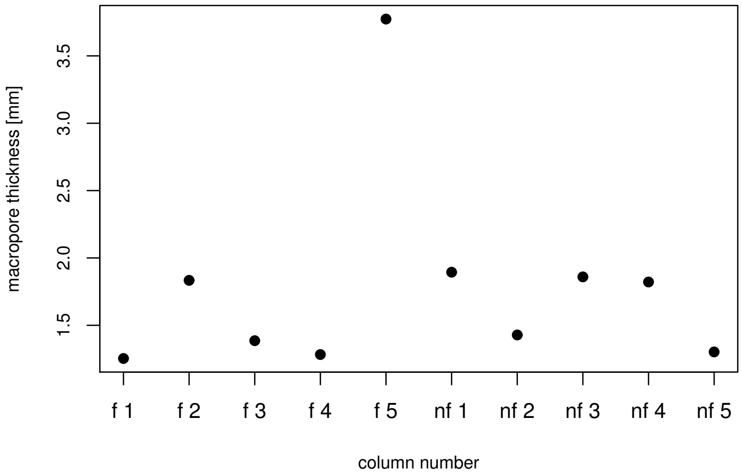

Figure 3.1.: Mean thickness of marcopores, f: group “frozen” nf: group “non-frozen”.

Following Graf and Hennings outlier test a value which differs more than four times standard deviation (± 4 sd) from the average (both calculated neglecting the suspected outlier) can be removed for further analyses (Rechenberg, 1982).

The mean macropore thickness of column f 5 was almost eight times the standard deviation higher than the average.

The results from column f 5 differed considerable from the results of the other columns, showing by far the highest measured concentrations and percentages of clomazone and propyzamide in the leachate. Column f 5 also behaved differently from the other frozen columns regarding temperature and water flow. Before the first irrigation event in the timespan between taking the samples out of the freezing room and starting the irrigation event, column number f 5 showed a much faster warming than the other frozen columns. This resulted in a temperature of around 3 °C throughout the column at the start of the first irrigation, so that the column could not be considered as frozen. Regarding the water flow, column number f 5 was the only column in the frozen treatment group that showed no or little delay of leachate compared to the non-frozen group during the second and third irrigation.

In the following sections the results from column f 5 were removed in favour of a better understanding of the effect of freezing. After removing column f 5 from the X-ray data the two treatment groups were once again compared regarding the measures of the macropore system. No significant differences could be observed and no further outlier could be found.

3.2. Water Flow

All leachate was collected during the experiments resulting in 220 samples weighing between 6 g and 60 g (mean 24 g).[1] Four to ten samples per column and irrigation event were taken. Figure 3.2 shows the cumulative leaching for each column over time in minutes after starting the irrigation. The amount of water applied during each irrigation event was approximately 20 mm. For a better comparability the amounts of drainage are also shown in millimeters. Surface ponding on the frozen columns was observed during the second and third irrigation, leading to a delay in drainage from the frozen columns.

The total amount of drainage for all three irrigation events varied between 30 mm and 60 mm per column. The large spread of the total amounts of drainage might be partly related to difficulties in setting fixed irrigation rates. The frozen columns showed a much larger variation in the amount of drainage during one irrigation event than the non-frozen columns. No statistically significant difference in the quantity of leachate could be observed between the treatment groups.

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[1] Excluding the samples from column f 5.

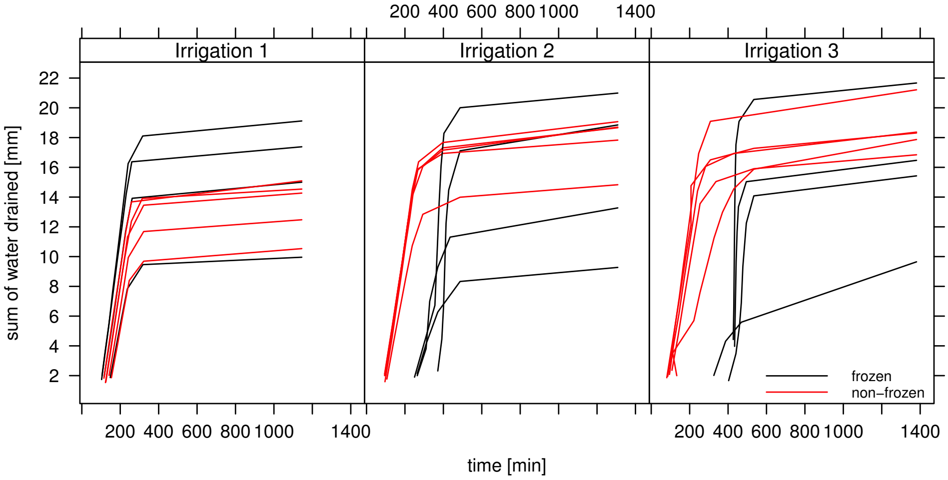

Figure 3.2.: Sum of water drained over time, t_0: start of irrigation event.

3.3. Temperature

The freezing of the soil took much longer before the first irrigation event when the soil was relatively dry (pressure potential of -30 cm) compared to the wetter soil before the second and third irrigation round. In general, the decrease in temperature in the frozen soil columns went from the surface towards the bottom, meaning that the insulation was sufficient to mimic field condition in that regard.

Furthermore, the measurements showed how the thawing proceeded during the irrigations. It was expected that the thawing during each irrigation would occur from the top towards the bottoms similar to the freezing. However, the thawing did not show a consistent pattern for all columns and irrigations events. Figure 3.3 illustrates the temperature measured in the frozen columns from the start of the irrigation events up to the point, when the last sample was collected.

The warming process went much faster as soon as zero degrees were exceeded. Overall, the thawing of the columns went quite fast despite of the insulation, so that the last leachate occurred when the columns of the frozen treatment group were not frozen anymore. One reason for the fast warming was that the irrigation water had a temperature of 20 °C.

