

Original Research

Core Ideas

- Significantly more pesticides leached from frozen than from unfrozen soil columns.
- Rapid breakthrough of pesticides indicated preferential flow in frozen soil.
- A strong negative correlation between K_f and leaching was observed.
- The effect of sorption properties is weaker in the presence of macropore flow.
- Macropore flow may be less important for highly mobile or highly sorbed pesticides.

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Leaching of Five Pesticides of Contrasting Mobility through Frozen and Unfrozen Soil

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Field and laboratory studies show increased leaching of pesticides through macropores in frozen soil. Fast macropore flow has been shown to reduce the influence of pesticide properties on leaching, but data on these processes are scarce. The objective of this study was to investigate the effect of soil freezing and thawing on transport of pesticides with a range of soil sorption coefficients (K_f). To do this we conducted a soil column study to quantify the transport of bromide and five pesticides (2-methyl-4-chlorophenoxyacetic acid, clomazone, boscalid, propiconazole, and diflufenican). Intact topsoil and subsoil columns from two agricultural soils (silt and loam) in southeastern Norway were used in this experiment, and pesticides were applied to the soil surface in all columns. Half the columns were then frozen (-3°C), and the other half were left unfrozen (4°C). Columns were subjected to repeated irrigation events where 25 mm of rainwater was applied during 5 h at each event. Irrigations were followed by 14-d periods of freezing or refrigeration. Percolate was collected and analyzed for pesticides and bromide. Pesticide leaching was up to five orders of magnitude larger from frozen than unfrozen columns. Early breakthrough ($\ll 1$ pore volume) of high concentrations was observed for pesticides in frozen columns, indicating that leaching was dominated by preferential flow. The rank order in pesticide leaching observed in this study corresponded to the rank order of mean K_f values for the pesticides, and the results suggest that sorption plays a role in determining leaching losses even in frozen soil.

Abbreviations: 2-MCP, 2-methyl-4-chlorophenol; LOQ, limit of quantification; MCPA, 2-methyl-4-chlorophenoxyacetic acid.

There is evidence that pesticides can leach through partially frozen soil during winter and early spring. Several field studies have shown large pesticide concentrations in leachate and drain water during freeze–thaw periods in Norway, Finland, and Sweden (Riise et al., 2004, 2006; Siimes et al., 2006; Ulén et al., 2013). Preferential flow is a nonequilibrium process (Jarvis et al., 2016) that is frequently triggered in soils containing large vertically continuous structural pores, termed *macropores*, generally having diameters of ~ 0.3 mm and larger (Beven and Germann, 1982; Jarvis, 2007). This includes biopores made by earthworms and plant roots and planar fissures caused by freeze–thaw and desiccation. Macropore flow can lead to increased leaching of pesticides to deeper soil layers or drainage systems, resulting in higher concentrations of pesticides in groundwater or surface water (Flury, 1996; Jarvis, 2007; Kjær et al., 2011). Compared with a slower and more uniform advective–dispersive transport process through the soil matrix, fast flow through macropores also reduces the influence of pesticide properties (e.g., degradation and sorption constants) on leaching (Jarvis, 2007; Larsson and Jarvis, 2000; McGrath et al., 2009). There is also some evidence that preferential flow may have a relatively larger effect on compounds that sorb moderately to soil than either more mobile or more strongly adsorbing compounds (McGrath et al., 2009).

Although soil freezing and thawing have been shown to influence the transport of solutes through soil, these processes are complex, and their effects on the fate and behavior of pesticides are not well understood (Hayashi, 2013; Ireson et al., 2013). In a soil column study that generated high-resolution data of leached concentrations during artificial

irrigation events, it was found that the nonreactive tracer bromide and the mobile herbicide 2-methyl-4-chlorophenoxyacetic acid (MCPA) were transported in large concentrations through macropores in partially frozen soil (Holten et al., 2018). The study showed that significantly more MCPA leached from frozen than unfrozen columns and that very little MCPA leached from unfrozen columns. The leaching patterns of bromide and MCPA were very consistent in frozen columns. A nonuniform pattern with concentrations peaking in the early leachate samples after the start of the first or second irrigation and decreasing concentrations later indicated preferential flow in open and connected macropores in the early stages of the experiment. Macropores are often air-filled when the soil first freezes (van der Kamp et al., 2003) and can hence have high infiltration capacities when the matrix is frozen. In unfrozen columns, the leaching pattern of bromide was much more uniform, with no distinct concentration peaks in the leachate, suggesting a slower advective–dispersive transport process through the soil matrix. In the same experiment, the leaching of the pesticides clomazone, boscalid, propiconazole, and diflufenican was also measured. In contrast to the high-resolution data reported for MCPA (Holten et al., 2018) with 25-mL subsamples of leachate analyzed during the course of several consecutive irrigation events, these pesticides were analyzed in bulk leachate samples, with each representing one irrigation event. The effect of freezing and thawing on the transport of pesticides with different sorption properties has to our knowledge not been investigated before. In this paper we report the results from the analysis of the bulk leachate samples from the experiment described in Holten et al. (2018). We hypothesize that leaching of pesticides in general will be larger from frozen soil columns with open and connected macropores compared with unfrozen columns and that the effects of freezing on leaching will be largest for moderately sorbing compounds.

Materials and Methods

Soil Sampling and Characterization

Intact soil columns were sampled in mid- to late May 2016 from two agricultural fields with different soil types in southeastern Norway (Kroer, 59°38'37" N, 10°49' 58" E; Hov, 60°12'45" N, 12°1'58" E) using aluminum cylinders (i.d., 9.2 cm; height, 20 cm). Fifty-six columns were sampled, 14 from both the topsoil (0–20 cm) and subsoil (20–40 cm) at each site. The cylinders were forced into the soil using a sledgehammer and dug out by hand.

Samples were stored at ~4°C. At the time of sampling the fields were under winter wheat. According to the farmers at Kroer and Hov, none of the pesticides included in our study had been applied during the 2 to 3 yr prior to sampling.

The Kroer loam has been characterized elsewhere (Tiberg, 1998), so no additional characterization was performed in this study. A simple soil characterization of the Hov silt was performed at the Division of Survey and Statistics at NIBIO. Soil characteristics are summarized in Table 1. This characterization was done according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2014).

To avoid disturbing the intact soil columns, soil water content was not measured at sampling or in the laboratory before the experiment started.

