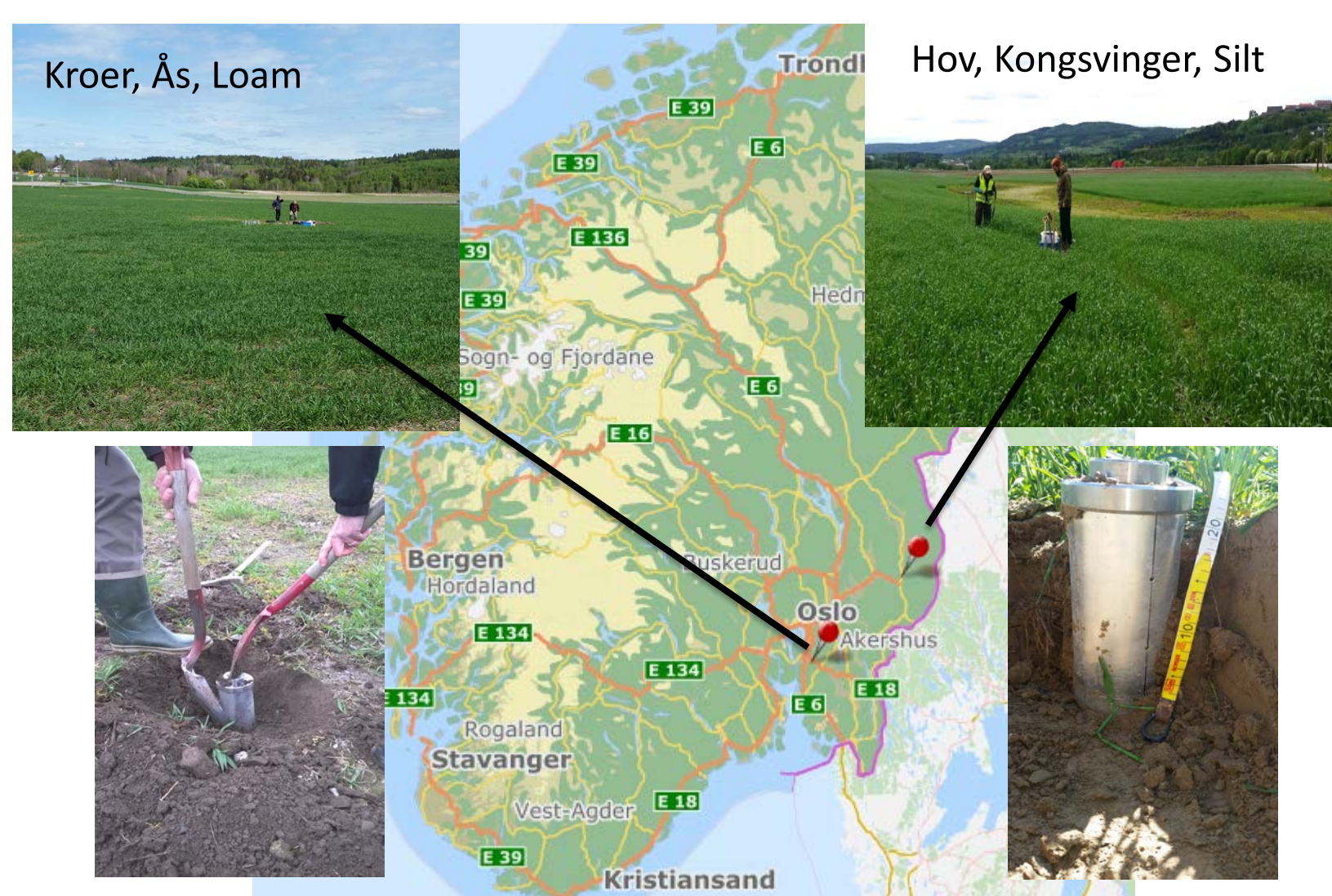


Introduction and objectives

- A leaching experiment with undisturbed soil columns from two different agricultural soils (silt and loam) was performed to study water flow and pesticide transport in frozen soils under cold climate conditions.
- The objective was to see whether the transport of water and pesticides in frozen soil was significantly different from transport in unfrozen soil.
- A selection of representative results from the bromide and MCPA analysis of the top 20 cm are presented here.



