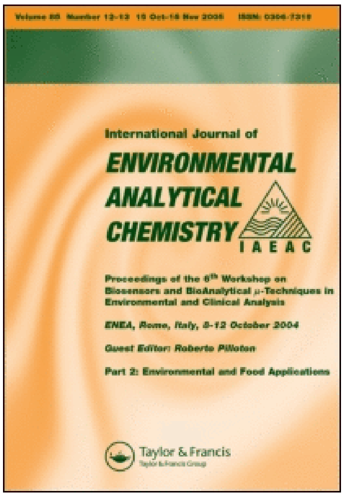

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SURFACE RUN-OFF OF MECOPROP

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Run-off of the phenoxyalkanoic acid herbicide mecoprop (2-(4-chloro-2-methylphenoxy) propionic acid) has been studied in Denmark on two locations having a mean slope of 10% and 12%, respectively. The herbicide has been sprayed out in the autumn where the most intense run-off events are expected. Mecoprop has been detected in run-off from both locations, the maximum concentrations were 1.62 µg/l and 23.34 µg/l, respectively. The content of mecoprop in run-off per ha was between 14 mg and 700 mg corresponding to between 0.02‰ and 0.97‰ of the applied amount. The mecoprop losses bound to sediment were only about 0.5% of the losses via the water phase. A modified version of the model CREAMS was used to test the model results against the observed at one of the locations. The modelled amount of losses was in good agreement with the observed.

KEY WORDS: Run-off, mecoprop, herbicide, pesticide, phenoxyalkanoic acid, CREAMS.

INTRODUCTION

When the amount of rain water exceeds the infiltration rate of the soil, surface run-off will take place. Primarily, pesticides having a high solubility[1–4] will be lost via the water phase through leaching or run-off. Pesticide transport via run-off is influenced by many factors including the time of application and the amount sprayed, the intensity and amount of precipitation, the texture and the slope of the soil. The amount of pesticide lost via run-off is related to the amount applied and is highest if the run-off takes place immediately after application[4–7]. Sibbesen *et al.*[8] stressed that the infiltration will be low, and the run-off proportional higher, if the soil is compact or frozen or if the surface structure of the soil is damaged.

Conventional tillage results in an increase in run-off according to Hall *et al.*[9], caused the disrupted macroporous spaces, opposite a no-tillage mulched surface having an intact macroporous matrix. This is in accordance with Danish trials at Foulum and Ødum[8] where surface run-off has shown to be more obvious from winter crops than from bare ground and grass areas. In this study run-off was studied by treating winter wheat, which was sown up and down the slope, with mecoprop in the autumn.

Many authors[5,10–13] have determined pesticides in run-off in concentrations up to 35 µg/l.

EXPERIMENTAL METHODS

Selection of localities

One of the two locations is situated at Ramsølille by the Langvad Stream just south of Roskilde in the centre of Sjælland (Zealand) (55°35'N, 12°04'E), the other is situated at Foulum north of Viborg in mid-Jutland (56°30'N, 9°34'E). The mean slope of location Langvad and Foulum is 12% and 10%, respectively.

Soil description

The physical properties of the 2 localities are given in Table 1. The content of humus in the plough layer was 2.1% at Foulum and 1.6% at Langvad, the soil types were loamy sand and sandy loam, respectively.

Table 2 shows the time of spraying and the dose of mecoprop.

Table 1 The soil physical properties.

Location	*Foulum*	*Langvad*
Slope %	10	12
Hydraulic conductivity (m/s)	$4.3 \cdot 10^{-6}$	$15.9 \cdot 10^{-6}$
Field capacity (vol. %)	16.7[a]	20.4[b]
Permanent wilting point (vol.%)	8.9	6.0
Porosity (vol. %)	42.5	44.4
Humus %	2.1	1.6
Clay % (< 2 μm)	8.8	14.4
Silt % (2–20 μm)	9.9	14.5
Fine sand % (20–200 μm)	35.6	43.8
Coarse sand % (20–2000 μm)	43.6	25.7
Soil classification[c]	Loamy sand	Sandy loam

[a] Measured at 0.10 bar. [b] Measured at 0.33 bar.
[c] After the classification established by the U.S. Department of Agriculture.