Chemicals

The pesticides MCPA (purity 99.5%), clomazone [2-(2-chlorobenzyl)-4,4-dimethyl-1,2-oxazolidin-3-one, purity 97.5%], boscalid [2-chloro-N-(4'-chlorobiphenyl-2-yl)nicotinamide, purity 98.4%], and propiconazole [(2RS,4RS;2RS,4SR)-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1H-1,2,4-triazole, purity 98%] were supplied by Dr. Ehrenstorfer GmbH. Diflufenican [2',4'-difluoro-2-(α,α,α -trifluoro-m-tolyloxy)nicotinamide, purity >99%] was supplied by Chiron AS. Two diflufenican metabolites were also included in the analyses: AE 0542291 (2-[3-(trifluoromethyl)phenoxy]pyridine-3-carboxamide, purity 99%) and AE B107137 (2-[3-(trifluoromethyl)phenoxy]pyridine-3-carboxylic acid, purity 98%), both supplied by Bayer CropScience. The MCPA metabolite 2-methyl-4-chlorophenol (2-MCP) (purity 96.0%; Sigma) was included. A mix of the five pesticides was prepared at concentrations of 282.6 mg L⁻¹ (MCPA), 7.1 mg L⁻¹ (clomazone), 41.9 mg L⁻¹ (boscalid), 19.6 mg L⁻¹ (propiconazole), and 18.8 mg L⁻¹ (diflufenican) in acetone (purity 99.7%; VWR Chemicals). These concentrations resulted in agriculturally relevant application rates. Ranges and mean values of degradation half-lives (DT₅₀) and soil sorption coefficients (K_p) for the studied pesticides are summarized in Table 2. The pesticides cover a wide range of degradation and sorption properties, from mobile and nonpersistent (MCPA) to slightly mobile and persistent (diflufenican).

A solution of artificial rainwater (Löv et al., 2017) was prepared [0.58 mg L⁻¹ NaCl, 0.70 mg L⁻¹ (NH₄)₂SO₄, 0.50 mg L⁻¹ NaNO₃, 0.57 mg L⁻¹ CaCl₂] and acidified with HCl (0.95 mL L⁻¹

Table 1. Selected characteristics of the studied soils.

Site	Classification†	Horizon	Depth	Soil texture‡	Clay	Silt	Sand	Total C	pH (H ₂ O)
			cm		%				
Kroer	Retic Stagnosol	Ap	0–23	loam	19.1	43.8	37.1	2.5	5.5
		Eg	23–40	silt loam	20.5	63.0	16.7	0.5	5.6
Hov	Dystric Fluvic Cambisol	Ap	0–20	silt	5.4	83.8	10.8	1.2	5.4
		Bw	28–50	silt	4.1	86.7	9.2	0.3	6.2

† IUSS Working Group WRB (2014).

‡ USDA soil texture calculator.

Table 2. Ranges of sorption coefficients (K_f) and laboratory degradation half-lives (DT_{50}) for 2-methyl-4-chlorophenoxyacetic acid (MCPA), clomazone, boscalid, propiconazole, and diflufenican. Values in parentheses are mean values.

Compound	K_f mL g ⁻¹	DT_{50} , 20°C d
MCPA	0.05–1.99† (0.94)	7–41† (24)
Clomazone	1.54–7.13† (4.33)	27–168§ (68)
Boscalid	3.3–27.8† (12.6)	108–384¶ (232)
Propiconazole	1.20–59† (15)	27–115† (72)
Diflufenican	13.5–48.9† (31.2)	44–238# (128)

† University of Hertfordshire (2018).

‡ European Commission (2005).

§ European Safety Authority (2007a).

¶ European Commission (2008).

European Safety Authority (2007b).

37%) to a pH of ~ 5 . The artificial rainwater was stored at $\sim 4^\circ\text{C}$ in 20-L plastic containers.

Experimental Setup and Sampling

Twenty of the sampled soil columns from each of the sites Kroer and Hov (40 columns in total) were included in the experiment. To ensure uniform initial conditions, the columns were placed in a box of water and allowed to absorb water until they were close to saturation. They were then placed on a sand box (Eikjeltkamp) at -30 cm pressure potential at the bottom to ensure that macropores were initially air filled.

Five columns were randomly chosen from each soil type and depth for the freezing treatment. Likewise, five columns were chosen from each soil type and depth for the nonfreezing treatment. More details on the preparation and selection of columns can be found in Holten et al. (2018). Thermistors were installed horizontally into the middle of the columns at depths of 7 and 14 cm from the soil surface in the columns that were subjected to freezing, and temperature was logged every 10 min throughout the experiment. The columns were insulated at the bottom and around the column walls to ensure freezing from the top downward (Fig. 1).

Five milliliters of the pesticide solution was applied as evenly as possible across the surface of each of the columns using a 5-mL pipette, giving rates of 2.1, 0.05, 0.32, 0.15, and 0.14 kg ha⁻¹ of MCPA, clomazone, boscalid, propiconazole, and diflufenican, respectively. The insulated columns in the freezing treatment were placed in a 1-m³ freezing cabinet at -3°C ; unfrozen columns were kept at $\sim 4^\circ\text{C}$ in a refrigerated room. Plastic lids were put on top of all the columns to reduce evaporation. The columns were incubated at these temperatures for about 4 wk. They were then subjected to repeated irrigation events in a separate room with the prepared artificial rainwater, followed by 14-d periods of freezing (or refrigeration for the unfrozen columns) between irrigations. The experiment lasted for a total of 8 wk for the silt soil (three



Fig. 1. Insulated soil columns in a Weiss freezing cabinet. The columns were placed on a polystyrene board. Thermistors were installed at two depths.

irrigations) and 10 wk for the loam (four irrigations). The columns were transported to the irrigation room in the morning of each irrigation event. The irrigation room and the artificial rain water were at temperatures of ~ 5 to 8°C and 2 to 4°C at the start of the irrigation, respectively. Temperatures increased to ~ 12 and 6°C in the room and water, respectively, during the day because it was difficult to obtain completely stable temperatures when working in the room. A temperature of -3°C was chosen for the freezing cabinet because it was considered low enough to ensure that any water present in macropores after the irrigations would be frozen.