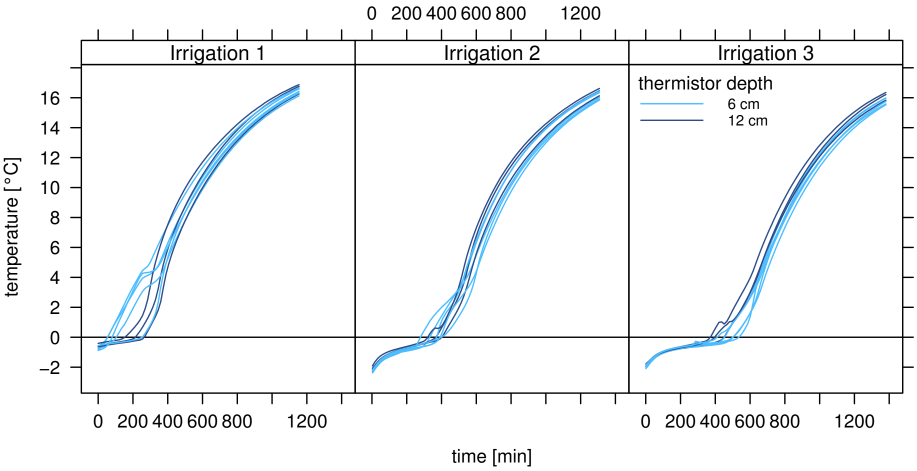

Figure 3.3.: Temperature of the frozen columns, t_0: start of irrigation event.

3.4. Bromide Transport

The concentration of bromide in the leachate was measured in all samples. The results are shown in figure 3.4, which presents the bromide concentrations at those points in time where the sample bottles were exchanged.

Bromide concentrations varied between 1.6 mg L^{-1} and 459.2 mg L^{-1}. The biggest difference between the treatment groups could be observed during the first irrigation, where bromide concentrations of more than 200 mg L^{-1} were solely found in leachate from columns of the non-frozen treatment group. During the second and third irrigation event lower bromide concentrations were found. All except two concentrations were below 100 mg L^{-1} in the latter two rounds. In addition, smaller differences between the treatment groups were observed. Statistically significant differences in bromide concentrations between treatment groups were only found during the first irrigation event with significantly higher concentrations in the drainage from the non-frozen columns.

To account for the different sample volumes the concentrations were converted to total weight and then normalized to the amount of bromide that was applied to each column. The results are shown in figure 3.5, where the sum of the leached bromide in percent of the applied amount is plotted over time in minutes after starting the irrigation events. Between 3.0 % and 39.3 % of the applied bromide leached during one irrigation event. For all three irrigation events leaching was between 24.6 % and 66.7 % with an average of 53.1 %.

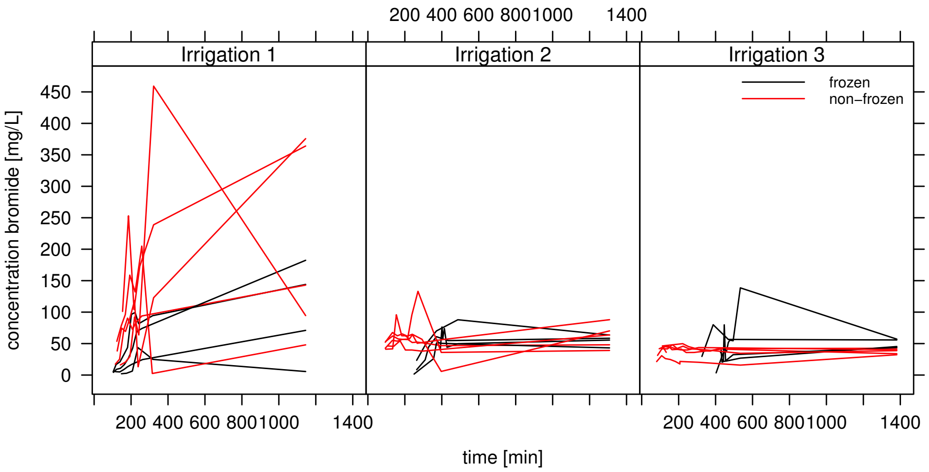

Figure 3.4.: Concentration of bromide over time, t_0: start of irrigation event.

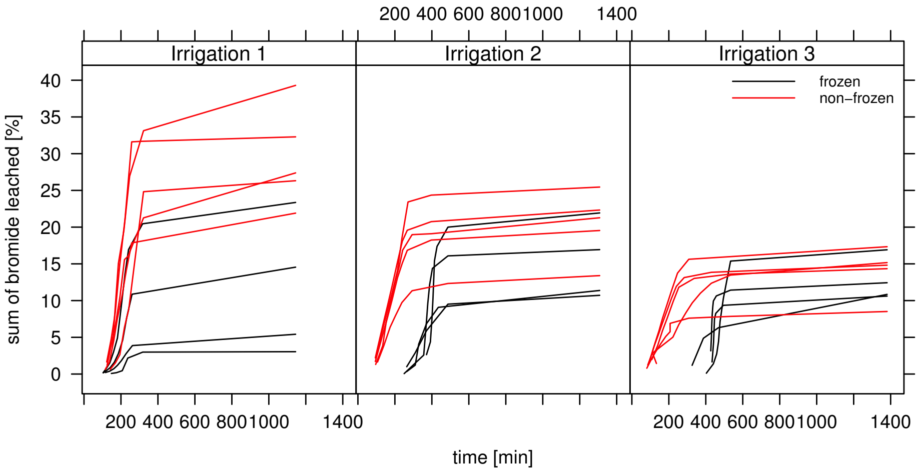

Figure 3.5.: Sum of bromide leached in percent of the applied amount, t_0: start of irrigation event.

During the first irrigation round significantly higher bromide leaching was observed in the non-frozen treatment group compared to the frozen columns.