Table 2 The applications of mecoprop.

Location	*Application time*	*Dose kg a.i. per ha*
Foulum plot 6	6.12.1993	0.720
Foulum plot 8	6.12.1993	0.720
Langvad	21.11.1991	0.584
Langvad	13.11.1992	0.584

Water sampling technique

Run-off from the Foulum plots was collected by placing a tank at the lower end of each plot. The tanks were emptied from time to time and the amounts of water were determined.

At Langvad the run-off reached a PVC-flume from where it drained to a vessel which was drained through a Thompson overflow. The water level in the vessel was measured every 30 s. Water samples were taken using a tilting vat sampling a fraction of the total run-off. In Table 3 amounts of run-off are given in litres from the test plot and in litres per ha together with the precipitation, which was recorded at both locations.

Analytical methods

The water samples were analysed by (GC-MS)[14] and calibration curves in the range 0.01 µg/l to 2.0 µg/l were prepared. In the light of these, the limit of detection were fixed according to Miller & Miller[15].

RESULTS AND DISCUSSION

Physical properties of the soil

As shown in Table 1, location Langvad is more steep than Foulum, which has a higher content of humus and sand and a lower clay and silt content than Langvad.

Table 3 Run-off and precipitation from the locations Foulum and Langvad.

Location	*Date*	*Run-off in l*		*Precipitation*	*Run-off in %*
		from the test plot	*per ha*	*in l per ha**	*of precipitation*
Foulum	04.01.1994	141$^{\Delta}$			
plot 6	10.02.1994	269			
	07.03.1994	1200			
	20.04.1994	359			
Σ		1969	342673	2948000	11.6
Foulum	04.01.1994	45$^{\Delta}$			
plot 8	10.02.1994	163			
	07.03.1994	662			
	20.04.1994	135			
Σ		1005	174904	2948000	5.9
Langvad	01.02.1992	3722$^{\Delta}$			
	14.02.1992	879			
	12.05.1992	1579			
Σ		6180	11236	2260000	0.5
	12.01.1993	23232$^{\Delta}$			
	04.02.1993	14633			
	23.04.1993	3623			
Σ		41488	75433	2227000	3.4

* Precipitation from the time of spraying until 20-4-94, 12-5-94 and 23-4-94, respectively.
$^{\Delta}$ Is the total amount of run-off from the time of spraying to the concerned date.

Run-off and precipitation

Run-off has been recorded before spraying in the autumn until April/May. In Denmark run-off events are normally very scarce in the summer. At Foulum run-off events have been registered at 2 plots, each having an area of 57.46 m^2 (Table 3). In the period from spraying (6-12-1993) until 20-4-1994 the total run-off from plot 6 and 8 amounted to 1969 1 and 1005 1, respectively. Converted into 1 run-off per ha, it amounts to 342673 1 from plot 6 and 174904 I from plot 8. In the same period the precipitation per ha was 2948000 1 (1 mm = 10000 l/ha). The amount of precipitation in the period December 1993—April 1994 was approximately 66% higher than the mean precipitation measured at Foulum in the period 1961–1990[16]. As shown in Table 3 the amount of run-off in per cent of the precipitation was 11.6% at plot 6 and 5.9% at plot 8, in spite of the fact that plot 6 and 8 are obviously uniform.

At Langvad the test field was 5500 m^2 (0.55 ha), run-off from this location has been recorded from autumn 1991 and 2 years further on. In Table 3 only figures from autumn, winter and spring are presented due to the fact that summer run-off events have been very limited.

In the first period - from spraying 21-11-1991 until mid-May 1992—run-off per ha was only 11236 1. In the following period—from spraying 13-11-1992 until late April—run-off amounted to 75433 1 per ha. The precipitation in the above mentioned periods was very much alike 2260000 1 and 2227000 1, respectively[16]. Both figures are below the mean precipitation. In 1991/1992 run-off amounted to 0.5% of the precipitation, in 1992/1993 to 3.4%.

