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Canadian Water Quality Guidelines for Glyphosate

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Abstract

A literature review was conducted on the uses, fate, and effects of glyphosate on raw water for drinking water supply, freshwater aquatic life, agricultural water uses, recreational water quality and aesthetics, and industrial water supplies. The information is summarized in this publication. From it, water quality guidelines for the protection of specific water uses are recommended.

Résumé

On a examiné la documentation relative aux utilisations, au devenir et aux effets du glyphosate sur l'eau naturelle utilisée comme eau potable non traitée, sur la vie aquatique en eau douce. sur l'utilisation de l'eau l'agriculture, sur la qualité de l'eau pour les loisirs et l'esthétique, ainsi que sur les approvisionnements en eau pour l'industrie. renseignements sont résumés dans cette publication. À partir de cette étude, des lignes directrices sur la qualité de l'eau sont recommandées pour la protection d'utilisations particulières de l'eau.

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SOURCES, OCCURRENCE, AND CHARACTERISTICS

Uses and Production

Glyphosate, the common name for N-(phosphonomethyl)glycine (IUPAC), is a colourless, crystalline solid with an empirical formula of C₃H₈NO₅P and a molecular weight of 169.1. The structural formula for glyphosate is shown in Figure 1. Its Chemical Abstracts Service (CAS)

O O II II HO C CH₂ NHCH₂ P(OH)₂

Figure 1. Structural formula for glyphosate

Registry Number is 1071-83-6. The isopropylamine salt of glyphosate (CAS Registry Number 38641-94-0) is the active ingredient in the water-soluble herbicides Roundup R , Vision R , Clear-it R , and Sidekick R . Roundup R and Vision R contain the equivalent of 356 $g \cdot L^{-1}$ of glyphosate (480 $g \cdot L^{-1}$ of the isopropylamine salt) (Worthing and Walker, 1983; Weed Science Society of America, 1983; Monsanto Company, 1987a). Three concentrations of glyphosate are marketed in the domestic products Clear-it^R and Sidekick^R. These are 9.4, 51.2, and 193 $g \cdot L^{-1}$ of the isopropylamine salt corresponding to 7, 38, and $143 \text{ g} \cdot \text{L}^{-1}$ of glyphosate as the carboxylic acid, respectively. The different concentrations are indicated by numbers associated with the trade name (i.e., $Clear-it^R-1$, -2, and -3; Sidekick R -1, -2, and -3). The isopropylamine salt of glyphosate at 144 $g \cdot L^{-1}$ is also combined with $227 \text{ g} \cdot \text{L}^{-1}$ of the isopropylamine salt of 2,4-D in the herbicide Rustler^R (Monsanto Company, 1987b; 1987c).

Glyphosate. introduced in 1971, has been registered in Canada since 1976. It is a nonselective, postemergence herbicide that applied to the foliage of target plants. Its mode of herbicidal action has not been completely elucidated, but it is known that glyphosate inhibits the synthesis of essential amino acids and promotes the destruction of photosynthetic pigments in foliage (Jaworski, 1972; Amrhein, Schab, et al., 1980; Amrhein, Deus, et al., 1980; Steinrucken and Amrhein, 1980). The commercial product Roundup R is registered in Canada for weed control in specific crops (barley, corn, oats, potatoes, soybeans, beets, and wheat) and industrial and nonagricultural areas (rights-of-way, industrial roadsides, pasture renovation, recreational land). Recommended application rates are $1.08 \div 1.68 \text{ kg-ai} \cdot \text{ha}^{-1}$ for annual weeds (ai = active ingredient), 1.20-5.76 kg-ai·ha⁻¹ for perennial weeds, and 1.44-2.88 kg-ai-ha⁻¹ for woody brush and trees (Monsanto Company, 1982b). Since 1987, Vision^R has replaced Roundup^R for forest use. $Vision^{\hbox{\it R}}$ is registered in Canada for control and suppression of herbaceous weeds, weedy brush, and trees in silviculture operations. Recommended application rates are $1.07-2.14 \text{ kg-ai-ha}^{-1}$. addition, Clear-it R and Sidekick R have been registered for domestic use.

Importation data are not available (Statistics Canada, 1986), probably because at the time statistics were collected Roundup^R was the only registered product containing glyphosate and the data were withheld to protect the manufacturer's interests. Results of the 1987 national registrant survey showed glyphosate was among the top ten herbicides in Canada as ranked by sales of active ingredient (Environment Canada/Agriculture Canada,

Glyphosate was reported sold to Quebec farmers in a 1982 survey, but the amount was not quantified (Environment Canada/Ministère l'Environnement du Québec, 1984). Glyphosate use for field crops, fruits, and vegetables in Ontario increased from 76 350 kg in 1983 (McGee, 1984) to kg in 1988 (Moxley, 1989). In New Brunswick, 53 868, 45 954, 59 083, and 36 505 kg-ai were applied by air under permit in 1985, 1986, 1987, and 1988, respectively (Shanks, 1985, 1986, 1987; W. Sexsmith, 1990, pers. comm.). Only 11 L of the Roundup^R formulation were reported sold in Yukon in 1986 (White, 1986). Currently, glyphosate is the most commonly used herbicide in forest management, accounting for 81% of the total forestry usage nationally (Campbell, 1990). A 1988 national survey of herbicide use in forestry lists Ontario as the largest user of glyphosate with 60 773 ha applied, followed by New Brunswick (40 025 ha), British Columbia (33 085), Quebec (29 759 ha), Nova Scotia (10 925), and Newfoundland (1010 ha) (Campbell 1990).

Glyphosate formulations can contain the microcontaminant M-nitrosoglyphosate. Treatment of soil with large quantities of sodium nitrate and glyphosate might lead to the formation of this compound, but this is not expected to occur under normal application practices (Khan and Young, 1977; Young and Khan, 1978; Khan and Marriage, 1979; Khan, 1981). Furthermore, M-nitrosoglyphosate is not considered to be persistent or carcinogenic (Corcoran et al., 1984).

Physical and Chemical Characteristics

The physical and chemical properties of glyphosate are presented in Table 1. In addition to the K_{OW} values reported in Table 1, a K_{OW} value of 5.6 x 10⁻⁴ has been calculated by Hunter et al. (1984). Glyphosate exhibits strong complexing properties toward divalent metal ions. This property is implicated in its inactivation by soils and possibly affects the enzyme-bound divalent metals in studies of glyphosate effects on plant biochemical processes (Buhler and Burnside, 1983; Glass, 1984).

Glyphosate in the Environment

Glyphosate can be introduced into the aquatic environment through spillage or accidental discharge or through possible waste disposal during production, packaging, storage, and use. When applied according to label instructions in agriculture or silviculture practices, chances of aquatic contamination are remote (Brønstad and Friestad, 1985). Glyphosate can, however, enter

Table 1. Physical and Chemical Characteristics of Glyphosate

| Physical state | solid crystal, odourless |
|--|--|
| Colour | white (1) |
| Molecular weight | 169.1 (1)(2) |
| Specific gravity | 0.5 g/cm ³ (1)(2) |
| Melting point | 200°C (decomposes) (2) |
| Boiling point | not determined (1) |
| Vapour pressure | 1.94×10^{-7} mm Hg at 45°C (3) |
| Aqueous Solubility | 12 g·L ⁻¹ at 25°C (1)(2) |
| Solubility in Organic Solvents | insoluble (1) |
| Partition Coefficient in Octanol/Water | 0.0017 at 20 $\mathrm{mg} \cdot \mathrm{L}^{-1}$ 0.0006 at 100 $\mathrm{mg} \cdot \mathrm{L}^{-1}$ |
| Incompatabilities | Corrosive to iron and galvanized steel (2) |
| | |

Sources: (1) Weed Science Society of America, 1983.

- (2) Worthing and Walker, 1983.
- (3) Monsanto Company, 1982a.
- (4) Concoran et al., 1984.

surface and subsurface waters by direct use near aquatic environments, or by runoff or leaching from terrestrial applications (Tooby, 1985). This has substantiated by reports indicating the presence of glyphosate residues in water from direct overspray in forestry operations (Newton et al., 1984; Feng et al., 1986b; Wan, 1986), from runoff (Edwards et al., 1980), and from irrigation canal discharges (Comes et al., 1976; Bowmer, Furthermore, the possibility of aquatic contamination from drift during agricultural or silviculture applications also exists (Yates et al., 1978; Feng et al., 1986a, 1986b; Beck, 1987). Despite the potential for introduction into the aquatic environment, there are no U.S. restrictions glyphosate-treated water for irrigation, recreation, and domestic uses (Reinert and Rodgers. 1987).

Levels in Water and Sediment

There is little information on glyphosate residues in environmental samples compared to many other herbicides. This has been attributed to the lack of a routine, quantitative technique for glyphosate analysis (Corcoran et al., 1984).

Following aerial applications (3.3 kg·ha⁻¹) to forest brush in Oregon, concentrations of glyphosate in stream water and sediments peaked at 0.27 mg·L⁻¹ (2 h posttreatment) and 0.05 mg·kg⁻¹ (between 10 and 20 d posttreatment), respectively. Glyphosate concentrations in the water declined rapidly after 2 h posttreatment. Glyphosate in sediment remained detectable throughout the 55-d study. The inactive glyphosate metabolite aminomethylphosphonic acid (AMPA) was detected at trace levels (0.01 and 0.05 mg·L⁻¹) in only 2 of 41 water samples, but was found consistently (concentrations not given) in sediments (Newton et al., 1984).