Materials and methods

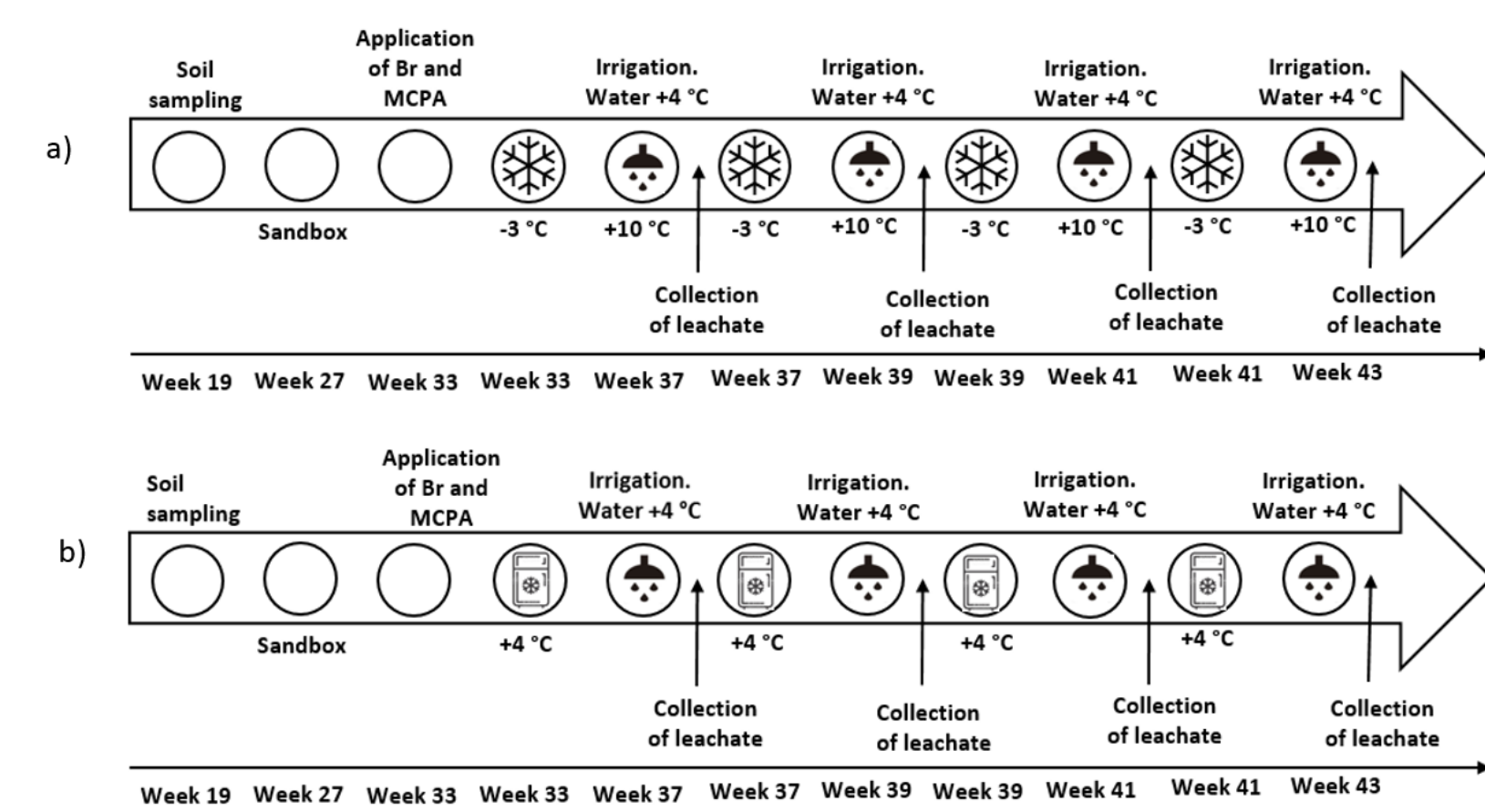


Figure 1: Timelines of the column experiment for frozen (a) and unfrozen (b) samples.