As described in Holten et al. (2018), the column setup allowed free drainage at the base of the soil columns. Irrigation water was distributed on the top of the columns using peristaltic pumps (Autoclude model VL) adjusted to give a rate of 5 mm h⁻¹ for 5 h, resulting in a total of ~ 25 mm of rainwater to each column per irrigation event. Water was dripped onto filter paper placed on the surface of the columns to ensure that it was distributed as uniformly as possible. The actual irrigation rates varied somewhat between columns, but there were no systematic differences between treatments, soils, or depths. Rough calculations suggested that the total amount of irrigation water supplied to the columns during the experiment would be equivalent to approximately one pore volume (Holten et al., 2018).

Leachate from the soil columns was sampled in polycarbonate bottles (Corning, VWR) at approximately every 25 mL (as reported in Holten et al. [2018]) and stored frozen (-20°C) in 60-mL amber glass bottles for later analysis. All subsamples were combined to one single bulk sample per irrigation for each column for further pesticide analysis (total volumes 20–140 mL).

Pesticide Analysis

The bulk water samples were preconcentrated and analyzed for the content of clomazone, boscalid, propiconazole, and diflufenican and for the diflufenican metabolites AE 0542291 and AE B107137. The MCPA metabolite 2-MCP was also analyzed for in selected leachate samples. The contribution from any particle-bound pesticides was not generally measured throughout

the experiment, but a preliminary test was performed to analyze potential residues on leached particles.

Each bulk leachate sample was preconcentrated using solid-phase extraction sorbents. In short, the water samples were thawed and centrifuged (5000 rpm, 15 min) in Teflon tubes to remove particles, and then internal standards propiconazole- d_5 (Dr. Ehrenstorfer GmbH, purity 99.4%) and diflufenican- d_3 (Chiron AS, purity 98%; 10 μL of a 1 $\mu\text{g mL}^{-1}$ mix) were added to each water sample. The samples were passed through preconditioned Oasis HLB columns (sorbent mass, 60 mg; Waters). Water (2 mL) was added to wash the sorbent, and then the analytes were eluted from the sorbent with 2 mL of acetone. The eluate was evaporated to dryness under a stream of N_2 and dissolved in 1 mL of acetone. Samples were filtrated with RC 0.45- μm syringe filters (Phenomenex, regenerated cellulose membrane) into liquid chromatography vials. The concentration of internal standards corresponded to 10 ng mL^{-1} in the final extracts. Blank and control samples was prepared from Milli-Q deionized water and preconcentrated simultaneously with each batch of samples. Control samples were spiked with 5 μL of a 1 $\mu\text{g mL}^{-1}$ acetone mix of all the analytes, giving a concentration of 5 ng mL^{-1} in the final extract. The recovery of the analytes with this extraction method was 79 to 116%, as measured from eight control samples.

Pesticide analyses was performed by LC-MS/MS (Waters Alliance 2695 LC-system coupled to a Quattro Ultima Pt triple quadrupole mass spectrometer, Micromass). A sample volume of 5 μL was injected, and the analytes were separated on a Phenomenex Gemini C18 column (100 \times 2 mm; particle diameter, 3 μm) with 5 mM formic acid or methanol as the mobile phase.

The analytes were detected in the positive ESI mode, with quantifier ion transitions 240 > 125 (clomazone), 343 > 307 (boscalid), 342 > 159 (propiconazole), 395 > 266 (diflufenican), 283 > 266 (AE 0542291), and 284 > 266 (AE B107137). All analytes were verified with a qualifier ion transition. Quantification was based on the peak area of the quantifier ion. Internal standard (propiconazole- d_5 and diflufenican- d_3) calibration was performed using quadratic regression analysis of the peak area ratios (quantifier ion/internal standard) vs. the concentration ratios. Bracketed calibration standards were set up in the range 0.2 to 300 ng mL^{-1} in acetone. The limit of quantification (LOQ) for the analytes was 0.5 ng mL^{-1} in the final extract. An LOQ of 0.5 ng mL^{-1} in the extract corresponds to 0.005 $\mu\text{g L}^{-1}$ in a 100-mL bulk water sample.

Mean measured concentrations of the pesticides are reported for each soil, soil depth, treatment, and irrigation event. For samples where no detections above the LOQ were made, concentrations were set to 0.001 $\mu\text{g L}^{-1}$, one fifth of the LOQ. In addition, the total mass transported through the soil columns is reported as a percentage of the applied amount.

Statistical Analysis

Statistical analyses of the differences in pesticide transport were performed with an ANOVA Type III test and a post hoc pairwise Tukey test (Tukey's HSD method) in R Commander (R

Core Team, 2016). Correlation analyses (Spearman's rho) were performed with Minitab v. 17.1.0. In the ANOVA for the effect of freezing on the amount of pesticides leached, log-transformed values ($\text{Ln}+2$) of mean total amounts of pesticides leached were used as response variables to get more homogeneous variances and thereby to comply with the prerequisite of normally distributed data. Soil type and treatment (frozen, unfrozen) were used as predictor variables (factors). Statistically significant results are reported at the 5% significance level unless otherwise stated.

Results

Temperatures

As presented in Holten et al. (2018), the temperatures in the frozen soil columns started to increase quickly toward 0°C when taken from the freezing cabinets and stabilized for a period before quickly increasing toward room temperature (Fig. 2). The period of stable temperatures around 0°C was longer during later irrigations. For the silt soil, this period increased from ~ 16 to ~ 26 h between the first and third irrigations for both topsoil and subsoil. It took some time before the first irrigation of the Kroer loam started; hence, the temperatures in the columns had risen to about 0°C at the beginning of the irrigation.

Infiltration, Drainage, and Bromide Leaching

The measurements of drainage and leaching of bromide in this experiment have been discussed in detail in Holten et al. (2018), but some of these data have also been included in Table 3 to help interpret the other results presented here. These data show that, contrary to the pesticide masses, significantly more water drained and more bromide leached from the unfrozen columns than from the frozen columns. This result applied to the loam topsoil and subsoil as well as to the silt subsoil.

In Holten et al. (2018), breakthrough curves of bromide in frozen columns showed high concentration peaks of bromide in leachate from columns during either the first or second irrigation, after only very little water had percolated through the columns ($\ll 1$ pore volume). In contrast, the leaching patterns in unfrozen columns were slower and more uniform, without clear concentration peaks.