Glyphosate residues were also monitored in water and sediments of streams following experimental forest spray operations in British Columbia. Aerial application (3.0 kg·ha $^{-1}$) over an unprotected stream resulted in maximum glyphosate concentrations in water of 0.023 mg·L $^{-1}$ and 0.100 mg·L $^{-1}$ at 2 to 3 h postspray and after the first rainstorm, respectively. The concentrations

of AMPA in water were consistently below the detection limit (5 μ g·L⁻¹). Glyphosate and AMPA residues in stream sediments were detected only following posttreatment rainstorms, indicating that deposition of the herbicide adsorbed onto soil particles from runoff had occurred. Glyphosate concentrations in sediments peaked at 0.400 mg·kg⁻¹ at periods of 21 d and 90 d posttreatment. These levels decreased to 0.04 mg·kg⁻¹ at the end of the 574-d study. A maximum AMPA concentration of 0.400 mg·kg⁻¹ in sediment was found 90 d after glyphosate application and declined $0.090 \text{ mg} \cdot \text{kg}^{-1}$ by the end of the study (Wan, 1986).

Glyphosate was monitored in water following an application of Rodeo (an aquatic herbicide registered in the U.S. containing 53.5% glyphosate) at a rate of 6.7 kg·ha⁻¹ to test plots in California for water hyacinth control. The maximum concentration detected was $60~\mu g \cdot L^{-1}$ at 4 h postspray at a site 6 m from the target area (Corcoran et al., 1984). Glyphosate residues were also measured after direct aerial application of 0.75 kg·ha⁻¹ over a lake. Immediately after spraying, maximum residues in the surface water did not exceed 0.70 mg·L⁻¹, and were not detected 1 h after application (detection limit not given) (Lund-Høie, 1985).

Glyphosate and AMPA were not detected in the first flow-through water from irrigation canals treated 158 or 172 d earlier with 5.6 kg·ha $^{-1}$ of glyphosate. The limit of detection was 2.5 μ g·L $^{-1}$. Soil samples collected 1 d prior to the filling of the canals contained 350 μ g·kg $^{-1}$ and 780 μ g·kg $^{-1}$ of glyphosate and AMPA, respectively (Comes et al., 1976).

A maximum glyphosate concentration of 5153 μ g·L⁻¹ in runoff was recorded from a watershed where 8.96 kg·ha⁻¹ of glyphosate were applied 1 d earlier. This concentration declined to 4 μ g·L⁻¹ at 122 d posttreatment. At application rates of 1.12-3.36 kg·ha⁻¹, the highest concentration detected in runoff was 100 μ g·L⁻¹, which decreased to <2 μ g·L⁻¹ within 2 months after treatment (Edwards et al., 1980).

Glyphosate and AMPA concentrations were monitored in surface waters in or adjacent to areas

of Manitoba forest receiving aerial applications of Roundup R (Beck, 1987). An application of 1.08 kg·ha⁻¹ of glyphosate produced glyphosate concentrations in a small water body (borrow pit) of 1088, 149, and 55 μ g·L⁻¹ at 1.5 h, 2 d, and 5 d, respectively, postspray. Glyphosate could not be detected after 30 d (detection limit 2.2 μ g·L⁻¹). Application of 1.44 kg·ha⁻¹ produced a residue of 11.3 μ g·L⁻¹ in a small borrow pit approximately 10 m from the boundary of the spray area. This residue occurred 2 d postspray. In another area, an application of 1.8 kg·ha⁻¹ produced residual concentrations of 18.8, 33.0, and 32.5 μ g·L⁻¹ at 1.5 h, 2 d, and 5 d, respectively, in a small borrow pit located 45 m from the spray zone.

Detection of AMPA in these surface waters following application was inconsistent. However, detection of AMPA residues in conjunction with glyphosate residues indicated that glyphosate biodegradation had occurred at some sites. The highest AMPA concentration recorded (44.7 μ g·L⁻¹) corresponded to a glyphosate concentration of 32.5 μ g·L⁻¹ and resulted from spray drift from the site receiving 1.8 kg·ha⁻¹ (Beck, 1987).

Aerial spraying of a Nova Scotia forest stream from a height of 20 m with Roundup R at 2.0 $kg=ai\cdot ha^{-1}$ resulted in a maximum stream-water glyphosate concentration of 39.0 μ g·L⁻¹ at 30 h postspray (Environment Canada, 1987). A pre-spray glyphosate concentration of 0.33 $\mu g \cdot L^{-1}$ was reported, but insufficient information concerning the analytical program was provided in the report to determine the validity of this value. The maximum concentration of AMPA observed in the stream $(0.55 \, \mu \text{g} \cdot \text{L}^{-1})$ also occurred at 30 h postspray. Concentrations of glyphosate and AMPA reported in the stream between the time of application and 30 h postspray were highly variable. Precipitation did not occur during this time and an explanation for the observed variability was not given.

Predicted glyphosate concentrations in the top 0.5 m of static water bodies are given by Payne et al. (1987) as the result of downwind drift of Roundup applications of 2.1 kg-ai·ha⁻¹ on a forest block in the Skeena River basin, British Columbia.

Glyphosate deposition on the surface of a water body was simulated with polyethylene sheets (0.3 X 1 m) pegged over areas cleared of vegetation at 25, 50, and 75 m downwind from the 100-ha site receiving the spray applications. Spray conditions were chosen for "worst case" drift effects with windspeeds averaging 0.8, 0.9, and 0.6 m·s⁻¹ at 22 m above ground level for the three trials. Predicted surface water concentrations varied by several orders of magnitude among the trials, but averaged 114, 15, and 6.4 μ g·L⁻¹ for distances of 25, 50, and 75 m downwind, respectively.

Similar work in the Carnation Creek basin on Vancouver Island, British Columbia, used 20 X 20 cm aluminum foil deposit plates to gauge the drift of glyphosate from aerial applications of Roundup^K with a Microfoil^R boom designed specifically to retard the drift of aerially applied pesticides. Spray applications of $363 \text{ g} \cdot \text{L}^{-1}$ of glyphosate as Roundup^R 2.118 $kg \cdot ha^{-1}$ from an elevation of approximately 18 m demonstrated that residue levels declined to 1% of direct spray application within 2-3 m from the edge of the spray zone. Deposition to water bodies 7-8 m from the edge of the spray zone is expected to be 0.1% of the typical operational treatment (equivalent to 0.002 kg·ha-1) (Feng et al., 1986a).

More intensive studies of glyphosate and AMPA in the surface waters of the Carnation Creek basin involved the direct overspray of two Carnation Creek tributaries (designated as tributaries 750 and 1600). Other forested areas in the basin were also sprayed, but a 10-m buffer between the spray zone and the tributary streams and the main stem of Carnation Creek was attempted. Direct overspray with Roundup^R at 2.0= $2.1 \text{ kg} \cdot \text{ha}^{-1}$ (about 252 L·ha⁻¹) resulted in glyphosate concentrations in tributary 1600 of >160 μ g·L⁻¹ at 2 h postspray. concentration rapidly dropped to 54.4 and $36.5 \, \mu g \cdot L^{-1}$ at 6.4 and 15.4 h postspray. respectively. AMPA concentrations peaked after 2 h at 4 μ g·L⁻¹ and decreased to 1.3 and 0.84 μ g·L⁻¹ at 6.4 and 15.4 h postspray, respectively. The magnitude and rate of decrease of glyphosate observed were comparable to other studies (Feng et al., 1986b).

Differences in glyphosate concentrations between the tributaries that received direct overspray input were apparently due to variables such as water surface area and overhanging riparian vegetation, which intercepted the glyphosate. These circumstances resulted in a peak concentration of only $1.5~\mu g \cdot L^{-1}$ in tributary 750. This concentration decreased below the quantification limit of $0.5~\mu g \cdot L^{-1}$ within 6 h. AMPA was not detected (i.e., <0.05 $\mu g \cdot L^{-1}$) in this tributary following 96 h postspray (Feng et al., 1986b).

Tributary 1450, which was protected from direct spray applications by a 10-m buffer zone, contained a concentration of 0.75 μ g·L⁻¹ at 1 h postspray due to spray drift. This concentration decreased to below limit of detection (0.1 μ g·L⁻¹) between 2 and 7.5 h postspray. A second peak concentration of 2.47 μ g·L⁻¹ occurred at 10 h postspray, which then decreased below 0.1 μ g·L⁻¹ after 16 h postspray. This delayed response was thought to have resulted from the slower subsurface flow of the tributary between the area receiving the spray drift and the sampling point (Feng et al., 1986b).