3.5. Pesticide Transport

The concentrations of clomazone, propyzamide and diflufenican were measured for one volumetric grab sample per irrigation round and column. The results are shown in figure 3.6, 3.7 and 3.8 for each substance separately.[2]

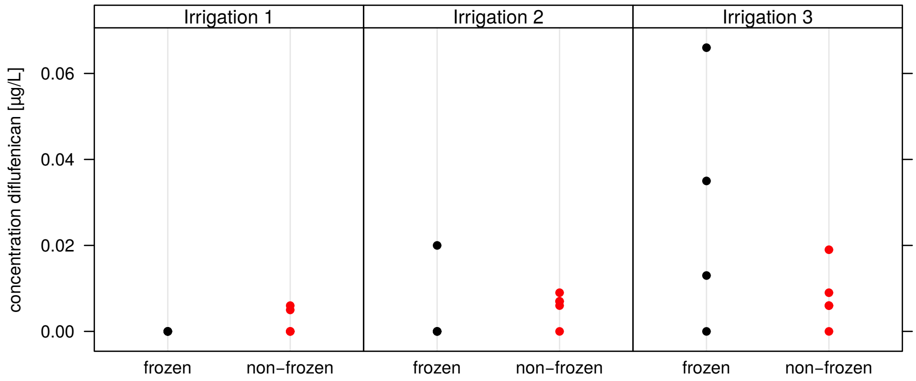

Figure 3.6.: Concentration of diflufenican.

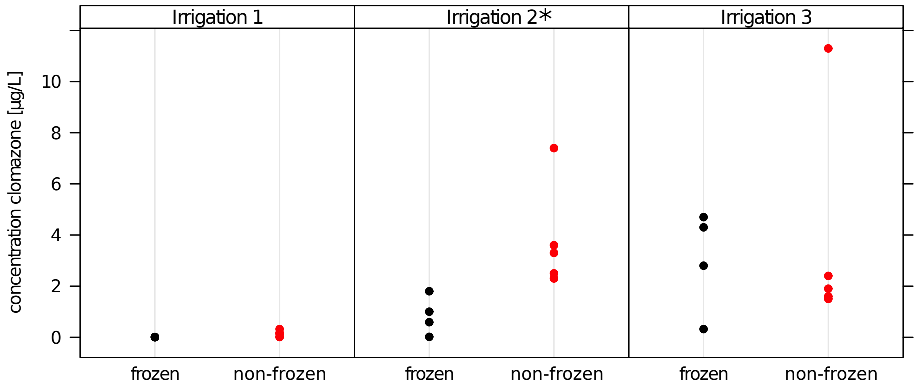

Figure 3.7.: Concentration of clomazone. *Significant difference.

For diflufenican all measured concentrations except one were below the limit of quantification (LOQ) of 0.05 µg L^{-1}. Therefore, no further statistical analyses were performed for diflufenican. In contrast, all measured concentrations of clomazone

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[2] Excluding the samples from column f 5.

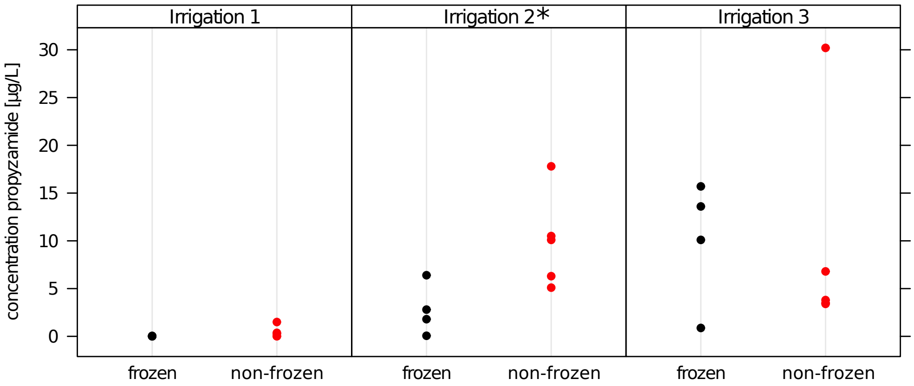

Figure 3.8.: Concentration of propyzamide. *Significant difference.

and propyzamide were higher than the limit of quantification (LOQ) of 0.002 µg L^{-1}. The highest measured concentrations were approximately 11.3 µg L^{-1} of clomazone and 30.2 µg L^{-1} of propyzamide.

For a better comparability between the pesticides with different doses applied and between the columns with different amounts of drainage the concentrations were converted into percent of the applied amount. The results are presented in figure 3.9 and 3.10. The amounts of pesticide leached per irrigation round varied between 0 % and 1.7 % (mean 0.3 %, STD 0.4 %) for clomazone and smaller than 1 ‰ and 1.1 % (mean 0.2 %, STD 0.3 %) for propyzamide. For both pesticides almost no leaching occurred during the first irrigation round, while leached amounts were similar during the second and third irrigation event.

The leaching of clomazone and propyzamide was significantly higher in the non-frozen treatment group during the second irrigation. Differences in pesticide leaching between the treatment groups during the first and third irrigation round as well as the cumulative amounts of all three rounds were not significant.

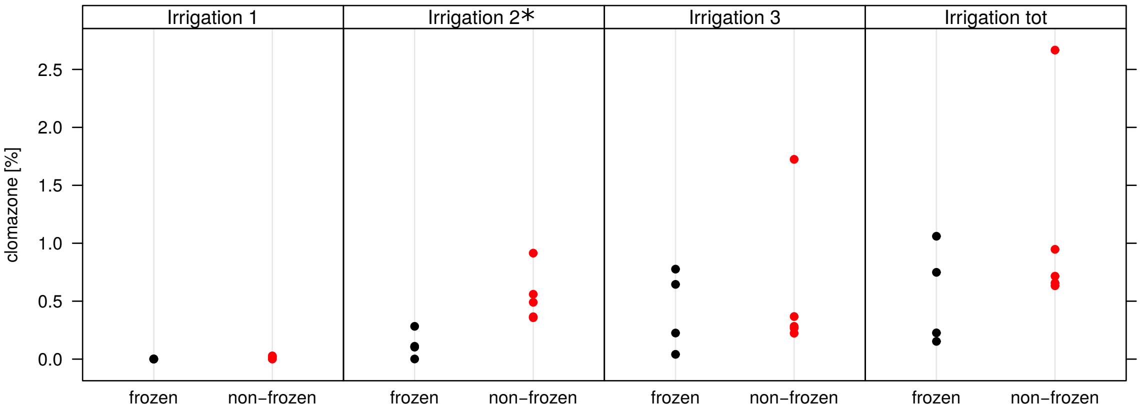

Figure 3.9.: Clomazone leached in percent of the applied amount. *Significant difference.

