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Fate of Glyphosate and Its Influence on Nitrogen-cycling in Two Finnish Agriculture Soils

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The fate of glyphosate (N-(phosphonomethyl)-glycine) in soil has been studied by many authors. According to SPRANKLE et al. (1975), HANCE (1976), NOMURA and HILTON (1977) and TORSTENSSON and AAMISEPP (1977) glyphosate mobility in soil is very limited. Glyphosate appears to be bound to the soil through the phosphonic acid moiety, and the strength of the adsorption correlates with the number of unoccupied phosphate sorption sites (HANCE 1976). The rate of glyphosate decomposition varies greatly in different soils. NOMURA and HILTON (1977) observed a 100-fold variation of degradation rate within a group of five Hawaiian sugarcane soils and TORSTENSSON and STARK (1979) also observed a large variation of degradation rate in Swedish forest soils under field conditions. Most of the persistence studies have been done using ^{14}C-labelled glyphosate in laboratory conditions. The degradation of glyphosate in soil occurs by microbial action (SPRANKLE et al. 1975, RUEPPEL et al. 1977, QUILTY and GEOGHEGAN 1976b), and the effect of glyphosate on different specific groups of micro-organisms has been discussed by several authors. In some cases very low concentrations of glyphosate have decreased activity of the microbium under study. JAWORSKI (1972) reported that the growth of Rhizobium japonicum was inhibited by glyphosate at 1.7 ppm and GROSSBARD (1974) observed an inhibition of Stachybotrys chartarum at a glyphosate concentration of 1 ppm. In several other studies, however, higher concentrations of glyphosate has been used without effect. QUILTY and GEOGHEGAN (1976a) have investigated the effect of glyphosate at concentrations of 300 ppm on nitrification in peat, TORSTENSSON (1978) has investigated glyphosates effect at a concentration of 100 ppm on nitrification and denitrification, and MARSH et al. (1977) have investigated the effect of glyphosate at a concentration of 100 ppm on NH_4 + NO_3 -amount in two different soils. No distinct inhibitory effects were observed in these studies.

During an energy forest experiment in Suomusjärvi, Kettula (located in Southern Finland) glyphosate was used to destroy indigenous flora, mainly quackgrass, before replanting. Since, the degradation rate of glyphosate and its biological impact are known to vary and field data was largely unavailable, it was decided that both the persistence of glyphosate and its effects on the nitrogen cycling processes fundamental to the energy forest experiment should be investigated.

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MATERIALS AND METHODS

Experimental fields and sampling

Some characteristics of the two experimental fields are given in table 1. Both fields, SK-1 (loam soil) and SK-2 (fine silt soil), were treated on the 14th of September, 1978 with glyphosate 2.6 $kg.ha^{-1}$. The vegetations consisted mainly of quackgrass, 20-30 cm high on SK-1 and sparse, about 10 cm high on SK-2. On the 6th of November, 1978, the fields were ploughed to the depth of 20-30 cm. Two sites (1 and 2 in tables) of ca 100 m^2 were chosen at each field and sampled immediately after the application of glyphosate, 28 d and eight months (249d) later on dates shown in table 2. Control samples were collected before glyphosate was applied. At each sampling three subsamples of one l were taken from 0-10 cm horizon before ploughing and from the 0-20 cm horizon after ploughing. These samples were pooled, mixed and divided into two parts, one for chemical analysis (air dried, stored at $-18^{\circ}C$) and one for microbial analysis (stored at $+4^{\circ}C$). From September 1978 to May 1979 the monthly mean temperatures in Kettula were: Sept. 8.0°, Oct. 3.4°, Nov. 1.9°, Dec, -12.2°, Jan. -8.8°, Feb. -10.1°, March -1.8°, April 1.5° and May $10.3^{\circ}C$.