The first rainfall in the area after spraying occurred between 21 and 24 h. The 39-mm rainfall event caused glyphosate concentrations in tributary 750 to increase from below 0.5 to 144 μ g·L⁻¹ at 27 h postspray. Subsequently, this concentration fell below $0.1 \, \mu \text{g} \cdot \text{L}^{-1}$ at 96 h postspray. AMPA peaked at 3.6 μ g·L⁼¹ at 27 h postspray and then declined to below the detection limit (0.05 μ g·L⁻¹) at 37 h postspray. These high values were thought to result from glyphosate washing off the riparian vegetation along the tributary. The other tributary (1600) that received direct overspray exhibited an increased glyphosate concentration of 109 μ g·L⁻¹ during the first rainfall, which then decreased to 1.3 μ g·L⁻¹ at 96 h postspray. AMPA concentrations were also increased by the rainfall to $1.8 \, \mu \text{g} \cdot \text{L}^{-1}$, which subsequently decreased to <0.1 μ g·L⁻¹ at 49 h postspray. Tributary 1450. which was protected from direct overspray by a 10-m buffer zone, showed a minor increase in glyphosate to $0.64 \, \mu \text{g} \cdot \text{L}^{-1}$ during the first $\frac{1}{2} \, \text{h}$ of the rainfall. Glyphosate was not detected in this tributary (i.e., <0.1 μ g·L⁻¹) at 47 h postspray (Feng et al., 1986b).

Although the conclusion was reached that direct applications of glyphosate and spray drift were the major sources of tributary water residues, sampling of the main stem of Carnation Creek downstream from the sprayed areas showed that the first rainfall after spraying produced glyphosate concentrations twice as high as those that resulted from the initial spraying (i.e., $1.4 \ \mu g \cdot L^{-1}$). This was thought to be due to the input of ephemeral streams draining the blocks of forest receiving direct spray (Feng et al., 1986b).

Continued monitoring of the study area through eight major storm events identified glyphosate concentrations in surface waters only during the storm at 23 d postspray. concentrations of 0.52 and $0.53 \, \mu \text{g} \cdot \text{L}^{-1}$ from tributaries 750 and 1600 were <0.5% of the first rainfall runoff concentrations. After 23 d postspray, glyphosate residues in surface waters of the study area were between the limits of quantification and detection (0.1 to 0.5 $\mu g \cdot L^{-1}$, respectively). AMPA was found only in trace concentrations (i.e., 0.05 to 0.2 μ g·L⁻¹) during continued monitoring. The persistence of glyphosate observed in this watershed study was similar to other reports of glyphosate persistence in runoff. However, these concentrations were than those reported for agricultural watersheds (Feng et al., 1986b).

Persistence and Degradation

Little published information is available on the persistence of glyphosate in surface waters. In their review of available information on the behaviour of glyphosate in the aquatic environment. Brønstad and Friestad (1985) concluded that a understanding of the various processes involved in glyphosate dissipation was necessary. conclusion was prompted by the lack of published comparative data with full descriptions of experimental conditions. From the available data, it was proposed that two major pathways for glyphosate dissipation in water were likely: (1) microbial breakdown to AMPA and (2) adsorption to sediments with subsequent microbial breakdown of bound residues anaerobic conditions (Tooby, 1985).

Degradation of glyphosate in water with abundant microflora under both aerobic and anaerobic conditions was described by Rueppel et al. (1977). The principal metabolite was AMPA. were characterized, metabolites Other | represented than 1% of the total less ¹⁴C-glyphosate originally added. Degradation was not recorded in sterilized water. The rate of degradation in water was expected to be slower than in soils due to the lower density of microbes found in water (Ghassemi et al., 1981). The availability of glyphosate to microorganisms for degradation both in soil and water was thought to be decreased by the formation of colloidal iron and aluminum precipitates (Moshier and Penner, 1978). microbial toxicity was not expected at recommended application rates (Carlisle and Trevors, 1986). Laboratory studies indicated that several species of microbes were able to degrade glyphosate (Talbot et al., 1984). One species, Arthrobacter sp., was able to utilize glyphosate as a sole source of Uptake and/or degradation of phosphorus. appeared subject to glyphosate, however, suppression or inhibition by orthophosphates and organophosphorus compounds (Pipke et al., 1987).

Dissipation of glyphosate in a Florida pond was observed to be rapid and followed first-order kinetics. The half-life was reported to be approximately 12 d (Sacher, 1978). Unpublished studies by the Monsanto Company, as reviewed by Ghassemi et al. (1981), found glyphosate half-lives of 7 weeks in sphagnum bogs (pH 4.23), 9 weeks in cattail swamps (pH 6.25), and 10 weeks in pond water (pH 7.33). No experimental details were provided in this review.

A detailed study of glyphosate dissipation in four Manitoba ponds and six outdoor microcosms demonstrated first-order half-lives ranging from 1.5 to 3.6 d (Goldsborough and Beck, n.d.). The ponds and microcosms received aerial applications of 0.89 kg·ha⁻¹ of glyphosate. Surface water samples collected immediately after spraying contained the highest glyphosate concentrations (range: 25-141 μ g·L⁻¹). Considerable variation existed between and within ponds for surface water glyphosate concentrations. At 11 d postspray, mean glyphosate residues had decreased to <3 μ g·L⁻¹. After 37 d, glyphosate was not detected (detection

limit $0.5 \ \mu g \cdot L^{-1}$) in any pond water sample. AMPA concentrations in pond water samples never exceeded $2.2 \ \mu g \cdot L^{-1}$ and generally were at or below the $0.5 - \mu g \cdot L^{-1}$ detection limit.

microcosms used in the study by Goldsborough and Beck (n.d.) were of two types: plastic-lined depressions made in forest soil only water and similar depressions containing containing water plus sediment. Observed mean glyphosate residues at 0.5 h postspray were 352 ± 25 $\mu g \cdot L^{-1}$ in the water-only microcosms and 215 ± 170 $\mu g \cdot L^{-1}$ in the water-plus-sediment microcosms. observations revealed increased Subsequent glyphosate concentrations in the water-only microcosms to 5 d postspray, which was attributed Glyphosate conceninputs. to allochthanous trations remained relatively stable for the next 10 d and decreased slightly by day 30. By glyphosate concentrations in the contrast, water-plus-sediment microcosms decreased rapidly in the first 8 d following application, but were still detectable at 30 d postspray (i.e., $8-11 \ \mu g \cdot L^{-1}$). The estimated half-life of glyphosate in the water-plus-sediment microcosms was 5.8 d.

AMPA concentrations in the microcosms were corresponding qlyphosate than 1ower exceed 20 μ g·L⁻¹. and did not concentrations Degradation of glyphosate to AMPA in microcosm water was apparently minimal. Initial postspray in water-only microcosms concentrations averaged 2 µg·L-1 and increased during the first $10 \quad \mu \text{g} \cdot \text{L}^{-1}$. 5-8 d to approximately water-plus-sediment the concentrations in microcosms increased from 2 to approximately $8 \mu g \cdot L^{-1}$ during the first 5 d postspray and decreased thereafter, remaining above the detection limit until day 30. The relative persistence of glyphosate in water-only microcosms, compared to the water-plus-sediment microcosms, indicated that adsorption to sediments played a major role in the removal of glyphosate from the water column (Goldsborough and Beck, n.d.).

A study that monitored glyphosate and AMPA in surface waters after glyphosate spraying in Manitoba forests (Beck, 1987) found that half-lives varied from 8 to 15 h. Given the minimal number of

data points and the absence of replicate samples, however, it was concluded that a half-life of less than 24 h was more appropriate to the study results.

Photodecomposition of glyphosate may occur in natural waters. Irradiation of 1.0 mg·L⁻¹ of glyphosate in sterilized, natural water for 1 and 14 d resulted in 18.4% and 86.7%, respectively, being transformed to AMPA (Brønstad and Friestad, 1985). The source of irradiation was not given. but natural sunlight was implied. Controls kept in the dark showed glyphosate to be stable. Lund-Høje and Friestad (1986) reported the photodegradation glyphosate in deionized water exposed to ultraviolet light (254 nm). Half-lives of 4 d and 3-4 weeks were reported for concentrations of 1.0 and $2000 \text{ mg} \cdot \text{L}^{-1}$, respectively. In addition. degradation of glyphosate (2.0 and 100 mg·L⁻¹) was found to occur in deionized and "polluted" waters exposed to natural sunlight (Lund-Høie and Friestad, 1986). The authors also reported that dissipation of glyphosate in water under dark conditions did not occur, although microbial activity (expressed as 14CO2 evolution $^{14}\mathrm{C} ext{-sucrose)}$ was high. A discussion of the results and how these data fit into the overall dissipation of glyphosate in water was not given. Although the results noted above indicate a potential for photodecomposition, they are, for the most part, inconclusive. From the available information, it be inferred, however, that the role of photolysis in the environmental degradation of glyphosate is a minor one.