- 10 undisturbed topsoil (0-20 cm) columns (h 20 cm, r 9.2 cm) sampled in spring from a loam and a silt soil (Table 1) under winter wheat.
- Applied -30 cm pressure potential to columns in sandbox to allow draining of macropores.
- MCPA applied at agronomical rate. Bromide applied as inactive tracer.
- Thermistors installed in half of the columns which then were insulated and frozen at -3 °C. The rest were stored at +4 °C (Figure 1 b).
- 3-4 freezing-thawing cycles (Figure 1 a). Columns irrigated with 25 mm artificial rainwater (5 mm/h) at each irrigation event (approx. 196 ml/irrigation).
- Irrigation room and rainwater temperatures were kept at approx. 10 and 4 °C respectively.
- Leachate was collected at ~25 ml intervals, weighed and analysed for bromide (Thermo, ion-selective electrode) and MCPA (LC-MS/MS).

Table 1: Soil characteristics of Kroer loam and Hov silt.

Site	Soil texture (USDA, 0-20 cm)	Class. (WRB 2014)	Horizon, cm	Clay, %	Silt, %	Sand, %	Org. C, %	pH (H ₂ O)	Pore vol., %
Kroer	Loam	Retic	Ap, 0-23	19.1	43.8	37.1	2.5	5.5	49.7
		Stagnosol	Eg, 23-40	20.5	63.0	16.7	0.5	5.6	39.4
Hov	Silt	Dystric	Ap, 0-20	5.4	83.8	10.8	1.2	5.4	48.5
		Fluvis	Bw, 28-50	4.1	86.7	9.2	0.3	6.2	48.0
		Cambisol							