TABLE 1

Soil characteristics of the experimental fields

Field	Soil type	pH	Organic carbon %(wt/wt)	P $\mu g/cm^3$	Respiration $\mu l\ CO_2/h/cm^3$ (s.d.)
SK-1	loam	5.1	44	12	2.6 (0.1)
SK-2	fine silt	5.5	1.5	6	1.5 (0.5)

Determination of glyphosate residues

The residues of glyphosate and its first metabolite, aminomethylphosphonic acid, were determined using the gas chromatographic method published in the PESTICIDE ANALYTICAL MANUAL (1977). Duplicate analysis where carried out on each sample. The soil samples were extracted with 0.5 M ammonium hydroxide. The residues were isolated from the extract by elution from an anion exchange resin and the resin fraction was further purified by charcoal treatment. Glyphosate and its metabolite were separated by elution from a cation exchange resin. Finally glyphosate and the metabolite were converted to the trifluoroacetyltrimethyl and trifluoroacetyldimethyl derivates, respectively, and determined quantitatively by gas chromatography using an alkali flame ionization detector. The results were calculated on dry weight basis.

Determination of biological activities

The potential acetylene reduction activity (~nitrogenase activity) was measured under ambient conditions from 2g soil samples amended with glucose and wetted to field capacity (NIEMI and WEBER, unpublished).

For determination of the potential nitrification activity 50cm^3 aliquots of soil were incubated at 20-23°C in open 250ml conical flasks. Soil moisture were adjusted to 50-70% of the water holding capacity and $(NH_4)_2SO_4$ was added to a concentration of 280 µg NH_4-N/ml in the soil solution. After 7 and 30 days the NO_3 concentration was estimated using a nitrate specific electrode. Nitrogen losses by denitrification under these incubation conditions were checked in a separate experiment and found to be negligeable.

The potential denitrification activity was determined by the acetylene inhibition method. Soil samples were amended with nitrate and incubated waterlogged in a N_2 atmosphere containing 2.5% C_2H_2 according to MÜLLER et al. (1980).

For determination of soil respiration activity an electrolytic respirometer, originally described by SWABY and PASSEY (1953) was used. Soil samples for the respiration assays were collected in September 1980.

Determination of other soil characteristics

The soil pH values were determined in a soil-water suspension (1:2 vol/vol). The carbon content was determined with an infrared carbon analyzer (URAS-2T) by high-temperature combustion (SALONEN 1979). Phosphorus was extracted with 1 M ammonium acetate at the pH of the soil sample, and determined according to BARTLETT (1959).

RESULTS AND DISCUSSION

Table 2 summarizes the results of the residue analyses. Immediately after the application about 17 ppm of glyphosate and 0.9 ppm aminomethylphosphonic acid (the first metabolite of glyphosate) were found in the loam (SK-1) soil. The corresponding values for the fine silt (SK-2) soil were 3.8 ppm and 0.1 ppm. Theoretically the applied glyphosate would give 18 ppm in the SK-1 soil and 4.2 ppm in the SK-2 soil, so that on an average 92% of the applied amount was found in both soils immediately after the application. Only a small amount had been taken up by the vegetation. During the following 28 days glyphosate degraded only slightly; about 76% of the initial amount was left in the SK-1 soil and 92% in the SK-2 soil. After eight months (249 days), over the winter period, concentrations of glyphosate fell considerably; about 10% of the initial amount was left in the SK-1 soil and about 53% in the SK-2

TABLE 2

Residues of glyphosate and its main metabolite, aminomethylphosphonic acid, in the soil from both experimental fields.