Another observation discussed in Holten et al. (2018) was a fast infiltration of ponding water in frozen soil columns as temperatures increased above 0°C. After thawing, 25-mL samples were collected at ~ 6 - to 7-min intervals, equal to flow rates of ~ 35 mm h^{-1} . In contrast, the interval between each sampling in unfrozen soil was typically ~ 30 min, equal to a flow rate of ~ 7 mm h^{-1} . As presented and discussed in detail in Holten et al. (2018), the data on the drainage of the columns showed that the outflow rates were quite constant during irrigation of the unfrozen columns (almost equal to the inflow rate) and that the outflow ceased rapidly when the irrigation stopped. This was clear for the loam topsoil and subsoil as well as the silt topsoil, but this difference was smaller for the unfrozen silt subsoil. In the frozen columns, the outflow started

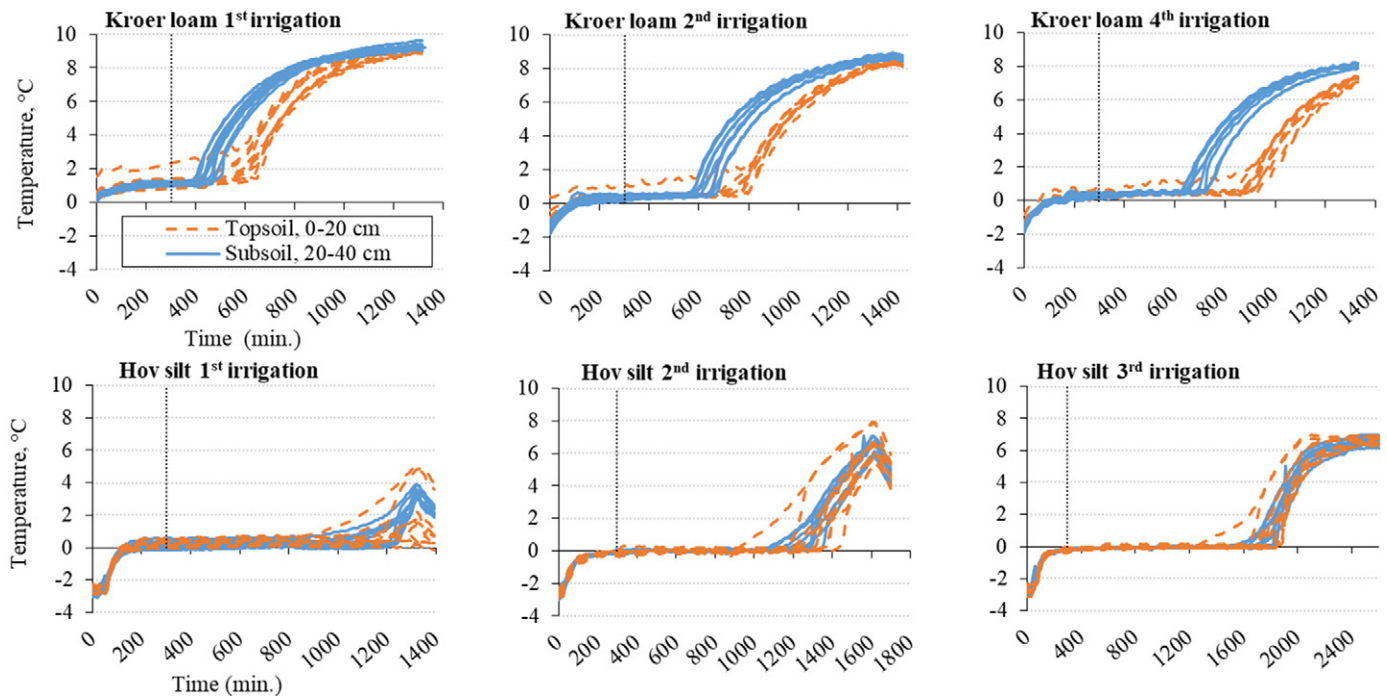


Fig. 2. Temperatures measured at 7 and 14 cm in frozen Kroer loam and Hov silt columns during three irrigation events. For the loam, the curve stops at the time the columns were put back in the freezing cabinet (temperatures then started to decrease). For the silt, the temperatures continued to increase even after the columns were put back into the freezing room (~1400 min). The end of each irrigation event (at 300 min) is symbolized with a dotted line. The same legend applies to all plots. Figure copied from Holten et al. (2018).

later, especially for the later irrigations, and many of the frozen columns continued to percolate slowly a long time after irrigation ceased. Data on the accumulated amount of percolated water plotted against time has been included in the supplemental material.

Pesticide Leaching

Figures 3 through 7 show the mean concentrations of the five different pesticides in leachate from all columns and irrigations (y axis on a logarithmic scale). Concentrations of all the pesticides

were in most cases much larger (but not necessarily significantly larger) in leachate from frozen columns than from unfrozen columns, with differences ranging up to five orders of magnitude. Concentrations in leachate from frozen columns increased from the first irrigation to the second before leveling out at a high level throughout the subsequent irrigations. In leachate from unfrozen soil columns, concentrations were lower (often \leq LOQ), more constant, or decreased throughout the experiment. In many cases, pesticides were detected in fewer samples from unfrozen than from

Table 3. Total amounts leached as percentage of applied amounts of water, bromide, 2-methyl-4-chlorophenoxyacetic acid (MCPA), clomazone, boscalid, propiconazole, and diflufenican leaching from Kroer loam soil columns during four irrigations and Hov silt soil columns during three irrigations.

Soil	Depth	Temperature	Water†	Bromide†	MCPA†	% of appl.‡			
						Clomazone	Boscalid	Propiconazole	Diflufenican
	cm	°C							
Kroer loam	0–20	–3	60.2b§	37.4c	24.5a	7.7a	1.0a	0.60a	0.13a
	0–20	4	91.2a	57.5b	0.4c	$7.8 \times 10^{-5}c$	$7.2 \times 10^{-6}c$	$1.9 \times 10^{-5}c$	$1.2 \times 10^{-4}c$
	20–40	–3	47.1c	28.2c	24.1a	1.0a	0.65a	0.15a	0.019b
	20–40	4	87.1a	72.1a	8.6b	0.049b	0.026b	$8.2 \times 10^{-3}b$	$6.2 \times 10^{-5}c$
Hov silt	0–20	–3	75.7B	25.2AB	16.4A	6.2A	1.3A	1.2A	0.19A
	0–20	4	94.0A	31.5A	0.5B	0.014C	$6.9 \times 10^{-4}C$	$4.8 \times 10^{-3}C$	nd¶
	20–40	–3	52.7C	13.1B	10.3A	1.7AB	0.32AB	0.25AB	0.03AB
	20–40	4	82.0AB	30.4A	10.6A	1.2B	0.19BC	0.15BC	0.026AB

† Data from Holten et al. (2018).