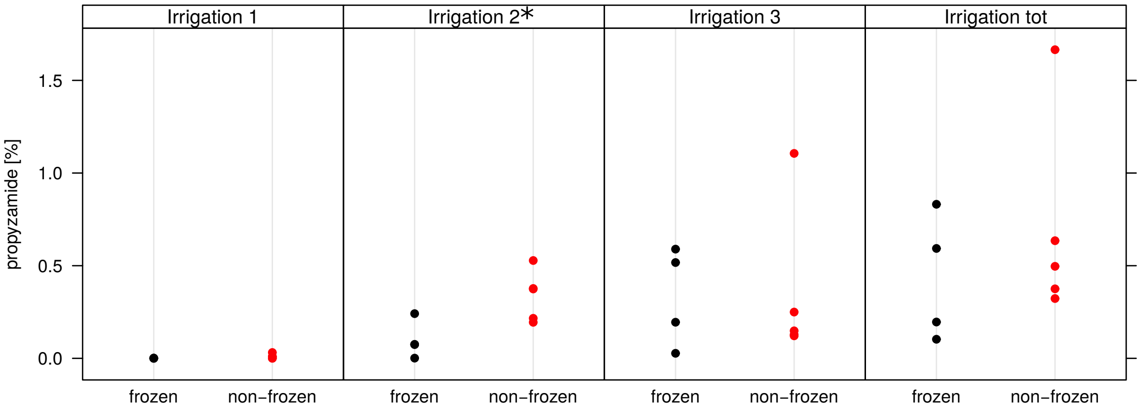

Figure 3.10.: Propyzamide leached in percent of the applied amount. *Significant difference.

4. Discussion

The discussion focuses on three issues concerning water flow and solute transport in frozen soils: (1) method performance and limitations of the laboratory experiments, (2) evaluation and comparison of the results with other studies and (3) implications of the findings and the need for further research.

4.1. Method Performance

This section includes an evaluation on how well the experimental set-up and the equipment fulfilled their purpose in the research about solute transport in frozen soil. Generally, advanced equipment such as a tractor-mounted sampling system, which lowers the risk of disturbing the soil structure, a large freezing room with the possibility to exactly set the temperature, a X-ray scanner to visualise and quantify soil macropores and a rain simulator were used in this study. However, few replicate columns and a relatively small amount of samples – especially for pesticide analyses – could be analysed due to financial reasons. The parts of the experimental set-up which were considered as most problematic are discussed below.

Water Temperature

The irrigation water had a temperature of 20 °C, since deionized water from the tap was used. Efforts to cool down the irrigation water with ice cubes failed due to the very large volume of the tank (1000 L). In addition, the room temperature was around 20 °C, which is much higher than expected air temperatures in spring during snow melt. The warm irrigation water as well as the high room temperature probably led to much faster thawing of the soil than can be expected under field conditions. Moghadas et al. (2016) claimed that the high water temperature was the most significant experimental limitation in their study about infiltration into frozen soils, even though their water had a temperature of 8–9 °C. Based on energy balance calculations for their experiments they stated that thawing of the whole columns (1.2 m high, 0.1 m diameter) would take around three to five times longer using water at 1.5 °C instead of 8 °C depending on the soil type.

Irrigation

Another weakness in the experimental set-up was related to difficulties in setting fixed irrigation rates in the rain simulator. All ten nozzles were connected to one hose. Before entering this hose the water passed through a regulator, where a constant pressure was set. To reach the requested rainfall intensity of 5 mm h^{-1}, the time a nozzles was on each minute was adjusted using a data logger. Since changing the settings for one nozzle influenced the pressure remaining for the other nozzles, calibrating the system in a way that all nozzles had the same intensity was a time consuming task. Even when using exactly the same settings irrigation intensities sometimes varied over time. The reasons for this problem are not clear. Possible explanations are that regulator at the inlet of the hose did not work in a robust way or that deposits in nozzles might have partly blocked the water flow at some times.

After each irrigation event one particular calibration round of the rain simulator was performed using exactly the same settings and the same duration (4 h) as in the preceding irrigation event. In the following, intensities determined by those calibration rounds are called calibration intensities. As explained before they might be different from the actually applied intensities during the irrigation experiments. Another way to estimate the amounts of water applied per column in all irrigation events is to add up the gain in column weight after the last irrigation, compared to the initial weight, and the amount of leachate. Unfortunately, the total applied amounts determined by this method are not consistent with the amounts calculated using the calibration intensities. One column (number f 1) showed a particularly large difference with more than 200 ml (corresponding to 16 mm) less irrigation when using the weight method. It is the same column showing by far the lowest amount of bromide leaching. An explanation for this large discrepancy could be that some water was lost through the holes in the column walls where thermistors were installed and was absorbed by the insulation. Similar observations were made by a research group at the Norwegian Institute of Bioeconomy Research (NIBIO) doing similar experiments. This group used non-absorbing insulation material and could observe irrigation water leakage through the holes for the temperature sensors and along the wires for many of the frozen columns (Roger

Holten, NIBIO, personal communication). This could also explain the larger spread in the amount of water drained in the frozen columns compared to the non-frozen columns (compare figure 3.2).

