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MCPA Residues in Developing Forest Ecosystem after Aerial Spraying

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In the spring 1970 there were exceptional number of reindeer deaths in Swedish Lapland. A herbicide treatment with 2,4-D and 2,4,5-T had been made about 8 months earlier. Analyses of the phenoxyacetic acid residues in deciduous trees revealed concentrations of 35 ppm (ERNE 1974).

After chemical brush control elsewhere in Sweden and Finland 0.5-6.9 ppm of 2,4-D and 2,4,5-T were found in berries and 2.3-60 ppm in their sprigs 24-32 days after treatment (ERNE and von HAARTMAN 1973). In foliage of birch and aspen the residue of 2,4-D varied from 0.15 to 31 ppm and that of 2,4,5-T from 0.1 to 30 ppm 13-43 weeks after herbicide spraying (SILTANEN and ROSENBERG 1978).

Because the chemical brush control has become a popular method of modifing the composition of forests, a project was started to investigate the phenoxyacetic acid residues at the different levels of forest. Analyses were made from birch, moss, leaf-litter and soil.

MATERIALS AND METHODS

The brush treatment was carried out on 10.8.1976 at the village of Lemivaara in Northern Karelia, Finland. The study area had been clearcut in 1968, ploughed and sowed with pine seeds in 1969. By the late summer 1976 there was a thick and uniform brush of birch and pine.

The commercial preparate used (Brush Killer MCPA, Kemira Oy) contained 500 g/l of the iso-octyl ester of 4-chloro-2-methyl phenoxyacetic acid (MCPA). The diluted herbicide was sprayed by plane, the concentration of the active substance being 2.5 kg/ha. The selected area for study was 50 m x 60 m.

Samples were collected 0, 15, 40, 261, 283 and 297 days after treatment.

The birch (Betula pubescens) twig , leaf-litter and moss (Pleurozium schreberii) samples were taken 15 randomy selected sites in the treated and the control area. Samples were homogenized and weighed into 2-5 gram lots. Ten milliliters of methanol was added to stop the activity of microorganisms.

Drill cores of 25 cm^2 were taken from 10 randomy selected sites of soil. The samples were divided into 0-3 cm, 3-6 cm and 6-15 cm portions, which were homogenized, divided into 15-20 gram lots and methanol (10 ml) was added.

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All samples were stored in a freezer (-20°C).

Before the residue analyses methanol was evaporated and 10 ml of distillated water was added to the soil samples.

The material was homogenized for 5 minutes in 30 ml of diethyl ether with an Ultra-Turrax homogenizer and pH was adjusted below 2 with conc. sulfuric acid (SILTANEN and ROSENBERG 1978, SUFFET 1973). The homogenate was stirred for 15 minutes and the ether was decanted into an evaporation bottle. Another portion of ether was added, and after pH control the sample was left to stand overnight. The combined ether extracts were evaporated to 5 ml and the residue was dissolved in 30 ml of iso-propanol and 30 ml of 0.2 M potassium hydroxide (PURKAYASTHA 1974, SILTANEN and ROSENBERG 1978, WOODHAM et al. 1974). The sample was hydrolysed in a hot water bath for half an hour. The pH of the cooled sample was adjusted below 2 with 0.7 M sulfuric acid. The phenoxyacetic acids were extracted with ether. After washing, the combined ether phase was evaporated and the residue was applied to an Al_2O_3-column (activity grade I)(LE ROY BJERKE et al. 1972, SILTANEN and ROSENBERG 1978). The acids were eluted with 40-50 ml of 4 % $NaHCO_3$ and after acidification with 0.5 M sulfuric acid the phenoxyacetic acids were extracted with ether. The ether was dried with anhydrous Na_2SO_4 and evaporated to 1 ml. The methyl esters were prepated by diazomethane method (LE ROY BJERKE et al. 1972, PURKAYASTHA 1974).