The higher run-off per cent in the period 1992/1993 was not caused by a break in the frost but was simply caused by precipitation with a high intensity and/or precipitation fallen on a frozen soil.

The mean precipitation (1961-1990) from November to May was 304 mm at Foulum and 294 mm at Roskilde (close to location Langvad), the Foulum precipitation is in average 3% higher than the Langvad precipitation[16].

Mecoprop run-off

Before spraying with mecoprop run-off samples were taken to check the background levels of this pesticide. At Langvad water sampled a few days before the first spraying (1991) contained 0.35 µg/l mecoprop, before the second spraying (1992) the concentration was 0.05 µg/l. The amount of mecoprop in the run-off sampled before the first spraying, could derive from wind drift in connection with a spot treatment with a mecoprop containing herbicide on a neighbouring field. Analyses of water samples from Foulum showed a content of mecoprop at 0.11 µg/l from plot 8 and below 0.07 µg/l from plot 6 before spraying (1993). Mecoprop has been measured in precipitation in Denmark[17] in concentrations up to 0.12 µg/l, therefore, the content of mecoprop in run-off could also derive from the precipitation.

The mecoprop concentrations in the run-off (water phase) sampled are given in Table 4 as total µg per test plot as well as in µg/l run-off and in mg per ha. Generally, the highest concentrations of mecoprop are seen in run-off samples taken just after spraying. The concentrations decreased during the winter and spring. In April/May the concentrations were below 0.7 µg/l.

At Foulum—plot 6—the highest concentration was 23.34 µg/l, at plot 8 the second highest concentration determined was 11.24 µg/l. Totally, at least 4.03 mg of mecoprop was carried with run-off at plot 6 (Table 5), this corresponds to 0.97‰ of the applied

Table 4 The concentrations of mecoprop in run-off given in μg/l (95% confidence limits), the total amount of mecoprop in run-off from the plots and the total amount of mecoprop in run-off per ha.

Location	*Date*	*Run-off*	*Mecoprop*		
		in l	*total μg*	*μg/l*	*mg per ha*
Foulum*	04.01.1994	141^Δ	3290.94	23.34(20.97;26.20)	573
plot 6	10.02.1994	269	513.79	1.91(1.83;1.99)	89
	07.03.1994	1200	O		
	20.04.1994	359	222.58	0.62(0.54;0.72)	38
Σ					700
Foulum*	04.01.1994	45^Δ	505.80	11.24(9.95;12.80)	88
plot 8	10.02.1994	163	185.82	1.14(1.07;1.22)	32
	07.03.1994	662	O		
	20.04.1994	135	48.60	0.36(0.33;0.41)	8
Σ					128
Langvad**	01.02.1992	3722^Δ	5437.39	1.46(1.08;1.84)□	10
	14.02.1992	879	1411.69	1.61(1.49;1.73)	3
	12.05.1992	1575	761.08	0.48(0.41;0.55)	1
Σ					14
Langvad**	12.01.1993	23232^Δ	37751.47	1.62(1.25;1.99)□	69
	04.02.1993	14633	3468.36	0.24(0.16;0.32)	6
	23.04.1993	3523	289.36	0.08(0.06;0.10)	1
Σ					76

* The test plot is 57,46 m^2. **The test plot is 5500 m^2. ^ΔIs the total amount of run-off from the time of spraying to the concerned date.
O Samples lost.
□ Originally samples were taken more frequent, but to compare the results from Langvad with the results from Foulum the content of mecoprop from single run-off events have been added and recalculated as one concentration deriving from the corresponding amount of run-off.

Table 5 The total amount of mecoprop in run-off from the test plots in mg and in ‰ of the applied amount.