Consequently, there is uncertainty about the exact irrigation intensities and the amount of water applied to each column. Since the amount of water and the irrigation intensity have crucial impact on water flow and solute transport through soil (Jarvis, 2007), this complicates the evaluation of the results of the study.

Analyses of Diflufenican, Water Content and Bromide Application

As described in the results (see section 3.5) diflufenican concentrations above the limit of quantification (LOQ) were only found in one sample. To study the behavior of immobile pesticides in leaching experiments diflufenican concentrations should be measured using gas chromatography coupled to a mass spectrometer (GC-MS) instead of the more cost-effective multiresidue method used in this study (see section 2.5). With GC-MS the LOD and LOQ for diflufenican concentrations can be lowered to $0.002\,\mu g\,L^{-1}$ and $0.004\,\mu g\,L^{-1}$, respectively (Jenny Kreuger, SLU, personal communication). This corresponds to a 2.5 times lower LOD and 12.5 times lower LOQ compared to the multiresidue method.

The columns gained weight in the four days on the sand bed, which means that the water pressure was lower than the set -30 cm. In my experiment the sand bed was used to make sure that all continuous macropores were air filled before the X-ray scanning. For setting a well defined water pressure before the experiments, saturation of the columns before placing them on the sand bed would have been necessary. In addition, the soil water content should be measured preferably before each freezing, since it is a critical factor controlling hydraulic conductivity of frozen soil and the thawing speed (Kane and Stein, 1983; Moghadas et al., 2016).

Another point that could be improved in the experimental set-up is the point in time of the bromide application. In contrast to the pesticides, which were applied just before the first freezing of the columns (group “frozen”), bromide was applied on frozen soil just before the first irrigation event. This means that effects of the freezing process on bromide distribution can not be evaluated based on the data for the first irrigation event.

4.2. Evaluation of the Results

In the following, observations about freezing and thawing of the soil, water flow and solute transport are set in a theoretical context and are compared to other experimental findings.

Freezing and Thawing

The time needed to reach around -2 °C throughout the soil of the frozen columns before the first irrigation event, when the soil was relatively dry (pressure potential of -30 cm), was more than twice as long as before the second and third irrigation round, when the soil was wetter. The opposite was expected due to the latent heat released during freezing of water. However, it seems that the low thermal conductivity of air (0.025 $\mathrm{W\,m^{-1}\,°C^{-1}}$) compared to water (0.59 $\mathrm{W\,m^{-1}\,°C^{-1}}$) was the critical factor and that the larger water content at the second and third freezing acted as a heat conductor (Weast, 1986).

The thawing during the irrigation did not always show the expected direction from the top towards the bottoms and was not consistent for all columns and irrigation events. It was not possible to keep the insulation underneath the columns during the irrigation and collection of the leachate, which means that both bottoms as well as surfaces were exposed to room temperature (20 °C). In addition, water and related heat transport through the column can be considered to be fastest along macropores (Jarvis, 2007), which are not equally distributed throughout the column.

The increase of temperature in the frozen columns went much faster as soon as zero degrees were exceeded (see section 3.3). Similar observations were made by Stähli and Stadler (1997) performing a study on water and solute dynamics in frozen soil columns. Their data showed that the soil temperature stayed around zero degrees for several days when thawing the soil columns from -5 °C to +3 °C. In the same time the liquid water content increased throughout the columns, showing that at 0 °C the energy is used for melting the ice rather than for temperature increase. Moghadas et al. (2016) reported that thawing of soils with higher water content took more time than in lower moisture soils. The temperature of the frozen columns in my experiments was higher when starting the first irrigation, due to a longer time needed to prepare the first irrigation, compared to the later two irrigation events, which makes it difficult to compare thawing rates.

Water Flow and Ponding

The drainage curves for the frozen and non-frozen treatment group (see figure 3.2) look very similar for the first irrigation event, even though the frozen columns were at least still partially frozen ($< 0\,°C$) when the largest part of drainage occurred (compare figure 3.3). That is in accordance with a conceptual model stating that the infiltration capacity of frozen soil is not limited as long as large air-filled pores dominate the permeability (Granger, Gray and Dyck, 1984). The two highest amounts of drainage during the first irrigation are actually found for two frozen columns, which could be related to reduced infiltration into the frozen soil matrix. Uncertainties about the applied irrigation amounts (see section 4.1) make it difficult to validate this assumption.

A delay in drainage and ponding on the frozen columns could be observed during the second and third irrigation event. These observations are consistent with results by Moghadas et al. (2016) who found that water breakthrough and attainment of steady percolation required much longer time in frozen soil columns with higher water content. Even though the water content in my study was not measured, it can be assumed that the water content of the soil was much higher after the first irrigation than before. Moghadas et al. (2016) explained this delay of drainage and ponding on the soil surface by ice blocking the pore system. Also, other studies have found extremely low hydraulic conductivities of frozen soil with high total water content (Kane and Stein, 1983).

In my experiments a large increase in infiltration rates of the ponded water into partially frozen soil was observed at a certain point during the later two irrigation events (compare figure 3.2 and 3.3). This might be explained by partial thawing of ice blocking the conducting macropores (Kane and Stein, 1983).

Several authors have pointed out the relevance of preferential water flow through macropores for infiltration into frozen soil (Granger, Gray and Dyck, 1984; Johnsson and Lundin, 1991; Stadler et al., 2000; Van der Kamp, Hayashi and Gallén, 2003). To evaluate, if preferential flow occurred in my study, the arrival time of the first leachate during the first irrigation was compared to the pore space and irrigation rate. Since the water pressure of the columns were set to -30 cm before starting the experiments, all pores with a diameter of more than approximately 0.1 mm (Young–Laplace equation) could be assumed to be air filled before the first irrigation. Calculating with the average macroporosity of 0.16 (see section 2.2), an average soil depth of 18 cm and an irrigation rate of $5\,\mathrm{mm\,h^{-1}}$, it would have taken around 340 min of irrigation to fill up all those pores. The first leachate occurred already after 100-150 min of irrigation. Since the first drainage samples of all columns contained bromide, obviously faster transport occurred in some parts of the pore system.