‡ Percentage of nominal applied amount.

§ Different letters denote significant differences based on pairwise comparisons (ANOVA III + Tukey test) of samples from frozen and unfrozen columns of the same soil. The statistics were done on log-transformed data.

¶ Not detected in any of the samples.

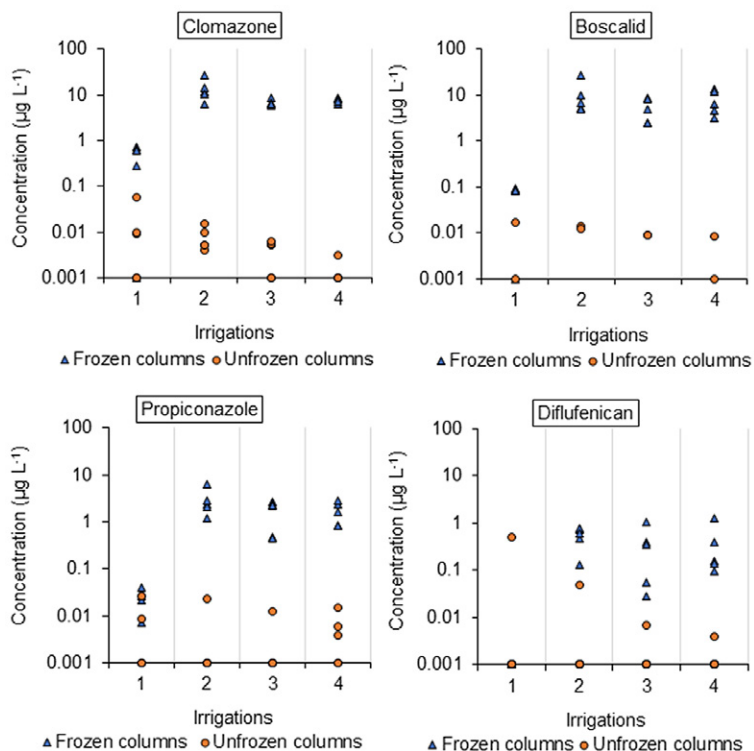


Fig. 3. Concentrations of the four studied pesticides in bulk leachate samples from frozen and unfrozen Kroer loam topsoil (0–20 cm) columns for each of four irrigation events. Concentrations are shown on \log_{10} scale. Detections below the limit of quantification ($0.005 \mu\text{g L}^{-1}$) are set to 0.001 in the plots.

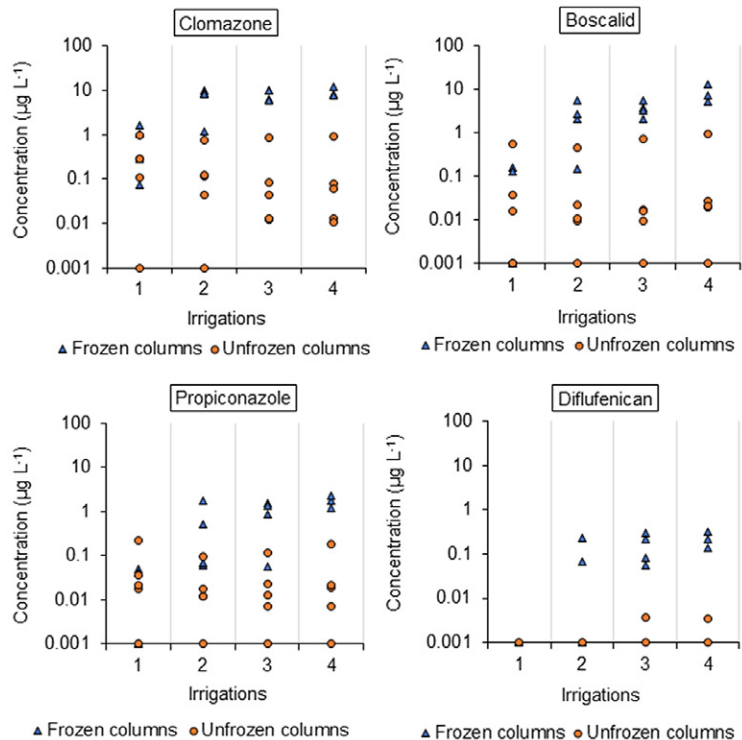


Fig. 4. Concentrations of the four studied pesticides in bulk leachate samples of leachate from frozen and unfrozen Kroer loam subsoil (20–40 cm) columns for each of four irrigations events. Concentrations are shown on \log_{10} scale. Detections below the limit of quantification ($0.005 \mu\text{g L}^{-1}$) are set to 0.001 in the plots.

frozen soil columns. These observations generally apply to both Kroer loam topsoil and subsoil and Hov silt topsoil (Fig. 3–6).

Concentrations varied between pesticides. For example, clomazone and boscalid leached at ~ 10 times larger concentrations than propiconazole and diflufenican in Kroer loam topsoil (Fig. 3). The results for the loam subsoil were similar, although the differences between the unfrozen columns were less clear (Fig. 4). Diflufenican was not detected in any leachate samples from the unfrozen loam subsoil columns. Many of the same trends as discussed above were also observed for the Hov silt topsoil (Fig. 5), but the differences were even less clear in the silt subsoil (Fig. 6) than in the loam subsoil, with no significant differences between the concentrations of the pesticides from frozen and unfrozen columns. Mean concentrations of MCPA subsamples weighted by volume (data from Holten et al. [2018]) have been added for comparison (Fig. 7). These results show that much larger concentrations of MCPA leached (approximately two orders of magnitude) compared with the other four pesticides (note the different scale of Fig. 7 compared with Fig. 3–6). With respect to the effects of treatment and soil type/depth, the results for MCPA were similar to the results for the other pesticides.

