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Triclopyr, Glyphosate and Phenoxyherbicide Residues in Cowberries, Bilberries and Lichen

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Foliar spraying with phenoxyherbicides for brush control has been practised in Finland for about twenty years. The use of 2,4,5-T has, however, been prohibited since January, 1980. In 1978, glyphosate was officially approved for brush control. Triclopyr has been used in official field tests, but has not yet been approved for use.

A report has been published in Finland concerning the residues of 2,4-D and 2,4,5-T in cowberries, mushrooms and tree twigs as a result of aerial spraying (MUKULA et al. 1978). A similar study has been carried out in Sweden (ERNE et al. 1973). 2,4-D, 2,4,5-T, MCPA and glyphosate residues following ground spraying of aerial spraying of small experimental plots in Sweden have also been reported (INGELÖG et al. 1977).

In Finland, an investigation was started in 1975 into herbicide residues in wild berries in forests using controlled ground spraying experiments. The herbicides studied during 1975–1976 were 2,4-D, 2,4,5-T, MCPA and glyphosate. The residues were analysed in cowberries and bilberries from small experimental plots, using increasing amounts of active ingredient. The interval between spraying and sampling was kept constant. The results of the investigations carried out during 1975–1976 have already been published (RAATIKAINEN et al. 1979).

In 1977, the above-mentioned investigation on small experimental plots was continued and the results are published here. The study was extended to include triclopyr, a new herbicide used for brush control. The residues of triclopyr were analysed in cowberries and bilberries under the same experimental conditions as in the previous study concerning 2,4-D, 2,4,5-T, MCPA and glyphosate. The effect of the date of treatment on glyphosate and triclopyr residues in cowberries and bilberries was also investigated. Berries were also sampled and analysed one year after the 1975 and 1976 experimental treatments, and the herbicides studied were 2,4-D, 2,4,5-T, MCPA and glyphosate. Glyphosate and triclopyr residues were also analysed in lichens sampled 9–13 months after treatment.

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METHODS

Field tests

The test sites were in two pine forests situated at Laukaa (about 62° 30' N and 25° 55' E) and Konnevesi (about 62° 40' N and 26° 05' E). In addition to pines, Pleurozium schreberi, Hylocomium splendens, Dicranum polysetum, D. scoparium and Cladonia rangiferina , the flora at Laukaa consisted of bilberry (Vaccinium myrtillus) 41 %, cowberry (V. vitis-idaea) 25 % and Calluna vulgaris 8 %, and at Konnevesi bilberry 14 %, cowberry 35 % and Calluna vulgaris 39 %. The experimental plots measured 2 x 10 m with four replicates. The herbicides used were the commercial preparations of triclopyr and glyphosate Garlon and Roundup. In 1977, the plots were treated using a portable Azo Propan knapsack sprayer. The herbicide doses in the active ingredient experiments were 0.25, 0.75 and 2.25 kg/ha, and in the application date experiments 0.75 kg/ha.

Residues of glyphosate, 2,4-D, 2,4,5-T and MCPA were also analysed from experiments at Laukaa carried out in 1975 and 1976 (RAATIKAINEN et al. 1979).

The total cowberry and bilberry yields and the lichen (Cladonia rangiferina) samples were picked from an area measuring 1.5 x 9.0 m in the centre of each experimental plot. After weighing, the berries and lichen samples were combined for each replicate, and deep frozen before chemical analysis.

Sample analyses

2,4-D (2,4-dichlorophenoxyacetic acid) and 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) residues were analysed as methyl esters by gas chromatography using the method of SILTANEN and ROSENBERG (1978). MCPA (4-chloro-2-methylphenoxyacetic acid) residues were determined using the same method but, in addition, MCPA was brominated after methylation (SILTANEN and ROSENBERG 1980). Triclopyr ((3,5,6-trichloro-2-pyridyl)oxyacetic acid) residues were determined as its methyl ester by gas chromatography using the same method as for 2,4-D and 2,4,5-T, with the exception that the acidic diethyl ether extraction was replaced with an alkaline methanol extraction according to the method developed by Dow Chemicals (FREEMAN 1978). Glyphosate (N-(phosphonomethyl)glycine) and its metabolite (aminomethylphosphonic acid) were analysed as N-trifluoroacetyl methyl esters by gas chromatography according to the method published in PESTICIDE ANALYTICAL MANUAL (1977).