Glyphosate strongly adsorbs to soil colloids and suspended solids in the water column and the adsorbed residues are removed from the water by sedimentation. Clay loam sediments were found to contain $11 \text{ mg} \cdot \text{kg}^{-1}$ glyphosate after 9 weeks of exposure to water containing 1.0 $mg \cdot L^{-1}$. findings of higher glyphosate concentrations in sediments corroborate reports indicating particulate matter had a high adsorptive capacity for glyphosate (Hance, 1976; Hensley et al., 1978; Lund-Høie and Friestad, 1986; Newton et al., 1984; Wan, 1986). Furthermore, they agreed with the results of Damanakis (1976), which showed the adsorption coefficient of glyphosate (concentration adsorbed/concentration in solution at equilibrium)

to increase as the ratio of soil to water was lowered. An adsorption coefficient of 11.1 was observed in a vessel with 40 g of soil and 80 mL of solution. The coefficient increased to 55.2 when only 5 g of soil were added to the 80 mL of solution.

persistence of glyphosate in Ontario boreal forest soils demonstrates dissipation with time and very little leaching. The time required for 50% glyphosate dissipation was approximately Residue values in the boreal forest sand soils were below 10% of their initial value after Under the study conditions used by Roy et al. (1987), no downslope (8°) movement in soil was observed when Roundup R (35.6% glyphosate) was applied at 1.789 kg·ha $^{-1}$. As well, glyphosate was not detected in runoff water during rainfall Research conducted by Torstensson and Aamisepp (1977) and reviews of other work (Ghassemi et al., 1982; Torstensson, 1985) related to the behaviour of glyphosate in soils supported the conclusions reached concerning glyphosate adsorption and degradation in the aquatic environment. Furthermore, the research conducted on glyphosate behaviour in soil has demonstrated that the extent of adsorption is correlated with the phosphate adsorption capacity of soil and that glyphosate adsorption is reversible (Torstensson, 1985). Whether or not similar behaviour occurs in the aquatic environment has not yet been determined.

One of the previously proposed pathways for glyphosate dissipation in water was "adsorption to sediments with subsequent microbial breakdown of bound residues under anaerobic conditions." Research in the soil environment showed that the microbial breakdown was a co-metabolic process and occurred under both aerobic and anaerobic conditions (Torstensson, 1985).

RATIONALE

Raw Water for Drinking Water Supply

Guideline

The maximum acceptable concentration (MAC) for glyphosate listed in the Guidelines for Canadian

Drinking Water Quality is $280~\mu\text{g}\cdot\text{L}^{-1}$ (Health and Welfare Canada, 1989). This value is based on a no-observed-effect level (NDEL) of 3 mg·kg⁻¹·d⁻¹ from a 2-year study with rats in which slight reductions in body weight occurred at higher doses.

The U.S. EPA recommends a limit of $500~\mu g \cdot L^{-1}$ of glyphosate in drinking water, which is calculated from an acceptable daily intake (ADI) of 0.10 mg·kg⁻¹·d⁻¹. The ADI is based on a NOEL of $10~mg\cdot kg^{-1}\cdot d^{-1}$ from a three-generation reproduction study with a 100-fold safety factor (U.S. EPA, 1982a, 1982b).

Freshwater Aquatic Life

Levels in Aquatic Biota

Glyphosate residues were measured in spawning rainbow trout (Salmo gairdneri) exposed to 0.02, 0.2, and 2.0 mg·L⁻¹ of the isopropylamine salt of glyphosate for 12 h in artificial streams (Folmar et al., 1979). Glyphosate and its major metabolic product, AMPA, were not detected in eggs or fillets of fish exposed to the technical material. Eggs and fillets of trout exposed to 2.0 mg·L⁻¹ of the formulated herbicide were reported to contain 60 and 80 μ g·kg⁻¹ of glyphosate, respectively.

Ten caged coho salmon (<u>Oncorhynchus kisutch</u>) fingerlings exposed to stream water that received an aerial application of 3.3 kg·ha⁻¹ (peak water concentration of 0.27 mg·L⁻¹ at 2 h posttreatment) did not contain detectable levels of glyphosate or its metabolic product, AMPA (Newton et al., 1984).

Toxicity to Aquatic Organisms

A summary of fish and invertebrate toxicity data related to glyphosate and Roundup R is presented in Appendix A. It should be stressed that the commercial formulation Roundup R also contains a proprietary surfactant (MONO818) at a concentration of approximately 15% v/v. The environmental toxicity data reported for Vision R by Monsanto Company (1987a) is identical to the same information reported for Roundup R (Monsanto Company, 1982b).

The toxicity data in Appendix A demonstrate that acute LC50 values for Roundup R are generally

an order of magnitude lower (i.e., more toxic) than acute LC_{50} values for glyphosate itself. A more dramatic comparison of toxicity data related to the surfactant used in Roundup^R, glyphosate, and the commercial formulation is presented in Table 2.

Table 2. The Toxicity of Glyphosate, Roundup^R, and the Proprietary Surfactant (Used in Roundup^R) to Four Aquatic Species¹

| | Chemical or | |
|----------------------------------|---|---|
| | Commercial | |
| Organism | Formulation | Exposure time - LC ₅₀ |
| Rainbow trout | Surfactant | 24 hr LC ₅₀ = 2.1 mg·L ⁼¹ |
| (Salmo | Glyphosate | 24 hr $LC_{50} = 140 \text{ mg} \cdot L^{-1}$ |
| gairdneri) | Roundup ^R | 24 hr LC ₅₀ = 8.3 mg·L ⁻¹ |
| | Surfactant | 96 hr $LC_{50} = 2.0 \text{ mg} \cdot L_1^{-1}$ |
| | Glyphosate | 96 hr $LC_{50} = 86 \text{ mg} \cdot L^{-1}$ |
| | Roundup ^R | 96 hr LC ₅₀ = 8.3 mg·L ⁻¹ |
| Fathead minnow | • | 24 hr $LC_{50} = 1.4 \text{ mg} \cdot L_1^{-1}$ |
| (<u>Pimephales</u> | Glyphosate | 24 hr $LC_{50} = 97 \text{ mg} \cdot L^{-1}$ |
| <u>promelas</u>) | Roundup ^R | 24 hr $LC_{50} = 2.4 \text{ mg} \cdot L^{-1}$ |
| | Surfactant | 96 hr $LC_{50} = 1.0 \text{ mg} \cdot L_1^{-1}$ |
| | Glyphosate | 96 hr $LC_{50} = 97 \text{ mg} \cdot L^{-1}$ |
| | Roundup ^R | 96 hr LC ₅₀ = 9.4 mg·L ⁻¹ |
| Channe1 | Surfactant | 24 hr $LC_{50} = 18 \text{ mg} \cdot L^{-1}$ |
| catfish | Glyphosate | 24 hr $LC_{50} = 130 \text{ mg} \cdot L^{-1}$ |
| (<u>Ictalurus</u> punctatus) | Roundup ^R | 24 hr LC ₅₀ = 13 mg·L ⁻¹ |
| | Surfactant | 96 hr $LC_{50} = 13 \text{ mg} \cdot L^{-1}$ |
| | G1yphosate | 96 hr $LC_{50} = 130 \text{ mg} \cdot L^{-1}$ |
| | Roundup ^R | 96 hr LC ₅₀ = 16 mg·L ⁻¹ |
| Bluegill | Surfactant | 24 hr $LC_{50} = 2.1 \text{ mg} \cdot L^{-1}$ |
| (<u>Lepomis</u> | Glyphosate | 24 hr $LC_{50} = 150 \text{ mg} \cdot L^{-1}$ |
| macrochirus) | Roundup ^R | 24 hr LC ₅₀ = 6.4 mg·L ⁻¹ |
| | Surfactant | 96 hr LC ₅₀ = 2.0 mg·L ⁻¹ |
| | Glyphosate | 96 hr $LC_{50} = 120 \text{ mg} \cdot L^{-1}$ |
| | Roundup ^R | 96 hr LC ₅₀ = 5.0 mg·L ⁻¹ |

¹ Data from U.S. Department of Agriculture, 1984.

This table shows the acute toxicity of the surfactant to be similar to that of the commercial formulation. The acute toxicity of glyphosate, however, is an order of magnitude lower (i.e., less toxic) than either the surfactant or the commercial formulation.

Studies conducted with the chemical glyphosate have shown that elevated pH and temperature increase its acute toxicity to rainbow trout (Salmo gairdneri) and bluegill (Lepomis macrochirus) (Folmar et al., 1979). Although adsorption of glyphosate onto suspended particulate material in the water column would generally be considered to reduce the bioavailability (and toxicity) of glyphosate to aquatic organisms. the reverse appears to occur in tests with Daphnia pulex. Laboratory toxicity tests conducted by Hartman and Martin (1984) demonstrated that the presence of $50 \text{ mg} \cdot \text{L}^{-1}$ suspended solids (as bentonite) actually increased the toxicity of the herbicide (locally Roundup R). The specific mechanisms purchased responsible for this response were not addressed. Consideration was not given, however, to the presence of the toxic surfactant in the commercial formulation or to the possibility that glyphosate and the surfactant might have been antagonistic in terms of their combined toxicity. If this were the case, removal of the glyphosate from solution by adsorption onto the clay suspension would have produced the observed increase in toxic response by the test organism.

This hypothesis was supported by Servizi et al. (1987), who used toxic units to assess the possibility of interaction between glyphosate and the surfactant in the Roundup^R formulation. Toxicity test results using natural lake water suggested the presence of antagonistic reactions between the surfactant (MONO818) and glyphosate. However, similar analyses of toxicity conducted in reconstituted water suggested the combined effects of glyphosate and MONO818 were "more than additive" (i.e., synergistic). difference in response was considered extremely important, as shown by Folmar et al. (1979), when the toxicity of Roundup R was investigated in a variety of freshwater organisms with reconstituted water used as the diluent. Reconstituted water is deionized water with the appropriate reagent grade

chemicals added to maintain a buffered pH at 7.2-7.5, an alkalinity of $30-35~\text{mg}\cdot\text{L}^{-1}$, and a hardness of $40-50~\text{mg}\cdot\text{L}^{-1}$ (Johnson and Finley, 1980). Generally, acute toxicity values for the formulated products tested are an order of magnitude lower (i.e., less toxic) than the active ingredient alone. The exact nature of the toxicity relationship between the active ingredient and the surfactant has as yet to be fully resolved.