Results

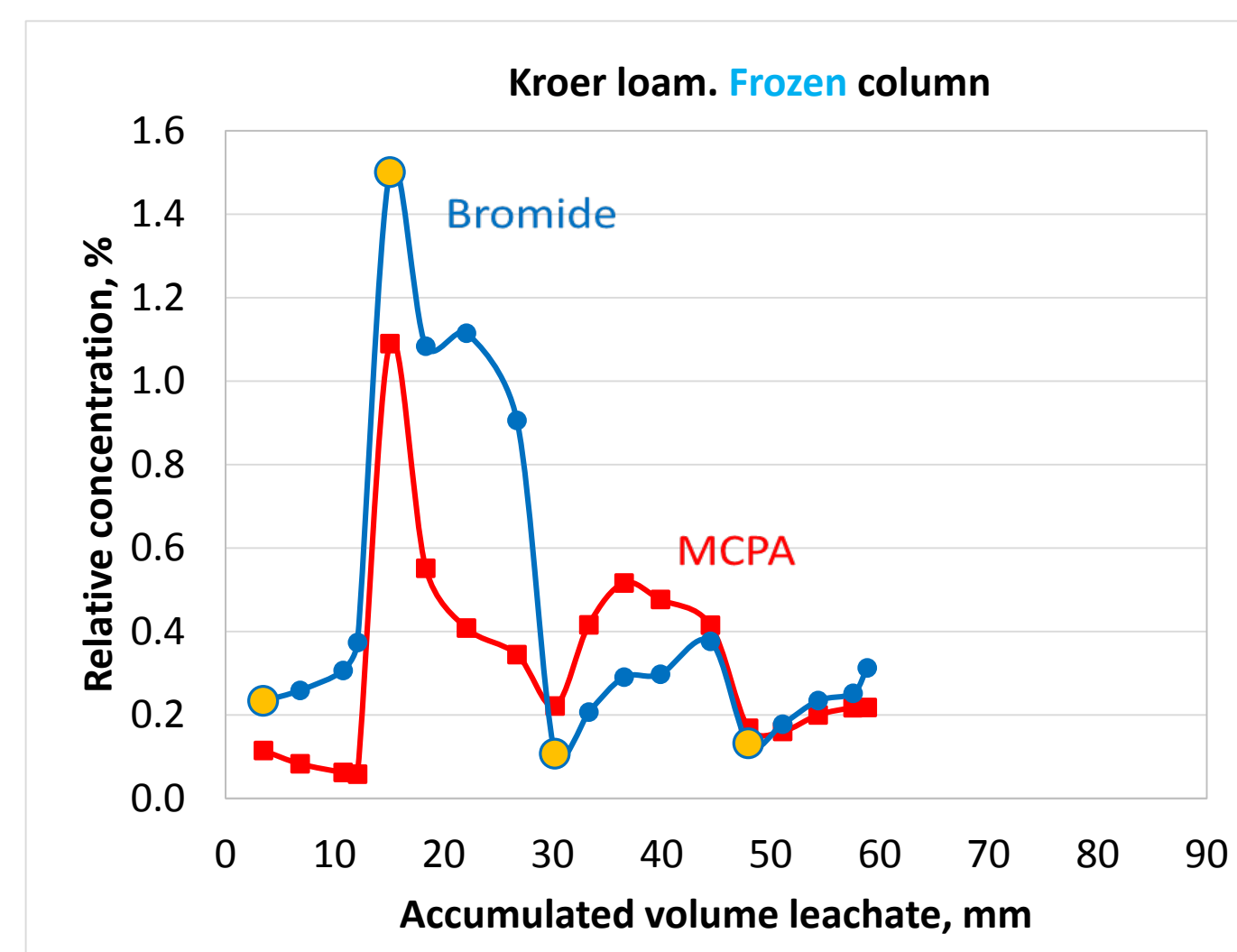


Figure 2: Kroer loam, 0-20 cm. Relative concentration (C/C_0 , in %) of bromide and MCPA in leachate from a frozen soil column. Yellow points on bromide curve mark the irrigation events.