Solute Transport

The hypothesis stated before conducting the experiments was that solutes might be transported faster in frozen soil due to limited lateral infiltration into the soil matrix and therefore enhanced preferential transport. However, the results of the solute transport experiments (see section 3.4 and 3.5) did not confirm this hypothesis, but rather indicate the opposite. Higher bromide concentrations during the first irrigation event and higher pesticide concentrations during the second irrigation event in the drainage of the non-frozen columns reveal that soil freezing might delay or even reduce solute transport.

The relative amount of bromide leached was significantly higher in the non-frozen columns during the first irrigation event and when considering the whole experiment. The higher leaching of bromide in the non-frozen columns during the first irrigation cannot be attributed to higher water flow (see section 3.2). A possible explanation is that the freeze-thaw treatment created medium sized pores. Such structures would increase the surface area of the mesopore system, which would potentially increase diffusion of the solutes into soil aggregates, and increase transport in mesopores, which is slower than macropore transport. Accordingly, creation of mesopores has the potential to reduce leaching. Validation of this theory would require high resolution X-ray imaging of the columns before and after the experiments to be able to compare the soil structure before and after the freeze-thaw cycles. Chamberlain, Iskandar and Hunsicker (1990) found that freezing and thawing of a silty clay soil changed the structure on microscopic scale, creating large voids where the structure was relatively homogeneous before the freezing.

As described in the method part (see section 2.5) there has been a problem with the bromide analyses using the ion chromatography (IC). Some of the measured bromide concentrations were extremely high. Using these values the amounts of bromide in the leachate would have been several times higher than the applied amount. The measurements were repeated using inductively coupled plasma mass spectrometry (ICP-MS) which generated much more reasonable results (see section 3.4). Unfortunately, the ICP-MS measurement could not be performed for three of the 247 samples, since not enough sample volume was left. For those samples the bromide concentrations measured with the IC were used in the analyses of the data. They did not belong to the extreme values of the IC measurements and the concentrations fit well into the range of the concentrations measured by the ICP-MS. Therefore, it seems unlikely that they caused the higher bromide leaching in the non-frozen group.

The transport of pesticides through the soil columns was delayed compared to bromide transport. Only very low amounts of pesticides leached during the first irrigation event, while the largest amounts of bromide were found in the drainage samples from the first irrigation event. This can be explained by the much higher mobility of bromide, which is considered to not adsorb to soil particles in considerable amounts. Therefore, faster transport of bromide through soil can be expected, since all used pesticides adsorb at least to a certain extent to soil organic matter. In addition, the pesticides were applied to the soil before the first freezing, while the bromide solution was applied just before the first irrigation. Accordingly, parts of the applied pesticides have probably diffused into soil aggregates and were hence less susceptible to infiltrating water and preferential flow than the bromide on the soil surface.

In general, measured propyzamide concentrations were much higher than clomazone concentrations. The difference can partly be explained by the more than four times higher dose applied of propyzamide (see section 2.3). The slightly higher percentages of leached clomazone can be explained by stronger sorption of propyzamide (higher Koc of propyzamide, see table 2.3). When comparing the relative leaching of the two pesticides clomazone and propyzamide during the three irrigation events (compare figure 3.9 and 3.10) it is remarkable how similar the patterns look. This is in consistence with results of other studies. For example Kladivko et al. (1991) found that losses of different pesticides were according to adsorption coefficients of the pesticides, but the timing of the leaching did not differ. The amounts of leached pesticides could not be clearly linked to the water flow, even though low leaching occurred in column number f1, which had also lowest amounts of drainage (see section 4.1).

In contrast to bromide, no significant difference in the total amount of leached pesticides considering all three irrigation events was found between the treatment groups. However, significantly higher pesticide transport through non-frozen columns during the second irrigation was observed. Theoretically, exclusion from the ice grid (Stähli and Stadler, 1997) together with freezing from large towards small pores (Johnsson and Lundin, 1991) could have led to a redistribution of pesticides towards smaller pores in the frozen soil columns. The ponding on the soil surface of the frozen columns together with the following fast drainage of the ponded water during the second irrigation (see section 3.2) could then have resulted in low pesticide concentrations in the drainage, since the water was bypassing the pesticide containing soil matrix. However, this process can not explain the higher leaching of bromide in the non-frozen columns during the first irrigation, since bromide was applied directly before the first irrigation and not before the freezing.

4.3. Implications and Further Research

The results of my study indicate that solute transport through the vadose zone might be reduced or at least delayed in frozen soil. Formation of fine voids and redistribution of solutes during soil freezing were discussed as possible explanations for these findings. Further research on structure formation due to soil freezing on micro scale and its impact on diffusion into soil aggregates is necessary to test these hypotheses. This could be achieved by combining transport studies in frozen soil with X-ray visualisation of structural changes due to freezing. Torrance et al. (2008) demonstrated that X-ray imaging can be used to visualise the formation of ice lenses in frozen soil samples. Further development of these methods, possibly in combination with visualisation of solute transport in soil (Koestel and Larsbo, 2014), could lead to an improved understanding of the processes happening in soil during freezing and therefore improve predictions of water flow and solute transport.

In addition, further studies about solute transport in frozen soil should be performed under more natural conditions. Important factors that should be adjusted are air- and water temperature, which can be expected to be much lower than in my study (both 20 °C) around the time of snowmelt.

In the presented study, only one soil with a very high clay content was included. Soil texture influences many processes related to soil freezing and water flow through frozen soil. Previous studies have shown that coarser textured soils need less time to reach a constant temperature regime during freezing than soils with finer texture (Stähli and Stadler, 1997) and differences in water flow between frozen and non-frozen columns were greater in finer textured soils (Moghadas et al., 2016). Including soils with different texture in further experiments about solute transport in frozen soil is essential to understand the controlling processes.