The field and laboratory 96-h static toxicity tests of Hildebrand et al. (1982) also demonstrated that mortality did not occur among caged rainbow trout fingerlings in streams that received applications of Roundup^R at rates of 2.2, 22.2, and 222.2 kg-ai·ha⁻¹. These were 1, 10, and 100 times the normally recommended application rate for forestry management.

Investigations of direct applications of Roundup^R to a pond containing caged <u>Daphnia magna</u> showed no effect, even at 100 times the recommended dose (Hildebrand et al., 1980). However, the various levels of exposure (1, 10, and 100 times the recommended dose for forestry management) were all conducted in the same pond without suitable controls or any mechanism of partitioning the treatment areas. In addition, the pond had an inflow and outflow that were not quantified, making the results questionable.

RoundupR Concern over use in forestry management and possible impacts on anadromous fish species returning to the sea (smoltification) resulted in laboratory experiments to determine the effects of this exposure. Concentrations of $\mathsf{Roundup}^\mathsf{R}$ as high as 10 times those reported in streams immediately after forest spraying did not affect the transition of yearling coho salmon (0. kisutch) to seawater. Ten-day exposures of coho salmon to 2.78 $\text{mg} \cdot \text{L}^{-1}$ did not alter plasma sodium concentration, hematocrit, or growth. As well, abnormal responses were absent when a 10-d freshwater recovery period was provided between RoundupR exposure and transfer to seawater (Mitchell et al., 1987a).

In addition to the North American toxicity data reported in Appendix A, a limited number of toxicity studies conducted with Asian fish species

exist. Singh and Yadav (1978) reported that $10~\text{mg}\cdot\text{L}^{-1}$ of glyphosate produced 100% mortality in major carp (Cirrhina mrigala) fingerlings after 2.5 h. A mortality of approximately 30% was reported for $5~\text{mg}\cdot\text{L}^{-1}$, but a time frame for this mortality was not given. Although the authors reported the results as glyphosate toxicity, it was not explicitly stated if glyphosate or the commercial formulation was used in the toxicity tests. It was implied that the test material was Roundup^R, in which case the reported $10~\text{mg}\cdot\text{L}^{-1}$ value would be similar to other reported values for the formulation toxicity.

Research into the effects of glyphosate on aquatic plants was generally directed toward two objectives: (1) the eradication of aquatic weed species and (2) concerns related to the impact of terrestrial applications of glyphosate to nontarget plants in aquatic environments adjacent to treated areas. Investigations into the elimination of nuisance aquatic plant growth with glyphosate revealed that spray applications of glyphosate (at 0.56 to 2.24 kg·ha⁻¹) to the floating leaves of the fragrant waterlily (Nymphaea odorata) and spatterdock (Nuphar sp.) eliminated these species within 2 months depending on the time of year and application rate. (It should be noted that these application rates are within those used in forestry spray programs.) While foliar application allowed plant uptake and translocation to the rhizomes, which were also killed, germination of seeds ocfollowing year and required an curred the additional application once the leaves had attained the surface to insure complete eradication (Welker and Riemer, 1973, 1982, 1983). Water hyacinth (Eichornia crassipes) required 2-6 kg·ha-1 applied to the foliage for complete elimination (Singh and Muller, 1979).

A review of glyphosate trials for the control of emergent aquatic and semiaquatic plant species from various regions around the world demonstrates that Roundup is able to control a wide variety of plants under a variety of conditions. Foliar applications, at rates of 1.8-3.0 kg-ae-ha⁻¹ (ae = acid equivalents) of glyphosate as the isopropylamine salt generally produce greater than 90% control of aquatic plant species. Some species,

such as alligator weed (<u>Alternanthera philoxe-roides</u>), exhibit a variable response and require in excess of 3 kg-ae·ha⁻¹ for control (Evans, 1978).

Control of submergent species [e.g., water (Myriophyllum spicatum) and curlyleaf milfoil (Potamogeton crispus)] by pondweed glyphosate much less effective. dissolved in water is Concentrations of approximately $1000 \text{ mg} \cdot \text{L}^{-1}$ and exposure times of at least 5 h are necessary for satisfactory control of these aquatic plants by Even concentrations of waterborne glyphosate. 5000 mg·L⁻¹ and 35-d exposures, however. are regrowth of both ineffective in preventing aforementioned species from the roots (Peverly and Crawford, 1975). As expected, $10 \text{ mg} \cdot \text{L}^{-1}$ of qlyphosate does not inhibit the growth of Potamogeton pectinatus. Growth stimulation was observed at 1.0 mg·L-1 for this species (Hartman and Martin, 1985). Details of experiments conducted with glyphosate and common submergent plants were not reported by Forney and Davis (1981) due to the lack of a toxic response.

The floating aquatic vascular plants of the genus Lemna (i.e., duckweeds) appear much more sensitive to glyphosate dissolved in water. Exposure to 8.5 mg·L⁻¹ of glyphosate for 7 d caused a 37% reduction in growth as measured by dry weight (Gianfagna and Foy, 1975; Cooley and Foy, 1986). An abstract of a study concerning glyphosate toxicity to Lemna minor reported an effective dose (ED) of 5 mg·L $^{-1}$ as toxic to 50% of the plants (Prasad, 1984). The exposure time, however, was not given. Hartman and Martin (1984) reported a 14-d ED50 of 2.0 mg·L⁻¹ of glyphosate for the same Addition of bentonitic clay for a solid concentration of $50 \text{ mg} \cdot \text{L}^{-1}$ suspended decreased the glyphosate toxicity over the same time period to $10 \text{ mg} \cdot \text{L}^{-1}$. Cell membrane permeability of Lemna minor fronds floating on glyphosate solutions of 1.69 and $16.9 \text{ mg} \cdot \text{L}^{-1}$ were apparently affected after 48-96 h, and 24-48 h, respectively (O'Brien and Prendeville, 1979). physiological or ecological However. the implications of this finding were not given.

The effect of glyphosate on enzyme extracts of $\underline{\text{Lemna}}$ $\underline{\text{gibba}}$ was studied by Hoagland (1978) and

Hoagland and Paul (1978). Enzyme activities were affected by 169.1 mg·L⁻¹ shortly after exposure. In some cases, the alteration of enzyme activities occurred prior to the appearance of observable damage and growth effects. This concentration of produced chlorotic areas fronds at 48 h posttreatment and inhibited growth by 30% at 72 h. An order of magnitude decrease in glyphosate (16.91 mg·L⁻¹) was also found to cause observable damage after 48 h. Within the 12- to 24-h exposure period, electron microscopic examination showed progressive damage of chloroplasts, mitochondria, and cell walls. studies and others involving the toxic effects of glyphosate on terrestrial plants were reviewed by Richardson (1985).

Concern over the possible alteration of the naturally occurring algal food base in aquatic ecosystems receiving glyphosate prompted field and laboratory investigations. The effects of direct spray application of 2.2 kg·ha⁻¹ on a forest stream and pool could not be detected by monitoring attached diatom communities (Sullivan et al., 1981). Unfortunately, measurements of glyphosate concentrations in the water were not made. Different types of algae varied in their responses to glyphosate solutions. The growth of the green alga <u>Chlorella</u> <u>sarokiniana</u> was inhibited by 3 mg·L $^{-1}$, whereas 203 mg·L $^{-1}$ were required to significantly reduce cell numbers in the flagellate Euglena gracilis (Richardson et al., 1979; Christy et al., 1981). Oxygen evolution inhibition was noted in E. gracilis exposed to glyphosate concentrations as low as 1 mg·L⁻¹ for 100 minutes. Longer exposures produced a stimulation of oxygen production (Richardson et al., 1979).

Compared to the above species, the cyanobacteria (blue-green algae) generally appeared more sensitive to glyphosate. The exponential growth rate of three species of cyanobacteria was reduced to 50% of the control by 2 $\rm mg \cdot L^{-1}$. Complete growth inhibition occurred at 10 $\rm mg \cdot L^{-1}$. Sensitivity varied widely among species of cyanobacteria. The data showed growth of one species of the genus Aphanocapsa to be inhibited by 2 $\rm mg \cdot L^{-1}$, while another species of the same genus required 100 $\rm mg \cdot L^{-1}$ for a similar response (Hutber et al., 1979).

A laboratory study of algal sensitivity to a variety of chemical compounds demonstrated that the glyphosate concentration that totally inhibited growth of 13 different algal species ranged from 2.8 to 23 $\text{mg} \cdot \text{L}^{-1}$. The median value was 11 $\text{mg} \cdot \text{L}^{-1}$ (Blanck et al., 1984).

