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Photodegradation of the Herbicide Glyphosate in Water

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Published information is sparse on the behaviour and fate of glyphosate (N-(phosphonomethyl)glycine) in the aquatic environment (Brønstad & Friestad 1984; Newton et al. 1984).

Early studies of glyphosate concluded that in comparison to microbial metabolism photodegradation plays a very minor role in the environmental decomposition of this herbicide (Rueppel et al. 1977). In this respect this paper, which reports the effect of artificial light as well as sunlight on glyphosate (Roundup^R) in water of varying qualities, contributes with some contrary findings.

MATERIALS AND METHODS

Solutions of 1 p.p.m. (a.i.) of glyphosate (1) in deionized water were exposed indoors to the following light qualities: a) sodium light with energy maximum peaks between 550 nm and 650 nm, b) mercury light with energy maximum between 400 and 600 nm, and c) UV-light with energy maximum at 254 nm.

2000 p.p.m. (a.i.) of glyphosate (2) was dissolved in deionized water and continuously exposed to a) darkness, or b) UV-light at 254 nm. The intensity of the light sources was 30 W/m^2 at water level. The temperature was 20^{o}C.

In an outdoors experiment (3) run from August 12 through October 15, 1983, under temperature conditions varying from 20^o to -5^{o}C, different water qualities with 1% glyphosate added were exposed to sunlight. The mean global radiation energy for the wave band 295 - 385 nm within the period referred to was 0.6 and 0.2 MJ/m^2/d for the first and the second half of the experiment respectively (Hegg 1983). The water samples included were: a) deionized water, b) as a) + silty clay loam (30-40% clay) (5% w/w), c) polluted water from an inland lake, d) as c) + 5% (w/w) silty clay loam.

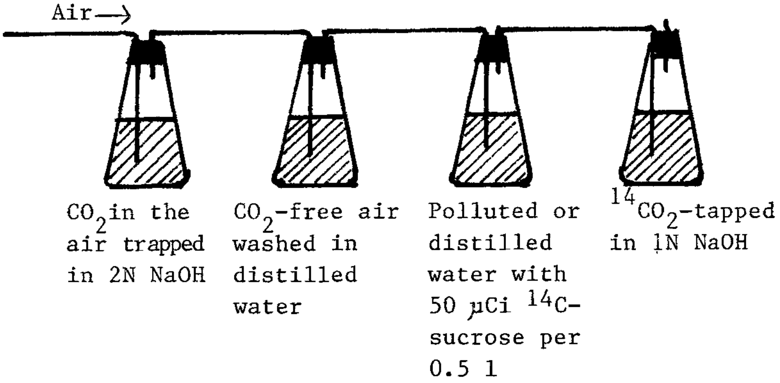
Glyphosate at 2 p.p.m. and 100 p.p.m. (4) was dissolved in deionized water or polluted water respectively (as described in experiment 3) and exposed to darkness or sunlight. The experiments were run in the period June 22 - August 25, 1984, during which the mean global radiation energy was 0.8 $MJ/m^2/d$. The temperature within this period varied between 11.2°C and 24°C with 15.9°C as a mean.

In experiments 1 to 3 the solutions were kept in 60 litre plastic containers covered by a thin film of polyethylene. In experiment 4, 10 litre containers were used.

For analysis of glyphosate residues (Friestad & Brønstad 1985), samples were taken at initiation of the experiments and thereafter at given intervals (see Figures). The solutions were stirred for about 2 minutes after each sampling. Samples of sedimented clay loam (Experiment 3) were analyzed at the end of the experimental period.

Samples of the solutions from experiments 2 and 4 were sent to Monsanto Co., U.S.A. for analysis of breakdown products of glyphosate. This company possesses the necessary competence and technique for identification of such products.

The sugardegrading properties of the polluted water were investigated by using ^{14}C-sucrose according to the following scheme:



The labelled sucrose had a specific activity of 10 mCi/mmol and was applied in 3% ethanol. Samples of 1 ml of the solution of trapped $^{14}CO_2$ were taken every 24 hours for scintillation counting.

RESULTS AND DISCUSSION

Experiment 1 shows that long-waved light does not have any photodegrading effect on glyphosate. UV-light, however, has a strong influence in this respect (Figure 1A). The half-life of glyphosate exposed to UV-light was about 4 days at the concentration used. At a starting concentration of 2000 p.p.m., the half-life of glyphosate was 3-4 weeks (Figure 1B).