RESULTS AND DISCUSSION

COWBERRY

Triclopyr. Triclopyr residues were analysed in cowberries after application rates of 0.25, 0.75 and 2.25 kg/ha of active ingredient. The cowberries were sampled 30 days after application and

the residues increased with increase in dose. The residues found were 0.3, 0.8 and 1.9 ppm, respectively (TABLE 1). The triclopyr residue level was of the same order of magnitude as those obtained with phenoxyherbicides and glyphosate (RAATIKAINEN et al. 1979). Triclopyr residues in cowberries were also determined for a constant application rate of 0.75 kg/ha of active ingredient and different application dates (TABLE 1). When the herbicide was applied in the middle of June or July and the berries were sampled 2-3 months after application the residues were low, 0.2-0.3 ppm. When the herbicide was applied in the middle of August and the cowberries were sampled one month after treatment the residues totalled 0.7-1.1 ppm. The residues were 2.4 ppm in berries sampled 6 days after treatment in September.

TABLE 1

Triclopyr residues in cowberries and bilberries from controlled field experiments (1977)

Sample	Application date	Active ingredient kg/ha	Interval between application and sampling, days	Residues ppm (mg/kg)
cowberry	16.8.77	0.25	30	0.3
	"	0.75	30	0.8
	"	2.25	30	1.9
bilberry	16.8.77	0.25	8	0.2
	"	0.75	8	0.8
	"	2.25	8	4.0
cowberry	15.6.77	0.75	98	0.3
	"	"	92	0.2
	13.7.77	"	70	0.2
	"	"	64	0.2
	16.8.77	"	36	1.1
	"	"	30	0.7
	15.9.77	"	6	2.4
bilberry	15.6.77	"	69	0.7
	13.7.77	"	41	0.4
	16.8.77	"	7	0.9

Glyphosate. Glyphosate was applied at a rate of 0.75 kg/ha in the middle of July, August and September and the berries were sampled 2 months, 1 month and 6 days after treatment, respectively (TABLE 2). The residues were low, 0.1-0.3 ppm in berries sampled 1-2 months after spraying and 1.6 ppm after 6 days. The amount of metabolite detected was very low, 0.01-0.02 ppm.

In addition, glyphosate was analysed in cowberries sampled 1 year after spraying, i.e. sampled during the following growing season in the autumn (TABLE 3). The application rate was 0.25 kg/ha and no residues were detected. The berry yield after the application with 0.75 and 2.25 kg/ha was small, and therefore analysis of berries from these application sites was not possible.

TABLE 2

Glyphosate residues in cowberries and bilberries from controlled field experiments (1977)

Sample	Application date	Active ingredient kg/ha	Interval between application and sampling, days	Residues, ppm (mg/kg) Glyphosate	Metabolite
cowberry	13.7.77	0.75	70	0.1	n.d. <0.01
	"	"	64	0.3	n.d. <0.01
	16.8.77	"	36	0.3	n.d. <0.01
	"	"	30	0.3	0.01
	15.9.77	"	6	1.6	0.02
bilberry	15.6.77	"	69	0.2	n.d. <0.01
	13.7.77	"	41	0.2	n.d. <0.01
	16.8.77	"	7	2.1	0.07

n.d. = not detected

BILBERRY

Triclopyr. Triclopyr residues were analysed in bilberries sampled 8 days after application of varying amounts of herbicide. The herbicide sprayed contained 0.25, 0.75 and 2.25 kg/ha of active ingredient (TABLE 1). The residues detected totalled 0.2, 0.8 and 4.0 ppm, respectively. The residue level in bilberries increases with increasing dosage in the same manner as in cowberries. The residue level was also the same as that found for phenoxyherbicides and glyphosate (RAATIKAINEN et al. 1979), but it should be observed that in the present investigation the berries were sampled only 8 days after treatment, whereas in the previous study

TABLE 3

Phenoxyherbicide and glyphosate residues in bilberries and cowberries from controlled field experiments (1975, 1976) after one year