Roundup $^{\mathbf{R}}$ was used as a toxicant in a comparison of the 2-3 week EPA bottle test and a 24-h algal oxygen evolution assay for the detection of waterborne contaminants. Dilutions of Roundup^R ranging from 0.75 to 75 μ g·L⁻¹ in an algal assay medium were used to find the concentration inhibiting oxygen evolution by 50% (10 $\mu q \cdot L^{-1}$) in unicellular chlorophyte Selanastrum capricornutum. The EPA bottle test demonstrated a 50% reduction in biomass at 3.83 μ g·L⁻¹. When Roundup^R was mixed with natural stream water, test concentrations ranging from 0.036 to 36 ug·L⁻¹ failed to provide an inhibitory response equivalent to 50% of the control in both test systems (Turbak et al., 1986).

Periphyton communities on acrylic rods from six small ponds bordering Lake Winnipeg were used to measure $\mathrm{H}^{14}\mathrm{CO}_3$ uptake in the laboratory during 4-h exposures to varying concentrations of Roundup^R. For those periphyton communities exhibiting a significant dose-response relationship, the concentration of glyphosate reported to produce a 50% inhibition of $^{14}\mathrm{C}$ -uptake ranged from 9.7 to 35.4 mg·L⁻¹ (Goldsborough and Brown, 1987, n.d.).

An aerial application of 2.0 kg·ha⁻¹ of glyphosate (as Roundup^R) over a small Nova Scotia forest stream failed to affect periphyton that colonized artificial substrates placed in the stream one month prior to spraying (Environment Canada, 1987). Comparisons of chlorophyll a. phaeophytin, total biomass, and ATP (adenosine triphosphate) upstream from and in the spray area failed to identify significant effects attributable to Roundup^R spraying. This survey for biological effects lasted 37 d postspray.

When Roundup R was applied to pools containing abundant aquatic macrophyte growth to achieve a glyphosate concentration of 200 mg·L $^{-1}$, suspended aquatic bacteria densities were depressed when measured as colony-forming units or CFUs. Maximum

depression occurred at 15 d posttreatment resulting in densities of 1 X 10^3 CFU·mL $^{-1}$ from an initial density of 2 X 10^5 CFU·mL $^{-1}$. After 20 d posttreatment, densities increased and attained control levels at 30 d posttreatment (Chan and Leung, 1986). Information was not given regarding aquatic macrophyte responses. Laboratory studies conducted with two bacteria species (Aeromonas hydrophila and Pseudomonas chlororaphis) isolated from these pools demonstrated extreme differences in glyphosate sensitivity. A concentration of 1500 mg·L $^{-1}$ apparently reduced the density of A. hydrophila to levels below the control, while the same concentration of glyphosate was lethal to P. chlororaphis (Chan and Leung, 1986).

Accumulation and Elimination of Glyphosate Aquatic Organisms

The published data indicated glyphosate had a low accumulation potential in aquatic organisms. A maximum bioconcentration factor (BCF) of 1.6 was reported for bluegill (Lepomis macrochirus) exposed to 0.6 mg·L⁻¹ of glyphosate for 28 d (Sacher, 1978). Channel catfish (Ictalurus punctatus). largemouth bass (Micropterus salmoides), and rainbow trout (Salmo gairdneri) exposed to 10 mg·L⁻¹ of glyphosate for 14 d had BCFs of 0.18, 0.04, and 0.03, respectively (Sacher, 1978). Exposure of fish to glyphosate at concentrations (not given) three to four times the recommended application rates for 10 to 14 d resulted in BCFs of 0.1 to 0.3 (Monsanto Company, 1984). The lack of information on experimental protocol and residue concentrations in the above studies, however, reduced their usefulness in the assessment of glyphosate uptake and retention.

The octanol-water partition coefficient for glyphosate was reported to be 0.0017 at 10 $\rm mg \cdot L^{-1}$ and 0.006 at 100 $\rm mg \cdot L^{-1}$ (Ghassemi et al., 1981). These low values support the available experimental data showing little tendency for glyphosate to accumulate in aquatic organisms.

Guideline

Specific provincial or federal objectives or guidelines for glyphosate in water for the protection of aquatic life do not exist. The U.S.

EPA does not have an objective, guideline, or advisory for glyphosate and does not plan to include this compound in future criteria development work (K. Potts, 1987, U.S. EPA Office of Water Regulations and Standards, Criteria and Standards Division, Criteria Branch, pers. comm.).

The California State Water Resources Control Board recommends an aquatic guideline of 130 $\mu g \cdot L^{-1}$ of glyphosate for waterborne residues of Roundup R "due to the increased toxic effect of the surfactant in the Roundup^R formulation[®] (Corcoran et al., 1984). This value is based upon application of a 10-fold safety factor to the 96-h LC₅₀ value of 1.3 mg·L⁻¹ for rainbow trout (Salmo gairdneri) fingerlings (Folmar et al., 1979). This recommendation sets a precedent for establishing a water quality related guideline, objective, or criterion with regard to glyphosate. The increased toxic effect of Roundup^R compared to glyphosate is readily apparent from the toxicity data included in this report. The lowest 96-h LC50 for a North American freshwater fish species exposed to glyphosate is 24 mg· L^{-1} for the bluegill (Lepomis By contrast, the lowest 96-h LC50 macrochirus). for a North American freshwater fish species exposed to Roundup^R is 1.3 mg·L⁻¹ for the rainbow trout (Salmo gairdneri) fingerling. Toxicity data for Vision^R is identical to that for Roundup^K (Monsanto Company, 1987a).

The available toxicity data are not sufficient to support a Canadian water quality guideline as chronic or long-term exposure studies with aquatic animals are not available. Most of the aquatic plant toxicity data are based on field observations of glyphosate use. Laboratory studies of cellular membrane permeability or enzyme activities are without any direct relation to toxicity endpoints. Some aquatic plant laboratory toxicity data have longer exposure times (i.e., 14 d) than those for animal studies. The effects of the surfactant in the Roundup^R formulation, however, are not as defined for plants as they are for animals. In addition, the plant toxicity data generally demonstrate a reduced sensitivity by these organisms compared to animals.

Available toxicity data have been used to generate an interim guideline. Given the amount of

data available for Roundup^R and the existence of an aquatic guideline for the formulation (i.e., as recommended by the California State Water Resources Control Board), it is appropriate that in this case a water quality guideline be set using the formulated product. The lowest 96-h LC50 generated from standardized tests of Roundup^R and a sensitive North American freshwater species is 1.3 $\rm mg\cdot L^{-1}$ (Folmar et al., 1979). The use of toxicity data from non-North American species is considered inappropriate. Using an application factor of 0.05 for nonpersistent substances (CCREM, 1987) produces an interim guideline of 0.065 $\rm mg\cdot L^{-1}$ or 65 $\rm \mu g\cdot L^{-1}$ of glyphosate.

Agricultural Uses

Livestock Watering

Guideline

Definitive studies are necessary before numerical concentrations of glyphosate in water can be proposed for the protection of livestock. complete assessment of the mammalian and avian toxicology data base with regard to glyphosate is not possible due to the proprietary information restrictions imposed by the manufacturer of Roundup^K. However, CCREM (1987) adopted the policy that the guidelines for pesticides in Canadian raw water for drinking water supply could be used as the maximum limits of pesticides in livestock drinking water "as a means of providing a margin of safety for livestock and preventing unacceptable residues in animal products." As a guideline for glyphosate in raw water for drinking water supply is available (280 $\mu g \cdot L^{-1}$), this value has been adopted as an interim guideline for livestock watering.

Irrigation

Glyphosate residues in irrigation water have the potential to affect crops adversely by way of transport through the soil (row irrigation) with subsequent root uptake or by aerial application (sprinkler irrigation) with subsequent foliar uptake. The manufacturer of Roundup^R stated that glyphosate dissipated rapidly in soils when applied at recommended rates to foliage (Ghassemi et al., 1981). This claim has generally been borne out by

several years of use of commercial products containing glyphosate in a wide variety of soils and by various scientific studies (e.g., Sprankle et al., 1975a, 1975b). It is recognized, however, that the degree and rate of glyphosate dissipation are dependent upon the constituents characteristics of the soil (e.g., clay content). In areas where the soil contains a high sand content (e.g., >80%), loss of glyphosate is at a rate (Eberbach and Douglas, 1983). experimental studies that reported the stunting and failure of crop species, 25 times the recommended glyphosate application rate was used (as a soil treatment). Thus, impacts of glyphosate residues in irrigation waters used with furrow irrigation techniques would most likely be insignificant under normal operating conditions (McKinnon, 1984).

Crop species sprinkler-irrigated with water that contained several times more glyphosate than would be expected as the result of normal spraying of irrigation ditch bank vegetation did not produce injury or apparent adverse plant health symptoms. The highest concentration used in these studies was $2.2~{\rm mg}\cdot {\rm L}^{-1}$ of glyphosate applied continuously for 8 h. This was equivalent to 1.1 kg=ai·ha⁻¹ (Bruns and Kelley, 1975; Comes and Kelley, 1979).