Location	*Mecoprop*	
	total in mg	*in ‰ of applied*
Foulum 1994 plot 6	4.03*	0.97*
Foulum 1994 plot 8	0.74*	0.18*
Langvad 1991/1992	7.61	0.02
Langvad 1992/1993	41.51	0.13

* The amount/‰ of mecoprop were at least the mentioned as water samples from March 1994 were lost.

amount, at plot 8 the corresponding figures are 0.74 mg and 0.18‰. At plot 6 the amount of run-off was approximately twice the run-off amount from plot 8. But more than 5 times as much mecoprop was carried from plot 6 than from plot 8. Unfortunately, samples taken on 7th March were lost, but the difference in losses between plot 6 and plot 8 would probably not be changed because of the missing samples.

At Langvad the highest concentration of mecoprop was 1.61 μg/l during the period 1991/1992 compared to 1.62 μg/l in 1992/1993. Totally, 7.61 mg mecoprop was carried with the run-off from Langvad in 1991/1992 corresponding to 0.02‰ of the applied amount. For Langvad 1992/1993 the corresponding figures were 41.51 mg and 0.13‰. In the period 1992/1993 the amount of run-off was nearly 7 times the amount in 1991/1992.

Calculating the mecoprop load in mg per ha (Table 4) or in ‰ of applied (Table 5) shows that run-off from Foulum contains much more mecoprop than run-off from Langvad.

The acute toxic concentrations of mecoprop to algae, dapniae and fish are between 100 mg/l and 1100 mg/l[18], which are at least 4000 times higher than the highest concentrations measured at Foulum.

Adsorption and degradation

The K_d-values for mecoprop in soil from Langvad was measured to 0.56 l/kg[13,19], corresponding to a K_{oc}-value of 50.9 l/kg. This means that the K_d-value for mecoprop in sediment from Foulum is 0.59 l/kg according to:

$$K_{oc} = \frac{K_d \cdot 100}{\%\ oc}$$

where oc is organic carbon.

Smith[20] has measured the half-live of mecoprop in 3 different soil typcs (clay, clay loam and sandy loam). The $T_{1/2}$-values were 7–9 days when measured at 20°C in soils saturated to 85% of the field capacity.

In this study mecoprop was applied in the autumn where the temperature was about 5°C. As the degradation time raises when temperature decreases, the degradation of mecoprop will be slower (about 37 days). Therefore, the potential pesticide load in run-off is greater after an autumn application than after a spring application.

The difference in pesticide load in run-off after autumn and spring application has been shown at Langvad[13] The autumn application caused a pesticide load which was at least 10 times larger than the spring application, in spite of the fact that the applied amount of spring herbicide was 5 times higher than the amount of autumn applied herbicide.

Mecoprop bound to sediment

Using the above K_d-values the total load of mecoprop bound to the sediment phase has been calculated for Foulum and Langvad (1992/1993). The calculations have been performed assuming equilibrium between mecoprop in soil and in water phase. At Foulum the total load was 1954 µg per ha corresponding to 0.5% of the mecoprop content in the water phase or 0.003‰ of the applied amount, at Langvad the total load was 862 µg per ha corresponding to 1.2% of the mecoprop content in the water phase or 0.002‰ of the applied amount. Thus the greatest loss was seen in the water phase.

Modelling

The results from location Langvad have been used to test the modified CREAMS model[21]. The period used for modelling cover nearly 2 years (November 1991-September

1993). The model results were tested against the observed run-off volume and against the observed soluble mecoprop loss in run-off[21]. The modelled cumulative amount of mecoprop losses was in good agreement with the observed cumulative losses, the calculated amounts of mecoprop losses via the water phase were 76% of the observed.

The calculated losses via sediment in the second period (November 1992—September 1993) were 99% of the observed.

CONCLUSION

The amount of mecoprop in run-off is reduced in time partly caused by the degradation and partly caused by the increased adsorption by soil in time. The content of mecoprop in run-off very much depends on the meteorological circumstances immediately after spraying.

The losses of mecoprop via run-off were very limited and far below 1% of the applied amount, the great majority of mecoprop was lost via the water phase.

In this study, the run-off volume, the run-off in per cent of precipitation and the load of mecoprop were greatest from the locations with the smallest slopes and the lowest hydraulic conductivity.

This study has shown a great variation between the two identical treated plots at Foulum, the difference might be due to different hydraulic conductivities in the plots.