The methyl ester of MCPA was analysed on a Perkin Elmer gas chromatograph F 22 equipped with a flame ionisation detector. The used glass columns (4 m) were packed with 4 % OV-17, 4 % Carbowax 20M, and 4 % GE-XE 60 (on Chromosorb W 80/100 mesh). The first samples were also analysed by a glass capillary column (36 m x 0.3 mm) coated with 3 % FFAP.

RESULTS AND DISCUSSION

The weather conditions in Northern Karelia immediatly after the MCPA-treatment are included in Table 1.

The characteristic toxicological symptoms of dicotyledons (van ANDEL et al. 1976) developed in birch between the first and second sample collection time. The leaf death was reflected in the water content of birch (Table 2), which was slightly lower at the time of the second sampling and markedly at time of the third. Forty days after treatment most of the birch leaves were dark brown or black in colour and some of them were falling. About 25 % of the treated birches were alive, the following spring.

There were no visible changes in mosses during the investigation period. The low water content of the last spring sample (Table 2) was caused by the preceding warm and nearly rainless period.

The ether soluble MCPA decreased 70 % in birch twigs and 75 % in mosses on a dry weight basis between the first and second sample collection (Table 3). These decreases may result in part from washing and perhaps photodecomposition. There was rain

TABLE 1

Weather conditions at the meteorological station, Ilomantsi kk. (N 62° 41', E 30° 57'). The mean air temperature (°C), the rainfall (mm) and the averages of the sum of total radiation (mWh/cm^2) of five-day periods after MCPA-treatment.

Dates	°C	mm	1) mWh/cm^2	Time of sample collection
9.-13.8.76	14.6	-	580	11.8.76
14.-18.8.76	15.6	-	549	-
19.-23.8.76	9.9	26.4	515	-
24.-28.8.76	10.1	-	448	26.8.76
29.8.-2.8.76	13.1	16.8	315	-
3.- 7.9.76	7.3	11.3	352	-
8.-12.9.76	7.5	25.3	190	-
13.-17.9.76	8.3	2.5	143	-
18.-22.9.76	5.3	-	323	20.9.76

Figures have been taken from the monthly publications of the meteorological bureau of Finland.

1) Recorded at Jyväskylä Airport

TABLE 2

The water content (%) of the birch twigs and mosses. Results are averages of three replicates.

Date	Birch	Moss
11.8.76	54.0±1.1	49.3±4.7
26.8.76	50.1±3.2	52.7±2.2
20.9.76	33.4±0.9	68.5±2.7
21.5.77	41.9±1.0	45.1±1.0
4.7.77	42.8±0.8	9.6±1.6

during the first two weeks after treatment and the total radiation was quite high (Table 1). If birch behaves like other susceptible plants, for instance sunflower or rape, it can be assumed that a large part of the herbicide was translocated from leaves to the rest of the plant and partly expelled through roots to the soil (COLLINS and GAUNT 1971, HALLMÉN 1974).

Six weeks after treatment only 25 % of the ether-soluble MCPA was left in twigs and 7 % in mosses on dry weight basis. There was only a slight difference between the second and the third birch sample.

No ether-soluble MCPA could be found in mosses in the spring 1977 with the method used.

TABLE 3

The content of MCPA residues in birch twigs and mosses on fresh weight (f.wt.) and dry weight (d.wt.) basis. Results are averages of five replicates.

Dates	Days after treat.	b i r c h		m o s s	
		ppm f.wt.	ppm d.wt.	ppm f.wt.	ppm d.wt.
11.8.76	0	344.2±94.2	784.6±214.0	73.9±31.7	144.3±60.5
26.8.76	15	119.2±19.3	238.8±38.6	17.1±2.0	36.7±4.2
20.9.76	40	131.7±8.6	197.8±12.9	3.1±0.9	10.2±2.7
29.4.77	261	25.2±3.1	44.6±5.5	-	-
21.5.77	283	32.0±8.2	55.1±14.1	0	0
4.7.77	297	43.6±5.4	76.3±9.5	0	0