Residues of glyphosate remaining in plant tissue at the time of harvest were also a concern. Furrow-irrigated and sprinkler-irrigated crops using water containing 5.51 mg·L⁻¹ and 2.21 mg·L⁻¹ of glyphosate, respectively, were found to contain glyphosate residues in some, but not all, of the Furrow irrigation crops tested. detectable residues of glyphosate $(0.15 \text{ mg} \cdot \text{kg}^{-1})$ only in a forage/grass/grain/sorghum crop treated at the highest rate $(2.8 \text{ kg} \cdot \text{ha}^{-1})$. Otherwise, furrow irrigation was ineffective in producing glyphosate residues in crop species. Sprinkler irrigation produced glyphosate residues in the forage/grass/grain/sorghum crop $(1.78 \text{ mg} \cdot \text{kg}^{-1})$ residue from 1.12 kg·ha⁻¹ glyphosate application) 2 d after treatment. Glyphosate residues were also found in sugar beet tops $(0.50 \text{ mg} \cdot \text{kg}^{-1})$ and field bean pods $(0.11 \text{ mg} \cdot \text{kg}^{-1})$ collected from plots sprinkler-irrigated at 1.12 kg·ha⁻¹. tomatoes, sugar beet roots, and the seeds of field beans failed to show detectable glyphosate residues (i.e., $>0.05 \text{ mg} \cdot \text{kg}^{-1}$) even after spray irrigation

with the highest glyphosate concentration used (2.21 ${\rm mg}\cdot {\rm L}^{-1}$, 1.12 ${\rm kg}\cdot {\rm ha}^{-1}$) (Bruns and Kelley, 1975).

normal spraying operations for the Under control of vegetation along drained irrigation canals (application rate: 5.6 kg·ha⁻¹ of glyphosate), glyphosate residues were not detected in the first flow of water through the canals approximately 23 d after treatment (Comes et al., 1976). Application of glyphosate to bank vegetation during irrigation canal use may produce residues in the water. The exact magnitude of the residues will be dependent upon factors such as channel dimensions and hydrology, the dosage of glyphosate used, the proportion of the applied glyphosate entering the water, and the dilution and dispersion during downstream movement. These interactive factors reduced 3600 mg·L⁻¹ glyphosate, applied at a rate of 5.3 $kg \cdot ha^{-1}$, from 0.41 $mg \cdot L^{-1}$ at the treatment site to 0.2 mg·L⁻¹ at a distance of 4 km downstream (average water velocity: 0.2 m·s⁻¹) (Bowmer, 1982a). Additional work by Bowmer (1982b) also demonstrated the removal of glyphosate from water by the adsorption onto suspended particulate material and the antagonistic effect on glyphosate adsorption by phosphate addition. The attenuation of glyphosate by adsorption onto suspended sediment downstream from spraying activities ranged from 13% to 31% per kilometre depending on site-specific water quality Loss of dissolved glyphosate by characteristics. adsorption was thought not to significantly reduce its phytotoxicity (Bowmer et al., 1986).

A criterion of 0.2 mg·L⁻¹ is used by the United Kingdom for glyphosate in irrigation water (Bowmer, 1982a), however, the rationale used to derive this level is not available for evaluation.

Guideline

Insufficient data exist to support the development of an irrigation water guideline for glyphosate at this time.

Recreational Water Quality and Aesthetics

Guideline

There is no recommended guideline for glyphosate in recreational waters.

Industrial Water Supplies

Guideline

There is no recommended guideline for glyphosate in industrial water supplies.

SUMMARY

Following an evaluation of the published information on the herbicide glyphosate. Canadian water quality guidelines were derived (Table 3).

Table 3. Recommended Water Quality Guidelines for Glyphosate

| Uses | Guidelines |
|---|---------------------------------------|
| Raw water for drinking water supply | 280 μg·L ^{=1*} |
| Freshwater aquatic life | 65 μ g·L ⁻¹ (Interim) |
| Agricultural uses | |
| Livestock watering | 280 μ g·L ⁻¹ (Interim) |
| Irrigation | No recommended guideline |
| Recreational water quality and aesthetics | No recommended guideline |
| Industrial water supplies | No recommended guideline |

^{*}Existing drinking water guideline (Health and Welfare Canada, 1989).

The background information on glyphosate in terms of uses and production, occurrence in the aquatic environment, persistence and degradation, and toxicity to nontarget organisms was reviewed. The rationale employed for the development of the recommended guidelines was summarized.

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Appendix A
Summary of Glyphosate and Roundup^R
Toxicity Data for Aquatic Organisms

Table A-1. Summary of Glyphosate and Roundup Toxicity Data for Aquatic Organisms

| Organism: | Chemical or Formulation | Exposure Time | Test Conditions | Effects | Comments ¹ | Reference |
|--|--------------------------|------------------|--------------------|--|--|--|
| INVERTEBRATES | | | | | | |
| Midge larvae (Chironomus plumosus) | Glyphosate | 48 h | u, s | $EC_{50} = 55 \text{ mg} \cdot L^{-1}$ | (31-97 mg·L ⁻¹) 22°C | Folmar et al., 1979 ² |
| Midge larvae (Chironomus plumosus) | Roundup ^R | 48 h | U, S | EC ₅₀ = 18 mg·L ⁻¹ | (94-32 mg·L ⁻¹) 22°C | |
| Grass Shrimp (Paleomonetes sp.) | Glyphosate, Technical | 96 h | NR | LC ₅₀ = 281 mg·L ⁻¹ NOEL at 210 mg·L ⁻¹ | (207-391 mg·L ⁻¹) | Monsanto Company, 1982a, and U.S. Department of |
| Fiddler crab (Crustacea) | Glyphosate, Technical | 96 h | NR | $LC_{50} = 934 \text{ mg} \cdot L^{-1}$ NOEL at 650 mg · L ⁻¹ | (555-1570 mg·L ⁻¹) | Agriculture, 1981 |
| Cladoceran (<u>Daphnia</u> sp.) | Roundup ^R | 48 h | NR | LC ₅₀ = 192 mg·L ⁻¹ | (181-205 mg·L ⁻¹) | U.S. Department of Agriculture, 1981 |
| Cladoceran (<u>Daphnia</u> sp.) | Roundup ^R | , 48: h | NR | $LC_{50} = 5.3 \text{ mg} \cdot L^{-1}$ | | Monsanto Company, 1982b |
| Cladoceran (Daphnia magna) | Roundup ^R | 48 h | บ, s | $EC_{50} = 3.0 \text{ mg} \cdot L^{-1}$ | (2.6-3.4 mg·L ⁻¹) 22°C | Folmar et al., 1979 |
| Amphipod (Gammarus pseudolimnaeus) | Roundup ^R | 48 h 96 h | u, s u, s | $LC_{50} = 62 \text{ mg} \cdot L^{-1}$ $LC_{50} = 43 \text{ mg} \cdot L^{-1}$ | $(40-98 \text{ mg} \cdot \text{L}^{-1}) 12^{\circ}\text{C}$ $(28-66 \text{ mg} \cdot \text{L}^{-1}) 12^{\circ}\text{C}$ | Folmar et al., 1979 |
| Crayfish (Crustacea) | Roundup ^R | 96 h | NR | $LC_{50} = >1000 \text{ mg} \cdot L^{-1}$ | | Monsanto Company, 1982b |
| Cladoceran (<u>Daphnia pulex</u>) | Roundup ^R | 96 h | M, s | EC ₅₀ = 25.5 mg·L ⁻¹ | 21°C | Servizi et al., 1987 |

¹ Values in parentheses are the 95% confidence limits.

² Some of the toxicity data reported by Folmar et al. (1979) were also reported by Johnson and Finley (1980).

3 pH of dechlorinated Vancouver city water (used for this bioassay) not measured during bioassay, but estimated from tests in which Roundup^R was found to reduce test water pH.

Hard = water hardness in $mg \cdot L^{-1}$ as $CaCO_3$

Cond = water conductivity

IPA = isopropylamine

PE = pulsed exposure; 2-h exposure and survival measured over subsequent 94 h

U = concentrations in test solutions not measured or not stated as being measured

M = concentrations in test solutions measured

S = static test

F = flow-through test

NR = not reported; generally these tests can be assumed to be U, S

Harpacticoid copepod (Nitocra spinipes)

Organism.

Cladoceran

(Daphnia sp.)

Atlantic ovsters

(yolk sac fry)

(eyed egg)