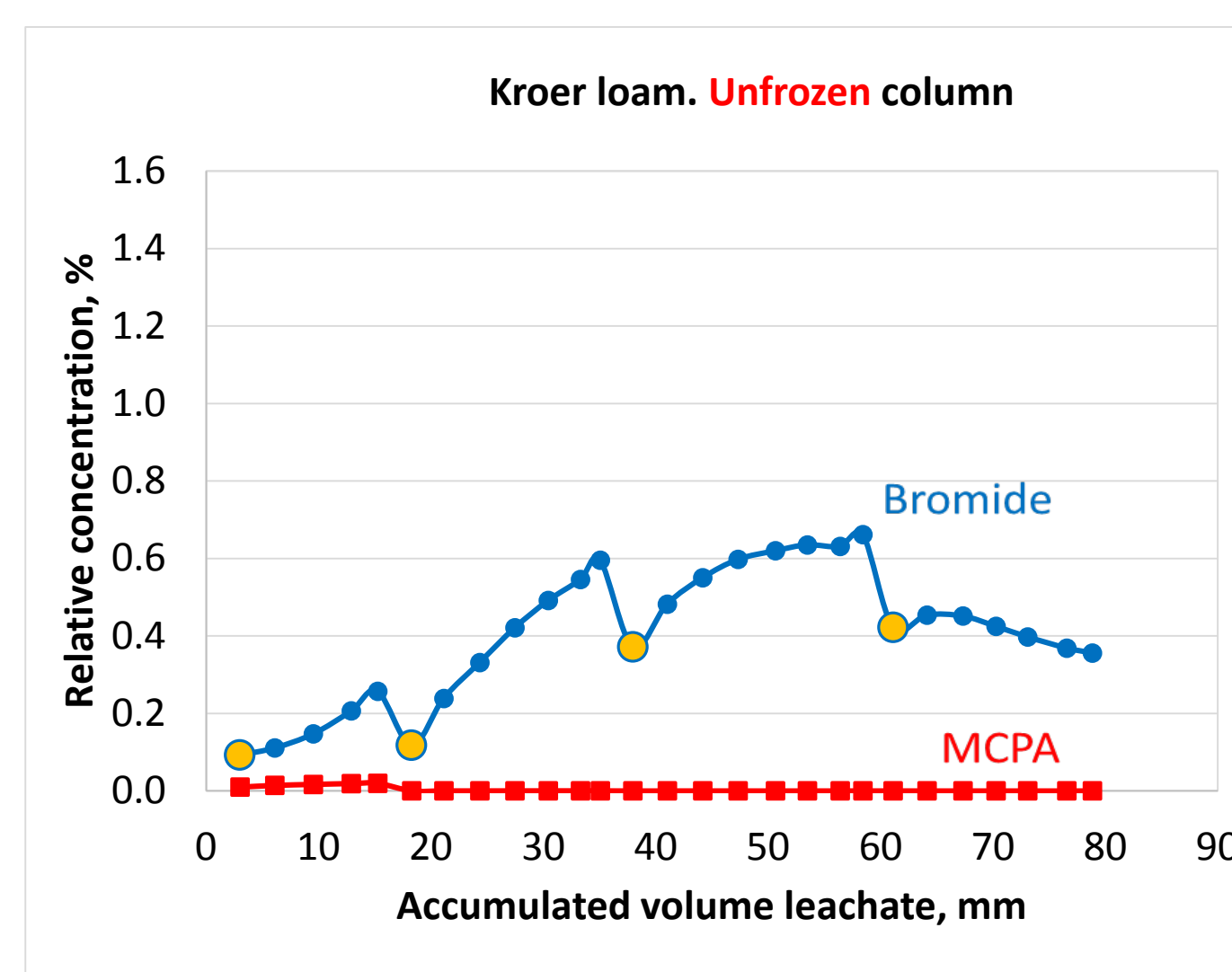


Figure 3: Kroer loam, 0-20 cm. Relative concentration (C/C_0 , in %) of bromide and MCPA in leachate from an unfrozen soil column. Yellow points on bromide curve mark the irrigation events.