Sample	Herbicide	Application date	Active ingredient kg/ha	Interval between application and sampling	Residues, ppm (mg/kg)
bilberry	2,4-D	17.8.76	0.25	1 year	n.d. < 0.05
	"	"	0.75	"	n.d. < 0.05
	"	"	2.25	"	n.d. < 0.05
	2,4,5-T	"	0.25	"	n.d. < 0.02
	"	"	0.75	"	n.d. < 0.02
	MCPA	"	0.25	"	n.d. < 0.05
	"	"	0.75	"	n.d. < 0.05
	glyphosate	"	0.25	"	glyphosate n.d. < 0.1 metabolite n.d. < 0.02
cowberry	"	6.8.75	0.25	"	glyphosate n.d. < 0.1 metabolite n.d. < 0.02

n.d. = not detected

the berries were picked 1 month after.
Triclopyr residues were analysed in bilberries sprayed at a constant rate, 0.75 kg/ha, but with varying application date (TABLE 1). The application dates were in the middle of June, July and August, giving sampling intervals of about 2 months, 1 month and 7 days. The residue totalled 0.7, 0.4 and 0.9 ppm, respectively. The residues did not seem to decrease with time, as might have been expected.

Glyphosate. Bilberries were sprayed with glyphosate at a rate of 0.75 kg/ha in the middle of June, July and August (TABLE 2). The residues after the first two applications, i.e. sampling intervals of about 2 months and 1 month, totalled 0.2 ppm and no metabolite residues were detected. In August, the berries were sampled 7 days after application and 2.1 ppm glyphosate residues and 0.07 ppm metabolite residues were found.

No glyphosate residues were detected in bilberries sampled one year after treatment (TABLE 3). As was the case with cowberries, bilberries could only be analysed from one application site (0.25 kg/ha).

2,4-D, 2,4,5-T and MCPA. In the present study, phenoxyherbicides were analysed in bilberries sampled one year after treatment with 0.25 and 0.75 kg/ha of active ingredient (TABLE 3). With the exception of 2,4-D treated berries bilberries from the areas treated with 2.25 kg/ha could not be sampled. No residue were detected.

LICHEN

Triclopyr. Triclopyr residues were analysed in reindeer lichen (Cladonia rangiferina) sampled in the autumn 13 months after treatment (TABLE 4). The lichens were taken from the bilberry plots. The application rates were 0.25, 0.75 and 2.25 kg/ha. The residues increased with an increase in dose beeing 0.15, 1.0 and 1.7 ppm respectively.

Glyphosate. Glyphosate residues were analysed in reindeer lichen (Cladonia rangiferina) sampled in the spring, 9 months after treatment (TABLE 4). Lichens were also taken from the bilberry plots. The application rates were 0.25, 0.75 and 2.25 kg/ha. The residues increased with an increase in dose. The glyphosate residues totalled 2.5 ppm, 14 ppm and 45 ppm, respectively.
The corresponding metabolite residues were 0.25 ppm, 0.85 ppm and 2.1 ppm. In addition, one sample was taken in the autumn, 13 months after treatment, from an area treated with 0.75 kg/ha. The residues were 6.4 ppm of glyphosate and 0.3 ppm of metabolite.
The results show that the glyphosate residues in reindeer lichen (Cladonia rangiferina) are significantly higher than the triclopyr residues. This phenomenon was not observed in berries.

TABLE 4

Glyphosate and triclopyr residues in reindeer lichen (Cladonia rangiferina) from controlled field experiments (1976, 1977)

Sample	Application date	Active ingredient kg/ha	Interval between application and sampling, months	Residues, ppm (mg/kg) Glyphosate	Metabolite
lichen	17.8.76	0.25	9	2.5	0.25
	"	0.75	9	14	0.85
	"	2.25	9	45	2.1
	16.8.77	0.75	13	6.4	0.30
				Triclopyr	
	"	0.25	13	0.15	
	"	0.75	13	1.0	
	"	2.25	13	1.7	

The results from this and the previous studies (MUKULA et al. 1978, RAATIKAINEN et al. 1979) show that the residues in berries were of the same order of magnitude when the same amount of any of the studied herbicides was used. In aerial spraying, the application rates for the different herbicides vary; the lowest is for glyphosate, 0.5-0.75 kg/ha, and the highest for phenoxyherbicides, 2.5 kg/ha. The application rate for triclopyr is about 1.2 kg/ha. As a consequence of this the residues in berries from aerially sprayed forests can be expected to be highest after phenoxyherbicide application and lowest after glyphosate application.

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