Table 3 shows that the leached amounts of the pesticides, expressed as percentages of the applied amounts, were in most cases significantly larger ($p < 0.05$) from the topsoil columns that were subjected to freezing than from the unfrozen topsoils. The differences between the amounts leaching from frozen and unfrozen columns were up to three to five orders of magnitude for the loam soil. The differences were less pronounced for the silt topsoil, with differences of up to three orders of magnitude between the two treatments. For the loam subsoil, the amount leached from frozen columns was about two orders of magnitude larger than from unfrozen columns, and the differences were statistically significant in all cases except diflufenican. For the silt subsoil, leached amounts were in the same order of magnitude in frozen and unfrozen columns, and the differences were not statistically significant.

2-Methyl-4-chlorophenoxyacetic acid was the pesticide that leached the most in all treatments, whereas diflufenican leached in the smallest amounts. The rank-order in pesticide leaching was the same for most treatments, soil types, and depths; MCPA > clomazone > boscalid > propiconazole > diflufenican.

The diflufenican metabolite AE 054229 was not detected in any of the leachate samples. However, the metabolite AE B107137 was detected in leachate samples from both soil types, depths, and treatments at a maximum amount of 0.15% of the applied amount of diflufenican. The maximum amount was detected in leachate samples from unfrozen loam subsoil columns. Other detections of this

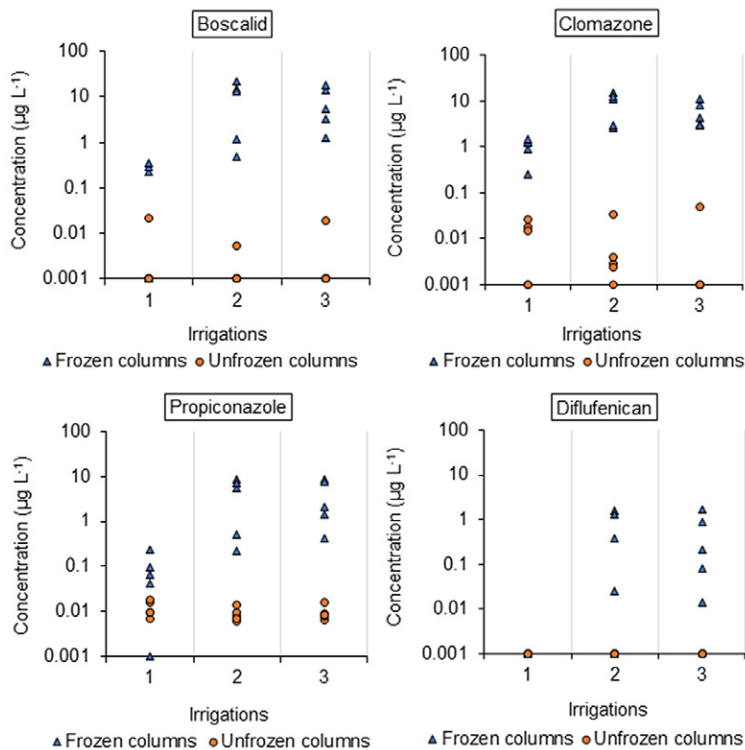


Fig. 5. Concentrations of the four studied pesticides in bulk leachate samples of leachate from frozen and unfrozen Hov silt topsoil (0–20 cm) columns for each of four irrigations events. Concentrations are shown on \log_{10} scale. Detections below the limit of quantification ($0.005 \mu\text{g L}^{-1}$) are set to 0.001 in the plots.

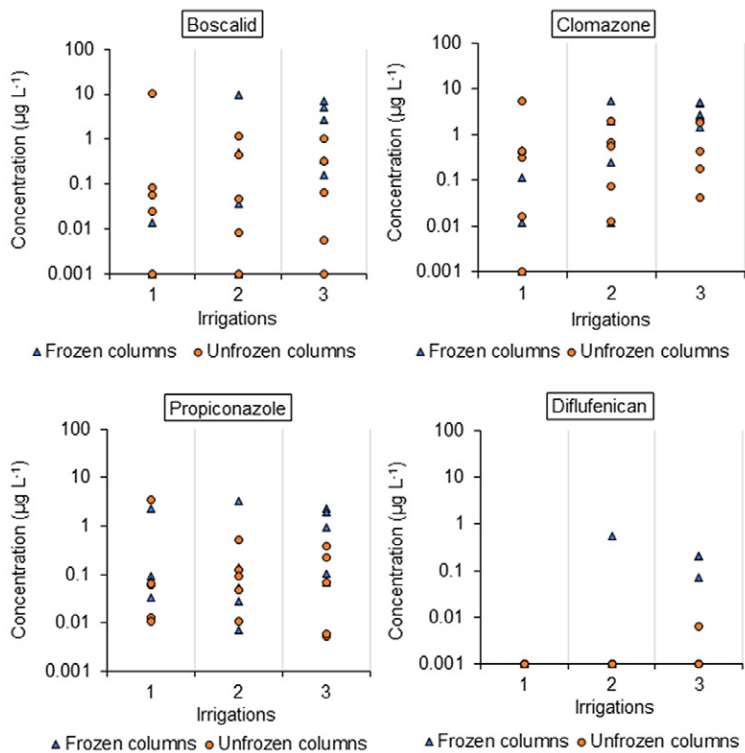


Fig. 6. Concentrations of the four studied pesticides in bulk leachate samples of leachate from frozen and unfrozen Hov silt subsoil (20–40 cm) columns for each of four irrigations events. Concentrations are shown on \log_{10} scale. Detections below the limit of quantification ($0.005 \mu\text{g L}^{-1}$) are set to 0.001 in the plots.

metabolite were generally $<0.04\%$ of the applied amount of diflufenican. In comparison, the MCPA metabolite 2-MCP was found at a maximum value of 0.003% of the applied amount of MCPA in leachate from frozen loam topsoil (Holten et al., 2018).

A general observation that was made during the experiment was that many of the leachate samples were visibly colored due to suspended particles. This was observed in leachate from both frozen and unfrozen columns. One water sample was tested for pesticide residues in the soil particles (after centrifugation) after extraction with acetone, but no pesticides were detected. The amount of soil particles was very low, and it was not considered worthwhile to extract and analyze the soil particles because pesticide concentrations were expected to be too low to detect.