The concentration in birch twigs decreased by about 77 % over the winter compared that with those of Sept. 20th. In part this marked decrease reflected the falling of leaves containing herbicide (WELLENSTEIN 1975), which began in late September. There was a slight increase in the ether-soluble MCPA in the spring and summer samples of 1977, however, but this increase wasn't statistically significant. This increase might be due to the breakdown of some MCPA-containing complexes. As COLLINS and GAUNT (1970, 1971) proved, the β-glycoside derivates of hydroxy-MCPA are ether-insoluble. If this kind of complex formation takes place in birch, the complexes might start to decompose the following summer. On the other hand, ERNE and von HAARTMAN (1973) found a decrease in the amounts of 2,4-D and 2,4,5-T residues in lingonberries during storage -18°C. The decrease was 60 % of 2,4-D and 50 % of 2,4,5-T within 1-2 years. They proposed a possible transport and binding of the herbicide into cell wall components. The complex formation of 2,4-D with pectic acid in citrus peel (MEAGHER 1966) and with protein (BUTTS and FANG 1956) has been reported earlier in litterature.

ERNE and von HAARTMAN (1973) found 2.3-60 ppm of 2,4-D and 2,4,5-T residues in the sprigs of berries 24-32 days after treatment. These values are much lower than our MCPA-results at 15 and 40 days. SILTANEN and ROSENBERG (1978) discovered that birch and aspen foliage contained 0.25-61 ppm of 2,4-D and 2,4,5-T 91-301 days after herbicide spraying. These results are comparable to our values for 261 and 283 days on fresh weight basis.

Soil samples taken immediatly after the treatment showed no traces of herbicide in any soil layer (Table 5). Two weeks later ether-soluble MCPA was found in all analysed layers. Calculated on a dry weight basis, 91 % of the ether-soluble residue appeared in the topmost layer (0-3 cm), about 7 % in the middle layer (3-6 cm) and 2 % in the bottom layer (6-15 cm). Thus most of the herbicide residue was concentrated in the uppermost layer where the content of organic matter was highest (Table 4). The same dis-

TABLE 4

The water content (w-%), the content of organic matter (o.m.-%) on a dry weight basis and the pH of the autumn 1976 and the spring 1977 soil samples.

Depth cm	Autumn 1976 w-%	o.m.-%	pH	Spring 1977 w-%	o.m.-%	pH
0-3	21.5±2.2	10.3±1.3	4.6	32.4±8.9	19.5±0.4	4.8
3-6	22.2±1.1	7.7±0.3	4.6	22.8±5.5	7.6±0.4	4.7
6-15	17.2±1.0	3.7±0.4	5.1	19.8±5.7	3.9±1.6	5.0

TABLE 5

The amounts of MCPA in the soil on fresh weight (f.wt.) and dry weight (d.wt.) bases and on the basis of organic matter (o.m.). Results are averages of four replicates.

Date	Days after treat.	Depth cm	ppm f.wt.	ppm d.wt.	ppm o.m.
11.8.76	0	0-3	0	0	0
		3-6	0	0	0
		6-15	0	0	0
26.8.76	15	0-3	3.2±0.3	4.0±0.3	36.0±3.0
		3-6	0.3±0.1	0.3±0.2	4.5±2.0
		6-15	0.1±0.1	0.1±0.1	3.8±1.6
20.9.76	40	0-3	0.9±0.2	1.1±0.3	12.1±3.1
		3-6	tr	tr	tr
		6-15	0	0	0
21.5.77	283	0-3	0.2±0.1	0.2±0.2	1.4±1.2
		3-6	tr	tr	tr
		6-15	tr	tr	tr
4.7.77	297	0-3	0.5±0.1	0.7±0.2	3.3±0.9
		3-6	0	0	0
		6-15	0	0	0

tr = < 0.1 ppm

covery was made by LUTZ et al. (1973) and STEWART and GAUL (1977) for 2,4-D and 2,4,5-T. In the lower layers the residues were nearly equal in amount relative to the organic matter content, indicating that organic matter is an important contributor to MCPA adsorption, as it is to 2,4,5-T adsorption (O'CONNOR and

ANDERSON 1974). The exceptionally high concentrations of residues in the soil at the time of the second sampling can be attributed to the rain which fell between Aug. 19th and 23rd and washed the chemicals from the above vegetation. The highest amounts of residues are usually found after the first rainfall (WHITE et al. 1976). Partly the residues have been mediated by plants (COLLINS and GAUNT 1971, HALLMÉN 1974).