Ponding of irrigation water occurred on the frozen soil surface during the later two irrigation events. In the field ponding can lead to higher surface runoff depending on the topography. Increased amounts of surface runoff have the potential to increase the transport of pesticides stored close to the soil surface towards surface waters and decrease transport of pesticides towards drainage systems and groundwater. The effect of soil freezing on the partition of precipitation into infiltration and surface runoff is important to be considered in risk assessment models.

5. Conclusion

An experimental study of pesticide and bromide transport through frozen soil was conducted in the laboratory with the objective of evaluating differences in solute transport and water flow between frozen and non-frozen soil.

No significant differences in the total amounts of pesticides leached between frozen and non-frozen columns were observed. However, amounts of pesticides in the drainage during the second irrigation were higher in the non-frozen columns. The trend was more apparent in the results for the non-reactive tracer bromide, which showed significantly higher bromide transport in the non-frozen columns during the first irrigation and for the total amounts transported during the whole experiment. These results are in contrast to the formulated hypothesis expecting faster solute transport through frozen soil. The hypothesis was based on the assumption that a frozen soil matrix would limit lateral infiltration and diffusion of solutes into soil aggregates and lead to fast preferential transport in macropores.

Ponding of irrigation water on the soil surface of the frozen soil columns led to a delay of drainage during the second and third irrigation. These observations are in consent with other studies reporting low hydraulic conductivities in frozen soils with higher initial water content. It shows that frozen soil can have an impact on the partitioning between infiltration and surface runoff during snowmelt, likely increasing the total amount of surface runoff. This aspect should be considered in risk assessment models.

The temperature of the irrigation water (20 °C) in this study led to fast thawing of the frozen columns during the experiments. This was one of the major limitations of the experimental set-up. Different times of pesticide and bromide application made it difficult to compare bromide and pesticide transport. Despite these problems the study demonstrated differences in water flow and solute transport between frozen and non-frozen soil. Additional studies including visualisation and comparison of the soil structure before and after the freeze-thaw cycles are essential to fully understand those differences.

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Appendix

A.1. Abbreviations

DT50: Degradation half-life
GC-MS: Gas chromatography/mass spectrometry
HPLC/MS/MS: High performance liquid chromatography/tandem mass spectrometry
IC: Ion chromatography
ICP-MS: Inductively coupled plasma mass spectrometry
Kfoc: Freundlich adsorption coefficients
Koc: Organic carbon sorption distribution coefficient
LOD: Limit of detection
LOQ: Limit of quantification
OMK: Organic Risk Pollutants Laboratory
USDA: United States Department of Agriculture

A.2. Pesticide and Bromide Transport

Table A.1.: Diflufenican transport.

Column	Irrigation 1 µg L^{-1}	Irrigation 2 µg L^{-1}	Irrigation 3 µg L^{-1}
f 1	0	0	0.013
f 2	0	0.020	0.066
f 3	0	0	0
f 4	0	0	0.035
f 5	0	0.040	0.030
nf 1	0.006	0.007	0.006
nf 2	0	0.007	0
nf 3	0	0.009	0.019
nf 4	0.005	0.006	0.009
nf 5	0	0	0.006

Table A.2.: Clomazone transport.

Column	Irrigation 1		Irrigation 2		Irrigation 3	
	µg L^{-1}	%	µg L^{-1}	%	µg L^{-1}	%
f 1	0	0	0.015	0.001	2.8	0.23
f 2	0.008	0.001	1.8	0.28	4.3	0.78
f 3	0.01	0.001	1.0	0.11	0.3	0.04
f 4	0.004	0.001	0.59	0.10	4.7	0.65
f 5	0.27	0.03	13.6	2.36	9.9	1.63
nf 1	0.17	0.02	3.6	0.56	2.4	0.37
nf 2	0.017	0.002	3.3	0.49	1.5	0.22
nf 3	0.32	0.03	7.4	0.92	11.3	1.72
nf 4	0.14	0.02	2.5	0.36	1.6	0.28
nf 5	0.008	0.001	2.3	0.37	1.9	0.27

Table A.3.: Propyzamide transport.

Column	Irrigation 1		Irrigation 2		Irrigation 3	
	µg L^{-1}	%	µg L^{-1}	%	µg L^{-1}	%
f 1	0.002	0.00004	0.062	0.001	10.1	0.19
f 2	0.02	0.0008	6.4	0.24	13.6	0.59
f 3	0.052	0.002	2.8	0.07	0.88	0.03
f 4	0.011	0.0004	1.8	0.08	15.7	0.52
f 5	0.67	0.020	42.1	1.74	31.4	1.24
nf 1	0.3	0.008	10.1	0.38	6.8	0.25
nf 2	0.021	0.0006	10.5	0.37	3.4	0.12
nf 3	1.5	0.032	17.8	0.53	30.2	1.11
nf 4	0.37	0.011	6.3	0.22	3.5	0.15
nf 5	0.012	0.0003	5.1	0.19	3.8	0.13

Table A.4.: Water flow and bromide transport in the frozen soil columns.