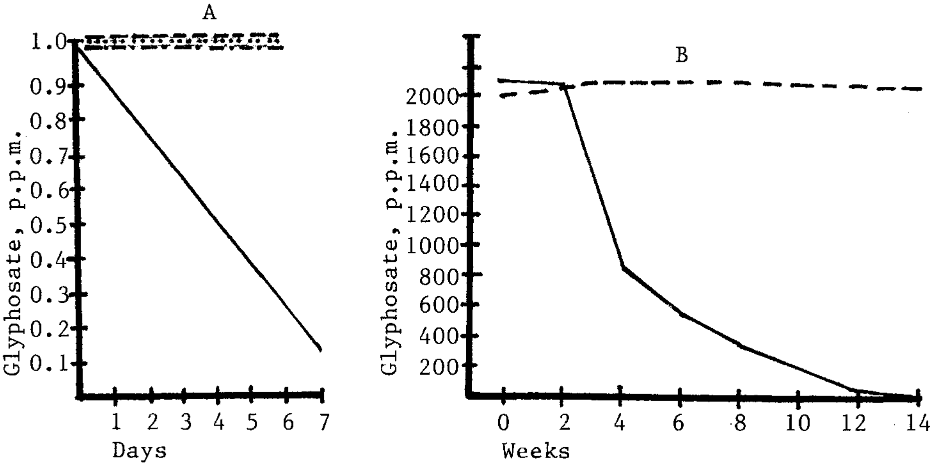


Figure 1. Degradation of glyphosate in deionized water when exposed to darkness (— — —), Na-light (• • • •), Hg-light (—•—•—) or UV-light (———) at two starting concentrations of glyphosate.

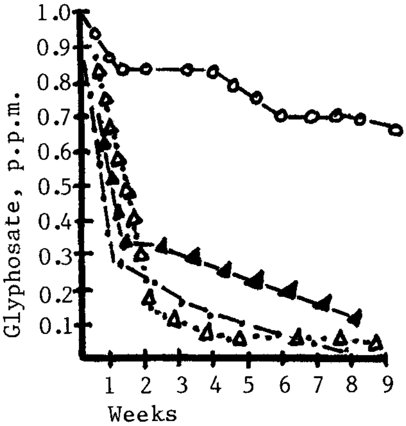


Figure 2. Degradation of glyphosate in deionized water (—Δ—Δ—), deionized water + 5% (w/w) silty clay loam (—▲—▲—), polluted water (—○—○—) or polluted water + 5% (w/w) silty clay loam (—●—●—) when exposed to sunlight.

The rapid photodegradation in pure water is also seen in the outdoor experiment 3 (Figure 2). Additionally, this figure shows that the degradation of glyphosate in deionized water occurs faster than in polluted water and that the disappearance is influenced by the presence of clay.

Analysis of the sediments at the end of this experiment showed that the content of glyphosate adsorbed to clay derived from deionized and polluted water was 12 p.p.m. and 10 p.p.m. respectively.

Since no dissipation of glyphosate took place under dark conditions even in polluted water (Figure 3), the microbial activity of the water was tested using sucrose as the substrate. It appears from Figure 4 that the polluted water possessed a high biological capacity for this substrate. Ten days after ^{14}C-sucrose was added to the two water qualities, the quantity of $^{14}CO_2$ evolved was about 20 times higher in polluted than in deionized water.

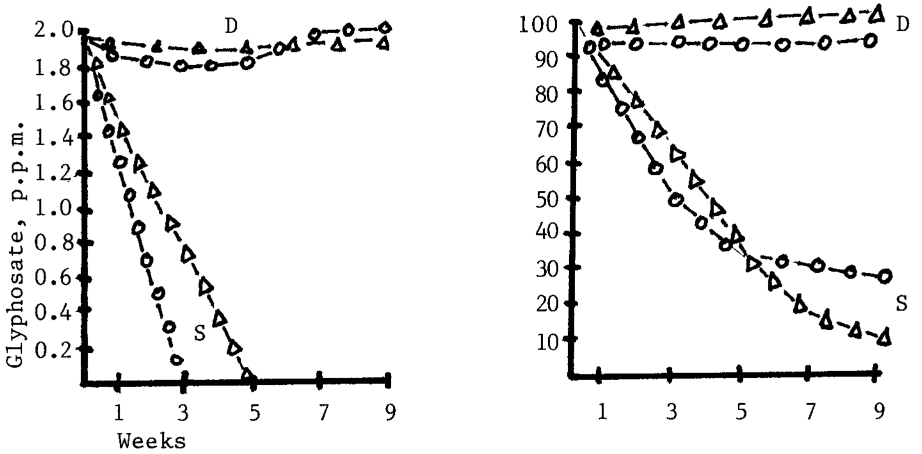


Figure 3. Degradation of glyphosate at two concentrations in deionized water (–Δ–Δ–) and polluted water (–o–o–) when exposed to sunlight (S) or darkness (D).