Sorption Coefficients and Leaching

The rank order observed for leaching follows quite closely the differences in the mean K_f values for the five compounds (Table 2). When combining results from frozen and unfrozen columns, a highly significant ($p < 0.001$) negative correlation was found between the fraction of pesticide leached and K_f in both Kroer loam and Hov silt, with correlation coefficients of -0.64 and -0.69 , respectively, indicating that substances with lower K_f values leached more than substances with higher K_f values (Fig. 8). This figure clearly shows that K_f has a strong effect on the leaching for both frozen and unfrozen soils, although the effect seems somewhat stronger for unfrozen subsoil than unfrozen topsoil.

Figure 9 shows a plot of the ratio of leaching from frozen and unfrozen columns against representative substance K_f values taken from the literature. It appears that the effects of freezing in enhancing leaching are strongest for the moderately adsorbing compounds and weaker for both weakly adsorbing (e.g., MCPA) and very strongly adsorbing compounds (e.g., diflufenican). This trend is especially apparent in the topsoil columns and somewhat weaker for the subsoils.

Discussion Infiltration, Drainage, and Bromide Leaching

The observation that less water drained and less bromide leached from frozen columns than unfrozen columns was unexpected because the frozen columns thawed completely during the period in the lysimeter room during irrigation events (Fig. 1), so any differences should have evened out. One likely explanation discussed in Holten et al. (2018) was that the frozen columns had not finished draining when they were returned to the freezing chamber and that some water may have been lost during the process

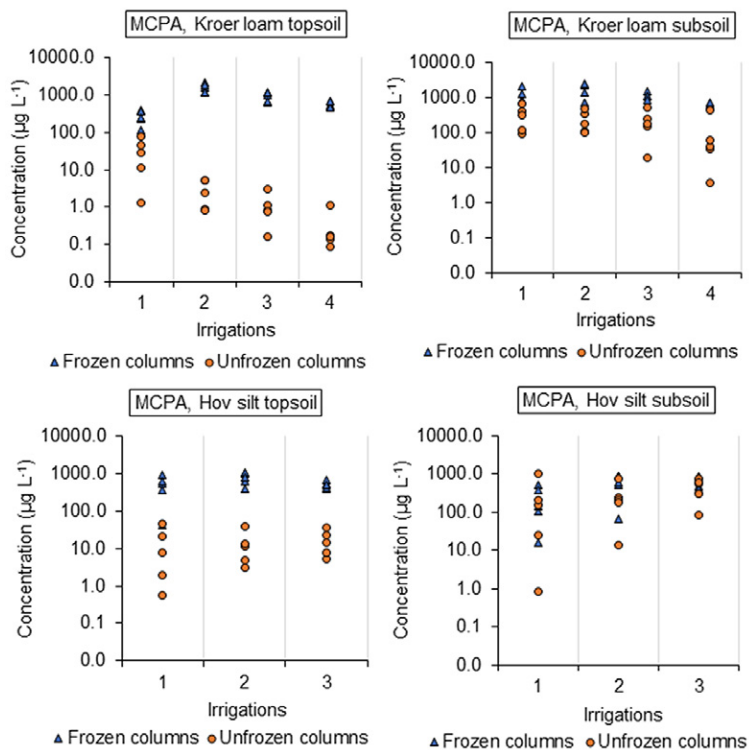


Fig. 7. Concentrations of 2-methyl-4-chlorophenoxyacetic acid (MCPA) in samples of leachate from frozen and unfrozen Kroer loam and Hov silt for each irrigation event. Concentrations were calculated as the sum of the amount of MCPA that leached from each column at each irrigation divided by the respective sum of leachate volumes. Concentrations are shown on a \log_{10} scale. Note the different scale compared with Fig. 3 through 6.

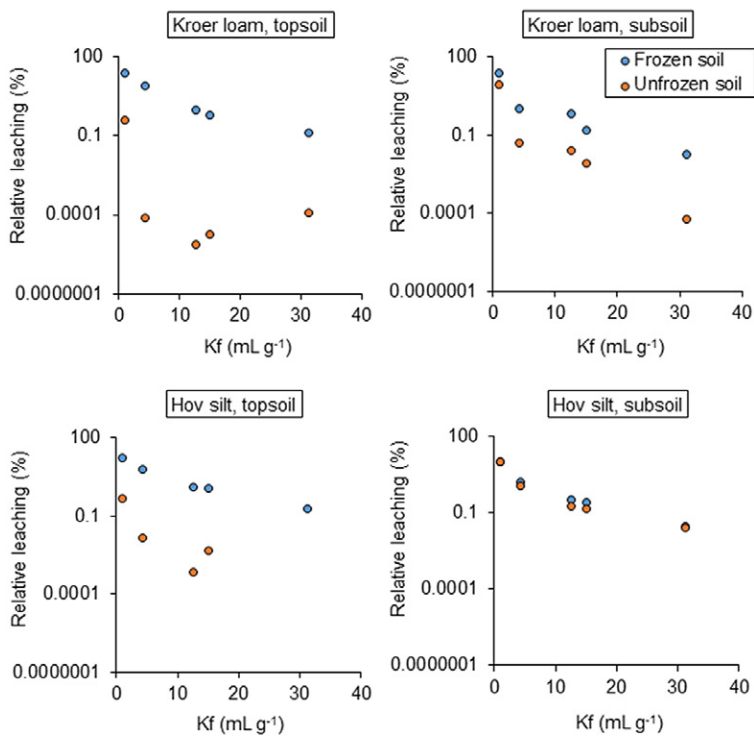


Fig. 8. Relative leaching from frozen and unfrozen soil columns plotted against mean sorption coefficient (K_f) values in Kroer loam and Hov silt topsoil and subsoil. The same legend applies to all four plots.

of moving the columns. Hence, thawing seemed to be faster than drainage. Continued sampling would have been desirable to sample more water from the frozen columns, but this was not possible due to time constraints.

Ponding was observed on all frozen columns, especially at later irrigations when the water content was higher, indicating that all pores were frozen. In these columns, infiltration started later, and percolating continued for a long time after the irrigation had stopped (Supplemental Fig. S1 and S2). As the temperature in the columns reached 0°C , infiltration could happen quite fast, with flow rates up to 35 mm h^{-1} , indicating that the ice in the macropores had at least partly melted. In addition, preferential flow was confirmed by bromide breakthrough curves presented in Holten et al. (2018), which in many cases showed significant concentration peaks in leachate samples during either the first or second irrigation after little water had percolated through the columns ($\ll 1$ pore volume). The leaching pattern of bromide in unfrozen columns was very different, indicating a slower and uniform flow and transport through the entire soil matrix, probably because the infiltration capacity of the unfrozen matrix was sufficient to prevent the generation of nonequilibrium preferential flow in soil macropores (Jarvis et al., 2016).