Column	Sample	Irrigation 1		Irrigation 2		Irrigation 3	
		Drainage [mm]	Bromide [%]	Drainage [mm]	Bromide [%]	Drainage [mm]	Bromide [%]
f 1	1	1.87	0.08	2.13	1.00	2.01	1.19
f 1	2	1.82	0.10	1.99	1.89	2.30	3.68
f 1	3	2.18	0.27	2.15	3.02	1.28	1.45
f 1	4	1.97	1.72	2.05	3.61	4.06	4.53
f 1	5	1.63	0.81	0.95	1.20		
f 1	6	0.50	0.06				
f 2	1	1.74	0.17	2.31	2.64	4.42	3.16
f 2	2	1.56	0.53	2.13	1.73	2.23	1.76
f 2	3	2.00	0.84	2.21	3.37	4.21	2.22
f 2	4	2.31	1.48	2.13	2.54	2.54	1.09
f 2	5	2.16	1.89	3.46	5.12	2.42	0.99
f 2	6	2.27	4.38	2.23	1.97	1.69	0.73
f 2	7	2.19	4.36	2.63	2.62	1.56	0.69
f 2	8	2.03	3.31	1.74	1.93	1.47	0.79
f 2	9	1.86	3.51			1.11	1.00
f 2	10	1.01	2.91				
f 3	1	1.92	0.21	2.00	0.34	1.66	0.11
f 3	2	1.87	0.19	1.81	0.87	1.82	1.27
f 3	3	1.84	0.33	3.19	2.86	1.80	1.36
f 3	4	1.78	0.46	2.28	2.78	1.63	1.69
f 3	5	1.88	0.63	2.03	2.22	2.42	2.69
f 3	6	2.40	0.97	1.96	2.30	2.92	3.18
f 3	7	2.22	1.09			1.83	5.08
f 3	8	1.08	1.54			1.34	1.53
f 4	1	2.00	0.17	1.90	0.06	3.97	1.64
f 4	2	1.58	0.29	4.82	2.52	3.48	1.67
f 4	3	1.96	0.42	4.60	4.65	2.21	0.99
f 4	4	2.15	0.72	2.27	2.41	2.00	3.20
f 4	5	2.20	1.18	2.49	2.53	1.69	0.76
f 4	6	2.10	1.81	2.19	2.21	1.69	1.09
f 4	7	2.22	3.07	1.72	1.70	1.43	1.26
f 4	8	2.16	3.21	0.99	0.85		
f 4	9	1.01	3.69				
f 5	1	1.88	1.11	2.29	0.67	1.87	0.39
f 5	2	1.92	1.24	2.79	1.74	2.50	1.08
f 5	3	2.17	1.79	2.31	1.35	2.57	1.09
f 5	4	1.88	3.46	2.40	1.39	2.94	1.06
f 5	5	2.20	4.81	2.30	1.19	2.00	0.78
f 5	6	2.30	3.93	2.09	1.05	2.61	0.99
f 5	7	1.73	5.68	1.89	0.99	1.60	0.83
f 5	8	0.58	0.06	2.08	1.62	1.79	1.17
f 5	9			1.68	1.46	1.22	0.95
f 5	10			0.79	0.59	0.61	0.34

Table A.5.: Water flow and bromide transport in the non-frozen soil columns.

Column	Sample	Irrigation 1		Irrigation 2		Irrigation 3	
		Drainage [mm]	Bromide [%]	Drainage [mm]	Bromide [%]	Drainage [mm]	Bromide [%]
nf 1	2	1.98	3.10	3.22	3.56	2.10	1.88
nf 1	3	1.87	3.61	2.17	2.34	2.00	1.85
nf 1	4	2.02	6.42	2.30	2.61	1.69	1.36
nf 1	5	2.40	6.35	2.53	2.90	2.18	1.78
nf 1	6	2.56	10.49	1.93	2.00	2.02	1.67
nf 1	7	1.54	0.08	1.67	1.75	2.33	1.67
nf 1	8	0.63	0.60	1.49	1.39	1.65	1.19
nf 1	9			1.35	1.30	0.87	0.72
nf 1	10					1.43	0.97
nf 2	1	1.83	0.63	2.10	2.19	2.00	1.44
nf 2	2	2.00	1.01	3.15	4.25	1.52	1.41
nf 2	3	2.00	2.91	2.19	2.73	2.18	2.17
nf 2	4	1.68	3.04	2.23	2.92	1.89	1.71
nf 2	5	2.20	3.20	2.54	3.14	1.95	1.64
nf 2	6	1.96	3.31	2.18	2.83	1.72	1.32
nf 2	7	2.00	3.75	1.49	1.51	1.73	1.32
nf 2	8	1.42	4.05	1.04	1.17	1.57	1.35
nf 2	9			0.90	1.58	1.32	1.11
nf 2	10					2.00	1.70
nf 3	1	1.86	3.76	1.77	1.63	1.86	0.79
nf 3	2	2.23	11.30	2.43	2.22	2.19	1.35
nf 3	3	2.17	4.52	2.31	2.52	1.62	0.85
nf 3	4	2.13	7.37	1.97	1.57	2.20	1.08
nf 3	5	1.30	6.19	2.26	1.80	2.37	1.02
nf 3	6	0.85	6.17	2.11	1.60	1.89	0.67
nf 3	7			1.15	0.99	2.63	1.14
nf 3	8			0.84	1.07	1.74	0.71
nf 3	9					0.77	0.24
nf 3	10					1.03	0.67
nf 4	1	1.57	1.20	1.59	1.31	1.96	1.22
nf 4	2	1.99	2.97	3.04	2.53	1.83	1.50
nf 4	3	1.81	2.51	1.78	3.42	1.71	1.55
nf 4	4	2.06	3.75	2.51	3.14	1.86	1.63
nf 4	5	2.18	5.15	1.87	2.33	1.95	1.69
nf 4	6	1.72	0.45	1.79	2.06	2.44	2.00
nf 4	7	2.13	5.23	1.61	2.08	2.05	1.64
nf 4	8	0.81	6.12	1.86	2.11	3.15	2.51
nf 4	9			1.10	0.13	2.16	1.89
nf 4	10			1.55	2.17	2.12	1.71
nf 5	1	2.01	0.65	2.04	2.18	2.35	1.97
nf 5	2	2.11	0.87	3.15	3.92	2.32	1.93
nf 5	3	1.88	1.12	2.60	2.98	2.09	2.02
nf 5	4	2.02	3.73	1.76	2.00	2.05	1.74
nf 5	5	1.91	2.44	2.66	3.00	2.45	2.25
nf 5	6	1.74	16.02	2.30	4.39	2.27	1.90
nf 5	7	0.79	1.49	1.87	4.97	1.49	1.20
nf 5	8			1.30	0.93	0.86	0.60
nf 5	9			1.40	1.10	0.94	0.73