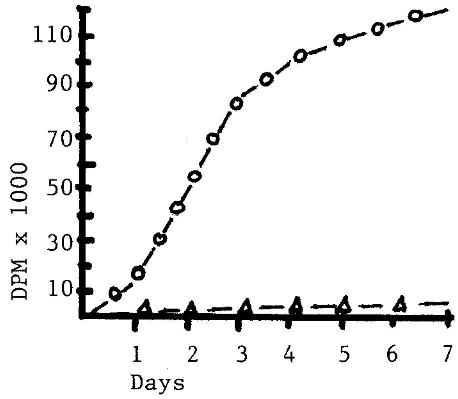


Figure 4. Evolution of $^{14}CO_2$ derived from ^{14}C-sucrose in deionized water (–Δ–Δ–) and polluted water (–o–o–) in darkness. Temp. 23 °C.

The results of analysis for photolytic degradation products of glyphosate are shown in Table 1 (Experiment 2 and 4).

Table 1. Glyphosate photolysis in two water qualities.

Water qual.	Exp.to sun (weeks)	Start conc. (p.p.m.)	Analytical results (p.p.m.)			
			Polarogr.	Chromatogr.		
			Glyphosate	Gly.	AMPA	NH_3
Deionized	5	2000	900	889	895	n.a.*
"	9	2000	300	256	1610	n.a.*
"	9	100	5.3	3.9	32.7	10.8
Polluted	9	100	24.0	22.2	16.2	5.5

* not analyzed

Several herbicides have been found to be photosensitive (Crosby 1976). Glyphosate, however, has been considered to be stable to sunlight (Rueppel et al. 1977). The present experiments show that this may not be true. Indeed the results show that UV-light possesses a high capacity for degrading glyphosate. The results also indicate that the rate of degradation proceeds faster in pure water than in polluted water (Figure 2).

It is well known that glyphosate is readily adsorbed to soil particles (Sprankle et al. 1975). Similar processes take place also when soil is suspended in water. The soil particles bind glyphosate, and the complexes disappear from the water by sedimentation (Siltanen & Rosenberg 1977). This was the case in the present experiment (Figure 2). Suspended soil particles showed the ability to glean glyphosate residues from the water.

As reported, the clay loam sediments in experiment 2 (Figure 2) contained, as a mean for the two water qualities, about 11 p.p.m. of glyphosate after 9 weeks of exposure to water containing originally 1 p.p.m. of glyphosate. This corresponds to 33 mg of glyphosate (3 kg clay loam per container). Of the 60 mg of glyphosate originally added to each container, Figure 2 shows that at the end of the period referred, about 90% had dissipated from the water. The clay loam sediments were probably responsible for about 2/3 of this dissipation. Hensley et al. (1978) and Newton et al. (1984) also report the ability of sediments to glean moderate amounts of glyphosate from water.

In pure water without suspended clay the photolytic degradation apparently exceeded the combined effect of photolysis and adsorption by clay (Figure 2). In the polluted water the opposite effect was observed, probably because the impurities in the polluted water reduced the penetration of the UV-light. By suspending clay loam in the water, the penetration was further decreased.

It is accepted knowledge that aminomethylphosphonic acid (AMPA) is the principal metabolite of glyphosate in soil and that this metabolite is further converted to formaldehyde via formylphosphonic acid (Rueppel et al. 1977). The photolytic products of glyphosate found (Table 1) could indicate a similar pathway of degradation. Besides demonstrating a very good agreement between results obtained for glyphosate in two different laboratories using different techniques, the table also indicates that AMPA is the main breakdown product in the photolytic process and that AMPA is far more stable to photodegradation than the parent compound.

The total concentrations of glyphosate residues and degradation products, calculated as glyphosate, are relatively close to the starting glyphosate cencentrations in Table 1. This indicates that CO_2-evolving processes may not be important in the photolysis of glyphosate.

Newton et al. (1984) found AMPA consistently in foliage in forest brush field ecosystems treated with 3.3 kg/ha glyphosate. In this connection, it may be hypothesized that the presence of AMPA could be a consequence of photolysis of glyphosate on the leaf surface with a subsequent penetration of this breakdown product into the leaf, rather than a result of glyphosate metabolism within the leaf.

Glyphosate is considered to be degradable by soil microflora (Rueppel et al. 1977). In the present investigation such degradation was not noted, not even in the polluted water which was found to possess a high potential for degrading sugar. Regarding AMPA, Harkness (1966) found that six out of ten strains of microorganisms examined could grow on this product as the sole phosphorous source. However, in the present study AMPA was found to be rather persistent to biodegradation. Evidently, active organisms of the type mentioned were not present in the water qualities used in our experiments.

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