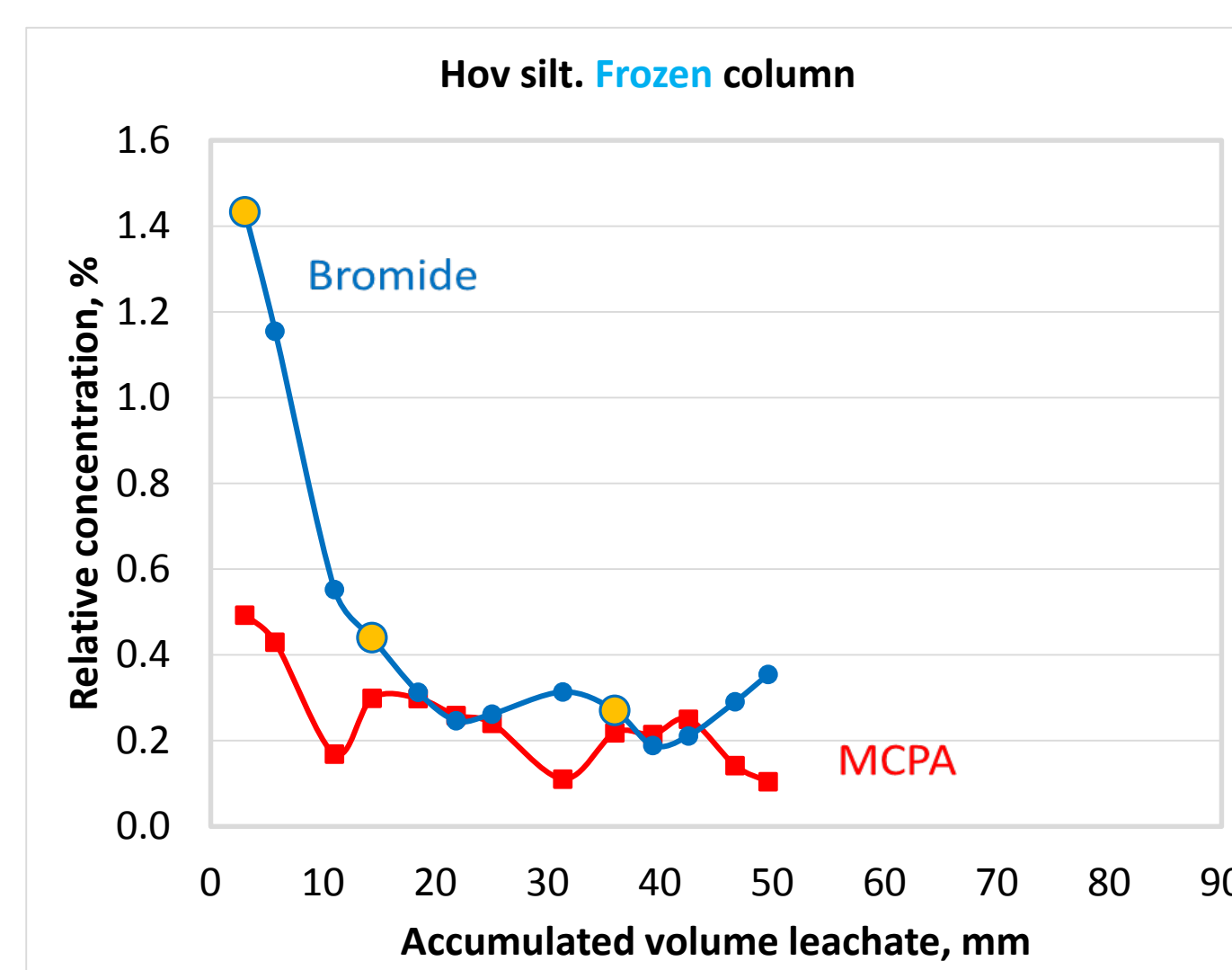


Figure 4: Hov silt, 0-20 cm. Relative concentration (C/C_0 , in %) of bromide and MCPA in leachate from a frozen soil column. Yellow points on bromide curve mark the irrigation events.