At Langvad the same amount of precipitation has resulted in very different run-off volumes in 1991/1992 and 1992/1993 caused by e.g. the intensity of the precipitation and the soil temperature (frozen soil).

According to the LC_{50} values there is no risk of acute toxic effects in water courses in consequence of the mecoprop load from run-off. On the other hand, the mecoprop load deriving from leaching is considerable greater, according to the model CREAMS the amount of mecoprop leached from the Langvad was approximately 70 times higher than the amount of mecoprop in run-off.

The above results lead to the conclusion that for relatively non-adsorptive pesticides (phenoxyalkanoic acids) the risk for leaching and pollution of groundwater is much higher than the risk for pollution via run-off even if the location is steep.

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References

1. K. R. O'Hara, in *T. D. Landis Proceedings*, (Intermountain Forest Nursery Association. US Department of Agriculture, Forest Service, Rocky Mountain Forest and Range Experimental Station, 1991) pp. 39–46.
2. S. Ebise, T. Inoue and A. Numabe, *Water Sci. Technol.*, **28**, 589–593 (1993).
3. T. Iwakauma, H. Shiraiski, S. Nohara and K. Takamura, *Chemosphere*, **4**, 677–691 (1993).
4. H. Klöppel, J. Haider and W. Kördel, *Chemosphere*, **4**, 649–662 (1994).
5. W. Nicholaichuk and R. Grover, *J. Environ. Qual.*, **12**, 412–414 (1983).
6. J. D. Gaynor, D. C. MacTavisk and W. I. Findlay, *Arch. Environ. Contam. Toxicol.*, **23**, 240–245 (1992).

7. B. T. Bowman, G. J. Wall and D. J. King, *Can. J. Soil Sci.*, **74**, 59–66 (1994).
8. E. Sibbesen, A. C. Hansen, J. D. Nielsen and T. Heidmann, in: *Soil Tillage and Environment* (P. Elonen and J. Pitkänen, ed., NJF-Utredning/Rapport, 88, 1993), pp. 29–38.
9. J. K Hall, R. O. Mumma and D. W. Watts, *Agric. Ecosyst. Environ.*, **37**, 303–314 (1991).
10. D. T. Waite, R. Grover, N. D. Westcott, H. Sommerstad and L. Kerr, *Environ. Toxicol. Chem.*, **11**, 741–748 (1992).
11. M. Sudo and T. Kunimatsu, *Water Sci. Tech.*, **25**, 85–92, (1992).
12. J. Kreuger, in: Pesticides in the Aquatic Environment. Appearance and Effect. (A. Helweg, ed., Statens Planteavlsforsøg. Beretning nr. S 2181, 1992), 137 pp.
13. G. Felding, J. B. Sørensen, B. B. Mogensen and A. C. Hansen, *Sci. Total Environ.*, **175**, 207–218 (1995).
14. G. Felding, *Sci. Total Environ.*, **168**, 11–18 (1995).
15. J. C. Miller and J. N. Miller, *Statistics for Analytical Chemistry*, (Ellis Horwood, Chichester, 1988) 2nd edn., 227 pp.
16. Meteorological data are from the Danish Institute of Plant and Soil Science, Research Centre Foulum.
17. E. Kirknel & G. Felding in: *Pesticides in Precipitation and in Surface Water Appearance and Effects*, (A. Helweg, ed., Nordic Council of Ministers. TemaNord 558, 1995), 188 pp.
18. Danish Environmental Protection Agency. Personal Communication (1994).
19. OECD Guideline for Testing of Chemicals Adsorption/Desorption **106**, (1981), 23 pp.
20. A. E. Smith, *Rev. Weed Sci.*, **4**, 1–24, (1989).
21 S. Rekolainen, G. Felding, J. B. Soerensen, B. B. Mogensen, and S. Salo, in: Pesticides in *Precipitation and in Surface Water-Appearance and Effects*, (A. Helweg, ed., Nordic Council of Ministers. TemaNord 558, 1995), 188 pp.