Later the amounts of ether-soluble traces decreased in soil and the residue in the uppermost layer at the third sampling was only 34 % of the corresponding value of the second time. The rapidity and extent of the decrease leads us to suppose that the decrease resulted more from chemical degradation and/or adsorption than microbial decomposition. Moreover, wheather conditions (Table 7) at this time were not so favourable for microbial activity. The microbial degradation of 2,4-D and MCPA in forest soil has been shown by TORSTENSSON (1975), who observed a faster degradation of herbicides after a second than after the first application in the unsterilized soil samples. KIRKLAND (1967) proved that the degradation capasity of MCPA persisted after drying and freezing of the soil. If a corresponding microbial activity had once developed in our forest soil during the autumn 1976, the residues would have been continuously degraded upon release from vegetation, litter or the upper part of the soil. Residual amounts would have been low if weather conditions had been favourable for microbial degradation. Concentrations in our later samples were low and the highest amounts were found in the uppermost layer of the soil (Table 5).

TABLE 6

The residual amounts of MCPA in the litter on fresh weight (f.wt.) and dry weight (d.wt.) bases. Results are averages of four replicates.

Date	Days after treat.	ppm f.wt.	ppm d.wt.
20.9.76	40	80.5±33.1	111.7±46.2
29.4.77	261	81.1±11.4	94.8±13.4
21.5.77	283	10.2±3.1	12.1±3.6
4.7.77	297	28.3±3.8	31.7±4.6

Excetionally high concentrations of ether-soluble residues were found in the autumn and first spring samples of birch leaf-litter on a dry weight basis (Table 6). There was no prominant decrease during the winter. At the same time the content of birch twigs decreased 77 % on a dry weight basis and the residual amount in the first spring sample of birch twigs was 47 ppm. The content of the ether-soluble MCPA in leaf-litter decreased by about 87 % between April and May, but it later (July) increased by about 20 ppm on a dry weight basis. What may cause this kind

TABLE 7

Weather conditions at the meteorological station, Ilomantsi kk. (N 62° 41', E 30° 57'), during the experiment period. The mean air temperature by month (°C), number of frost days/month, total monthly precipitation (mm), and the snow cover depth (cm) on the 15th day of month.

Month	Mean air temperature °C	Frost days	Total precipitation mm	Depth of snow cover cm
August	12.5	0	75	-
September	5.8	12	45	-
October	-1.9	28	10	-
November	-2.7	21	42	-
December	-6.4	28	54	12
January	-9.6	31	25	37
February	-11.2	28	24	45
March	-4.7	23	31	48
April	1.1	19	40	34
May	8.4	6	62	-
June	13.5	1	42	-
July	15.6	0	83	-

of fluctuation ? The birch leaf-litter was flexible and resistant in structure in the autumn and in the first and second samples of spring, but breakable by July. LÄHDE (1974) has shown that cellulose decomposes fast during spring and early summer in Nordic forest soils. So we may suppose that during winter the leaching and decomposition of litter was quite limited because of the snow-cover and low temperature (Table 7), and residues remained high. Leaching of the dead leaf material began with the melting of the snow during late April and early May and continued with the spring rains of May. Because the temperature was quite low the (microbial) degradation processes of litter were limited and the residues remained low. During June, however, the ground temperature rose and moisture conditions were favourable for the decomposition of litter to begin. At this stage the bounded MCPA began to release from the ether-insoluble complexes (COLLINS and GAUNT 1971, HALLMÉN 1974), and higher concentrations of free residues appeared in the litter samples.

In part the released residues were leached to the soil, where they concentrated in the uppermost layer and were degraded further (Table 5). MCPA may also be degraded in litter, as has been shown for 2,4-D and 2,4,5-T (NORRIS 1966).

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