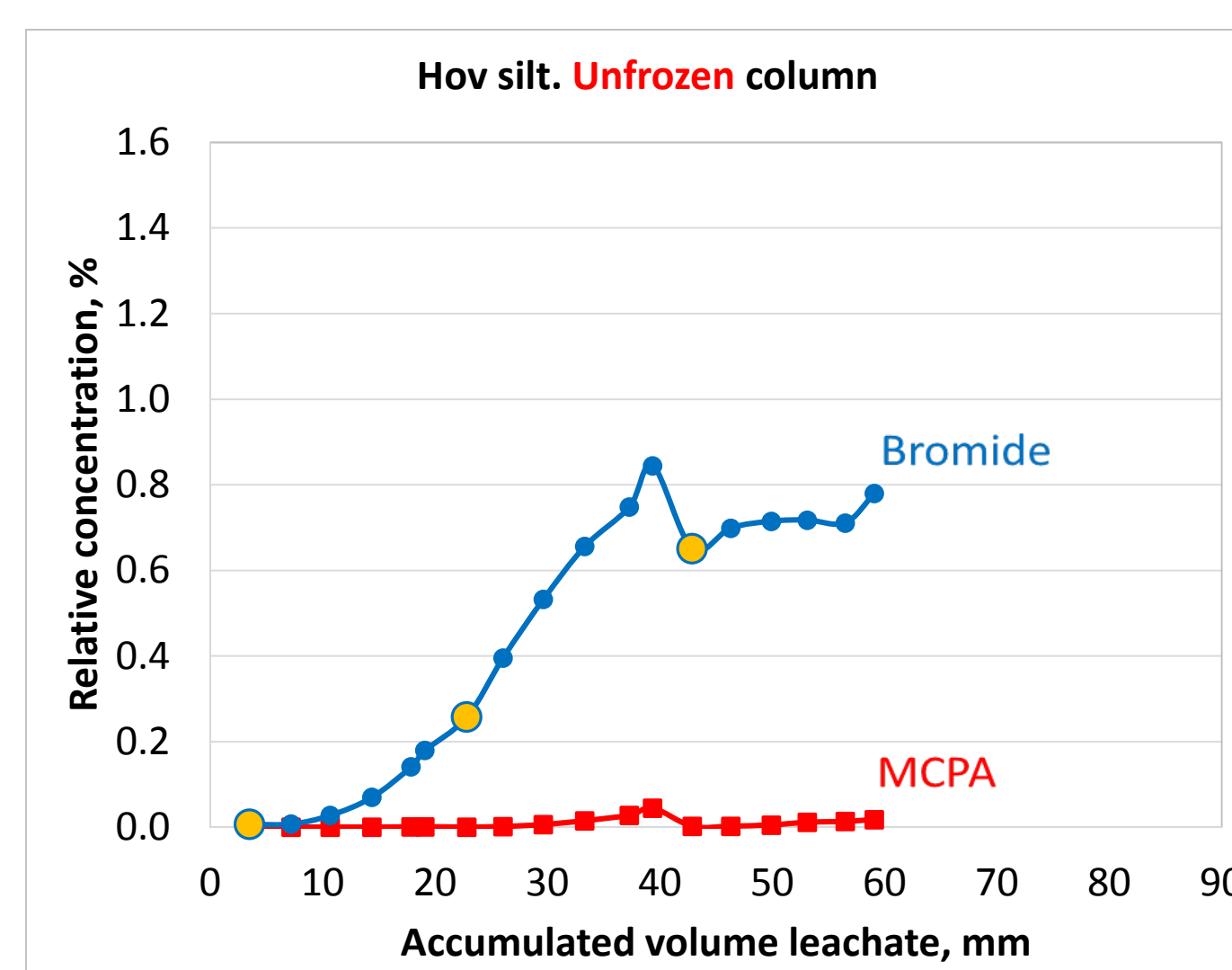


Figure 5: Hov silt, 0-20 cm. Relative concentration (C/C_0 , in %) of bromide and MCPA in leachate from an unfrozen soil column. Yellow points on bromide curve mark the irrigation events.

Table 2: Water drained and bromide and MCPA leached (average of 5 columns) from frozen and unfrozen Hov silt and Kroer loam soil columns after 3 and 4 irrigations

		Average amount water drained, mm (STD)	Bromide leached, % of applied (STD*)	MCPA leached, % of applied (STD*)
Kroer, loam	Frozen	52.6 (5.4)	37.4 (3.3)	24.5 (6.9)
	Unfrozen	77.2 (2.9)	57.5 (10.3)	0.4 (0.3)
Hov, silt	Frozen	48.3 (5.1)	25.2 (8.8)	16.4 (3.4)
	Unfrozen	59.8 (1.6)	31.5 (9.7)	0.5 (0.2)

* Percent point.



- Sharp peaks in breakthrough curves or high concentrations leaching at the first irrigation in the frozen soil columns, indicate bypass of sorption sites and fast preferential transport through open macropores (Figure 2 and 4).
- Similar results were observed for both loam and silt although less clear for MCPA in the silt soil, probably due to smaller macroporosity.
- Smoother breakthrough curves for bromide leaching from unfrozen columns indicating slower transport through the whole of the soil matrix (Figure 3 and 5).
- Compared with frozen soil, considerable less MCPA than bromide leached from unfrozen soil columns after about one pore volume had drained (Table 2).

Conclusions

- Preferential transport of MCPA and bromide was observed in frozen soils. Sorption of MCPA was probably much weaker in frozen soil as transport was confined to the larger (still unfrozen) pores.
 - This might be due to smaller surface area and faster water flow in these pores so that equilibrium was not reached (i.e. kinetic effects).
- Preferential flow of pesticides in macropores during thawing of frozen soils can lead to fast vertical transport of relatively high concentrations of pesticides towards groundwater or to surface water through drains.



Key references

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