Pesticide Leaching

In this study, only bulk leachate samples were analyzed; therefore, breakthrough curves, such as the ones presented for MCPA and bromide by Holten et al. (2018), could not be presented. Nevertheless, significantly larger concentrations in leachate and leached amounts of these pesticides from the columns subjected to the freezing treatment indicate that the transport of all five pesticides investigated in this study was enhanced in partially frozen soil (Fig. 3–7). For an advective–dispersive transport process and with the K_f values reported in Table 2, one would not expect any breakthrough until after many pore volumes had passed through the columns. The relatively rapid breakthrough of bromide, as presented in Holten et al. (2018), and the adsorbing pesticides in this case ($\ll 1$ pore volume) indicate that the leaching process was dominated by preferential flow through soil macropores that presumably remained air-filled, confirming the hypothesis that leaching of pesticides in general will be larger from frozen soil columns with open and connected macropores compared with unfrozen columns and that the effects of freezing on leaching will be largest for moderately sorbing compounds. Conversely, the much smaller concentrations of the pesticides in leachate from unfrozen columns can probably be attributed to a more uniform transport process through the bulk of the soil, such that the pesticides were exposed to more soil surfaces and binding sites, hence resulting in stronger sorption.

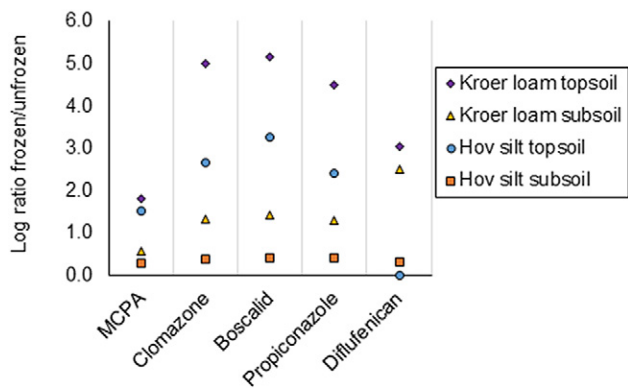


Fig. 9. The logarithm of the ratio of the percentage of the applied amount leached from frozen and unfrozen soil columns of five different pesticides.

The effects of freezing were much less clear in the silt subsoil (Fig. 4), where the amounts leached were not significantly different between the treatments. This can probably be attributed to a lack of connected macroporosity in the silt subsoil, as shown and discussed in Holten et al. (2018).

Suspended particles were observed in some samples, but the concentration of particle-bound pesticides was not analyzed in all samples due to particles being filtered out during sample preparation. This could have influenced the recovery of the more strongly adsorbing compounds like diflufenican, which may partly explain the low amounts detected in the leachate. However, a preliminary test indicated that no pesticides were adsorbed to particles extracted with acetone, although leaching losses through particle-bound transport cannot be completely ruled out.

The concentrations of the diflufenican metabolite AE B107137 and the MCPA metabolite 2-MCP detected in leachate samples were generally small. One exception was the leachate from unfrozen Kroer loam subsoil columns, where the amounts AE B107137 of leached reached a level of 0.15% of the applied amount of diflufenican. The amounts of diflufenican were very low in leachate from the same columns, but this metabolite is very mobile, with typical K_f values of 0.11 to 0.42 mL g⁻¹ (University of Hertfordshire, 2018). This indicates that diflufenican was subject to some degradation during the experiment, despite the low temperatures. Nevertheless, the amounts of the metabolite were generally low, and degradation was not considered to be the reason for the differences observed between frozen and unfrozen columns.

Sorption Coefficients and Leaching

This study showed higher mobility for most pesticides in frozen soil columns compared with unfrozen columns. The rank order in pesticide leaching observed in this study (MCPA > clomazone > boscalid > propiconazole > diflufenican) corresponds well to the rank-order of mean K_f values of the pesticides from a range of different soil types, both in frozen and unfrozen soils. The data in this study also show a strong negative correlation between pesticide

sorption properties (K_f) and leaching (Fig. 8). This dependency has also been shown in field studies where leaching behavior of different compounds has been compared in the presence of macropore flow (Jarvis, 2007), suggesting that compound sorption properties have a certain effect, although this will be weaker when macropore flow is present (Larsson and Jarvis, 2000). Plotting the logarithm of the ratio between the mean amounts of pesticides that leached from frozen columns and unfrozen columns (Fig. 9) indicates that MCPA and diflufenican are less influenced by macropore flow because the leaching ratios for these substances in general are lower than for substances with more intermediate sorption. This relationship seems clearer for the topsoils of both the Kroer loam and Hov silt than for subsoils, perhaps due to smaller and less well-connected macropores in these subsoils (Holten et al., 2018). These results indicate, although rather indirectly, that macropores play a larger role for the transport of substances of more intermediate mobility, as argued by McGrath et al. (2010), and that this also applies to frozen soil. More mobile substances may leach regardless of the presence of macropores, whereas more or less immobile substances adsorb strongly to the soil in any case and are transported either particle-bound through macropores toward drains (Kjær et al., 2011; Øygarden et al., 1997) or via surface runoff/erosion (Larsbo et al., 2016). The fact that diflufenican was found in very low concentrations in leachate in this study may, among other reasons (sorption, degradation), be due to loss via particle-bound transport.

The data in this study indicate higher pesticide mobility in frozen soil than unfrozen soil. This is partly in line with a study where lower K_d values were found for the mobile pesticide metribuzin at -5°C than at 5°C (Stenrød et al., 2008). However, the presence of macropore flow probably explains most of the differences observed between leaching from frozen and unfrozen columns in this study.

Conclusion and Recommendations

This study shows that air-filled and connected macropores can facilitate fast transport of high concentrations of pesticides vertically through a partially frozen soil profile. The studied pesticides had a range of K_f values, and the results suggest that sorption plays a role in determining leaching losses even in frozen soil. To our knowledge, these relationships have not been investigated in detail before, at least not in frozen soils, and the findings here show that further investigation may be worthwhile. Modeling with an appropriate model could also help to interpret some of the results (Mohammed et al., 2018). In addition, these relationships are worth considering when assessing the fate and behavior of pesticides during the cold period of year and may be worth taking into account in pesticide monitoring programs.

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