Sampling date and days after application	Sampling depth (cm)	Site	Residue ppm (mg/kg of air dry soil)			
			Field SK-1 (loam soil)		Field SK-2 (fine silt soil)	
			Glyphosate[x]	Metabolite[x]	Glyphosate[x]	Metabolite[x]
14.9.-78						
0	0-10	1.	17, 19	0.8 -	3.9, 4.1	0.1, 0.1
		2.	14, 18	1.0 0.9	3.8, 3.4	0.1, 0.1
			(17)	(0.9)	(3.8)	(0.1)
12.10.-78						
28	0-10	1.	17, 19	3.5, 3.3	3.5, 4.3	0.3, 0.3
		2.	6, 10	2.9, 2.9	2.6, 3.5	0.6, 0.4
			(13)	(3.2)	(3.5)	(0.4)
21.5.-79						
249	0-20	1.	0.8, 1.0	0.3, 0.2	0.8, 1.2	0.1, 0.1
		2.	0.9 -	0.4, 0.3	0.9, 1.1	0.4, 0.2
			(0.9)	(0.3)	(1.0)	(0.2)

x) duplicate estimations on soils from sites 1 and 2, and in parenthesis their means.

soil. To obtain this information from table 2 the results from the final sampling have been doubled to allow for greater sampling depth (20 cm). TORSTENSSON and STARK (1979) followed the degradation of glyphosate in similar experimental conditions (but at higher temperatures) in eight Swedish forest soils. Glyphosate was applied in August, and according to their results on average 20% (2.4-92%) was still present in samples taken in May of the following year. Both LÖNSJÖ et al. (1980) and TORSTENSSON and STARK (1979) found a positive correlation between soil respiration activity and degradation rate of glyphosate. Our results also show (Tables 1 and 2) this correlation: glyphosate decreased more rapidly in the soil with higher respiration activity (SK-1).

No significant accumulation of aminomethylphosphonic acid occurred during the experimental study. Although a fourfold increase in level of this metabolite occurred during the first 28 days after application, the levels then declined. After eight months the residue level in the SK-1 soil decreased to about 1/5 of the highest value, while the level in the SK-2 soil remained constant. The results have again been doubled to allow for greater sampling depth as done in the comparison of the glyphosate results.

The acetylene reduction results are shown in table 3. A Significant decrease in the acetylene reduction activity of SK-1 soil occurred between the second and third sampling. In the SK-2 soil acetylene reduction was not affected. This effect may be an indirect one, since in killing the existing plant cover, glyphosate could have altered the ratio of available C and N more in the SK-1 field where the plant cover was denser, than in the SK-2 field.

TABLE 3

Potential acetylene reduction activities

Sampling field and site	Ethylene production n mol·g^{-1}·h^{-1} (s.d.)		
	0.5 h before application of glyphosate	0.5 h after application of glyphosate	28 d after application of glyphosate
SK-1 1	148 (19)	131 (1)	73 (13)
" 2	101 (11)	85 (18)	24 (16)
SK-2 1	34 (1)	35 (1)	37 (2)
" 2	29 (2)	31 (3)	37 (2)

No strong effect of glyphosate on the potential nitrification or denitrification activities can be seen from tables 4 and 5, respectively.

TABLE 4

Potential nitrification activities

Sampling field and site		NO_3^--N $\mu g \cdot g^{-1}$ (s.d.)			
		0.5 h before application of glyphosate		0.5 h after application of glyphosate	
SK-1	1	542	(25)	544	(12)
"	2	555	(12)	470	(12)
SK-2	1	23	(1)	52	(4)
"	2	15	(2)	20	(3)

TABLE 5

Potential denitrification activities

Sampling field and site		N_2O-N $\mu g \cdot g^{-1} \cdot d^{-1}$ (s.d.)					
		0.5 h before application of glyphosate		0.5 h after application of glyphosate		28 d after application of glyphosate	
SK-1	1	64	(4)	54	(9)	75	(4)
"	2	61	(3)	73	(11)	70	(4)
SK-2	1	8	(0.7)	11	(2.0)	9	(0.1)
"	2	5	(1.2)	6	(1.4)	6	(1.1)

It is concluded that glyphosate degraded even at low temperature conditions, and it is not to expected, that the application of glyphosate will affect directly nitrogen fixation, nitrification or denitrification activity in these soils.

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