Chemical or

Formulation

Glyphosate,

Glyphosate,

Technical

Roundup^R

Roundup^R

RoundupR

Test

Conditions

U, S

NR

NR

Effects

 $LC_{50} = 22 \text{ mg} \cdot L^{-1}$

 $LC_{50} = 780 \text{ mg} \cdot L^{-1}$

NOEL at 10 mg·L-1

 $LC_{50} = 4.3 \text{ mg} \cdot L^{-1}$ $LC_{50} = 4.3 \text{ mg} \cdot L^{-1}$

 $LC_{50} = 43 \text{ mg} \cdot L^{-1}$

Comments 1

No effect on

Reference

Monsanto Company, 1982a

Monsanto Company, 1982a,

 $(17-29 \text{ mg} \cdot \text{L}^{-1})$ 21.1°C Linden et al., 1979

Exposure

Time

96 h

48 h

48 h

24 h

96 h

24 h

U, S

U, S

U., S

Table A-1. Continued

| Organism | Chemical or Formulation | Exposure Time | Test Conditions | Effects | ${\tt Comments}^1$ | Reference |
|---|----------------------------|------------------|--------------------|--|--|---|
| Bluegill (Lepomis macrochirus) | RoundupR | 24 h 96 h | U, S U, S | LC ₅₀ = 6.4 mg·L ⁻¹ LC ₅₀ = 5.0 mg·L ⁻¹ | (4.8-8.6 mg·L ⁻¹) 22°C (3.8-6.6 mg·L ⁻¹) 22°C | |
| Bluegill (Lepomis macrochirus) | Roundup ^R | 96 h | NR · | $LC_{50} = 14 \text{ mg} \cdot L^{-1}$ | | Monsanto Company, 1982 |
| Carp (Cyprinus carpio) | Roundup ^R | 96 h | NR | $LC_{50} = 3.9 \text{ mg} \cdot L^{-1}$ | | |
| Rainbow trout (<u>Salmo gairdneri</u>) | Roundup ^R | 96 h | NR | $LC_{50} = 11 \text{ mg} \cdot L^{-1}$ | | |
| Channel catfish (<u>Ictalurus punctatus</u>) | Roundup ^R | 96 h | NR | $LC_{50} = 16 \text{ mg} \cdot L^{-1}$ | | |
| Fathead minnow (<u>Pimephales promelas</u>) | Roundup ^R | 96 h | NR | $LC_{50} = 9.4 \text{ mg} \cdot L^{-1}$ | | |
| Rainbow trout (<u>Salmo gairdneri</u>) | Roundup ^R | 96 h | NR | $LC_{50} = 48 \text{ mg} \cdot L^{-1}$ | | U.S. Department of Agriculture, 1981 |
| Bluegill (<u>Lepomis</u> macrochirus) | Roundup ^R | 96 h | NR | $LC_{50} = 24 \text{ mg} \cdot L^{-1}$ | | |
| Rainbow trout (<u>Salmo gairdneri</u>) | Roundup ^R | 96 h | Մ, Տ Մ, Տ | $LC_{50} = 54.8 \text{ mg}$ $LC_{50} = 52.0 \text{ mg} \cdot L^{-1}$ | 12°C (Field test) 11°C | Hildebrand et al., 198 |
| Rainbow trout (Salmo gairdneri) | Glyphosate | 24 h 96 h | Մ, Տ Մ, Տ | $LC_{50} = 140 \text{ mg} \cdot L^{-1}$ $LC_{50} = 140 \text{ mg} \cdot L^{-1}$ | $(120-170 \text{ mg} \cdot \text{L}^{-1}) 12^{\circ}\text{C}$ $(120-170 \text{ mg} \cdot \text{L}^{-1}) 12^{\circ}\text{C}$ | Folmar et al., 1979 |
| fathead minnow Pimephales promelas) | Glyphosate | 24 h 96 h | u, s u, s | $LC_{50} = 97 \text{ mg} \cdot L^{-1}$ $LC_{50} = 97 \text{ mg} \cdot L^{-1}$ | $(79-120 \text{ mg} \cdot \text{L}^{-1}) 22^{\circ}\text{C}$ $(79-120 \text{ mg} \cdot \text{L}^{-1}) 22^{\circ}\text{C}$ | |
| Channel catfish Ictalurus punctatus) | Glyphosate | 24 h 96 h | U, S U, S | $LC_{50} = 130 \text{ mg} \cdot L^{-1}$ $LC_{50} = 130 \text{ mg} \cdot L^{-1}$ | $(110-160 \text{ mg} \cdot \text{L}^{-1})$ 22°C $(110-160 \text{ mg} \cdot \text{L}^{-1})$ 22°C | |
| Bluegill (Lepomis macrochirus) | Glyphosate | 24 h 96 h | ប, s ប, s | $LC_{50} = 150 \text{ mg} \cdot L^{-1}$ $LC_{50} = 150 \text{ mg} \cdot L^{-1}$ | $(120-190 \text{ mg} \cdot \text{L}^{-1}) 22^{\circ}\text{C}$ $(120-190 \text{ mg} \cdot \text{L}^{-1}) 22^{\circ}\text{C}$ | |
| dainbow trout Salmo gairdneri) fry) | Glyphosate Technical | 96 h | NR | LC ₅₀ = 50 mg·L ⁻¹ | 3 lb. ai/gal. | Folmar, 1976 |

Table A-1. Continued

| Organism | Chemical or Formulation | Exposure Time | Test Conditions | Effects | Comments 1 | Reference |
|---|--------------------------|-------------------|--------------------|---|--|---|
| Bleak (Alburnus alburnus) | Glyphosate, Technical | 96 h | U, S | LC ₅₀ = 16 mg·L ⁻¹ | (15-18 mg·L ⁻¹) 22°C | Linden et al., 1979 |
| Rainbow trout (Salmo gairdneri) | Glyphosate Technical | 96 h | NR | $LC_{50} = 38 \text{ mg} \cdot L^{-1}$ | | U.S. Department of Agriculture, 1981 |
| Bluegill (<u>Lepomis</u> <u>macrochirus</u>) | Glyphosate, Technical | 96 h | NR | LC ₅₀ = 78 mg·L ⁻¹ | | |
| Bluegill (<u>Lepomis</u> <u>macrochirus</u>) | Glyphosate, Technical | 96 h | NR | $LC_{50} = 24 \text{ mg} \cdot L^{-1}$ | | |
| Bluegill (Lepomis macrochirus) | Glyphosate, Technical | 96 h | NR | $LC_{50} = 120 \text{ mg} \cdot L^{-1}$ | | Monsanto Company, 1982a |
| Bluegill (Lepomis macrochirus) | Roundup ^R | 96 h | u, s | $LC_{50} = 5.6 \text{ mg} \cdot L^{-1}$ | (4.2-7.5 mg·L ⁻¹) 22°C | Johnson and Finley, 198 |
| Trout (Species unknown) | Glyphosate, Technical | 96 h | NR | $LC_{50} = :86 \text{ mg} \cdot L^{-1}$ | | Monsanto Company, 1982s |
| Carp (Cyprinus carpio) | Glyphosate, Technical | 96 h | NR | $LC_{50} = 115 \text{ mg} \cdot L^{-1}$ | | |
| Harlequin fish (Rasbora heteromorpha) | Glyphosate, Technical | 96 h | NR | $LC_{50} = 168 \text{ mg} \cdot L^{-1}$ | | |
| Carp (Cyprinus carpio) | Glyphosate, Technical | 96 h | NR | $LC_{50} = 119 \text{ mg} \cdot L^{-1}$ $LC_{1} = 96.7 \text{ mg} \cdot L^{-1}$ $LC_{99} = 146 \text{ mg} \cdot L^{-1}$ | | U.S. Department of Agriculture, 1981 |
| Carp (Cyprinus carpio) | Glyphosate, Technical | 96 [:] h | NR | $LC_{50} = 115 \text{ mg} \cdot L^{-1}$ $LC_{1} = 105 \text{ mg} \cdot L^{-1}$ $LC_{99} = 125 \text{ mg} \cdot L^{-1}$ | | |
| Rainbow trout (Salmo gairdneri) (fry) | Roundup ^R | 96 h | M, S | $LC_{50} = 28.0 \text{ mg} \cdot L^{-1}$ $LC_{50} = 25.5 \text{ mg} \cdot L^{-1}$ | рн <6.3, 15°C ³ рн <6.3, 14.5°C ³ | Servizi et al., 1987 |
| Coho salmon (Oncorhynchus kisutch) (fry) | Roundup ^R | 96 h | M, S | LC ₅₀ = 42.0 mg·L ⁻¹ | pH <6.3, 15°C ³ | |

| Organism | Chemical or Formulation | Exposure Time | Test Conditions | Effects | Comments ¹ | Reference |
|---|--------------------------|------------------|--------------------|--|--|-----------------------|
| Sockey salmon (Oncorhynchus nerka) (Ery) | Roundup ^R | 96 h | M, S | LC ₅₀ = 28.8 mg·L ⁻¹ | pH = 7.7, 4.5°C | |
| (fingerlings) | Roundup ^R | 96 h | M, S | $LC_{50} = 26.7 \text{ mg} \cdot L^{-1}$ $LC_{50} = 27.7 \text{ mg} \cdot L^{-1}$ | рн = 7.95, 4.2°C рн = 8.00, 4.2°C | |
| Rainbow trout (Salmo gairdneri) | Roundup ^R | 96 h: | M, S | LC ₅₀ = 26 mg·L ⁻¹ | (12-38 mg·L ⁻¹), 10-12°C, pH = 6.1, Hard = 4.5 mg·L ⁻¹ , Cond = 12 μ mhos·cm ⁻¹ | Mitchell et al., 1987 |
| | Roundup ^R | 96 h | M, S | $LC_{50} = 22 \text{ mg} \cdot L^{-1}$ | (12-38 mg·L ⁻¹), 10-12°C, pH = 7.6, Hard = 85 mg·L ⁻¹ , Cond = 132 μ mhos·cm ⁻¹ | |
| | Roundup ^R | 96 h | M, S | LC ₅₀ = 15 mg·L ⁻¹ | (12-38 mg·L ⁻¹), 10-12°C, ph = 7.7, Hard = 81 mg·L ⁻¹ , Cond = 132 μ mhos·cm ⁻¹ | |
| | Glyphosate (IPA salt) | 96 h | M, ·s | LC ₅₀ = 12 mg·L ⁻¹ | $(5.7-18 \text{ mg} \cdot \text{L}^{-1})$, $10-12^{\circ}\text{C}$, pH = 6.1 , Hard = $4.5 \text{ mg} \cdot \text{L}^{-1}$, $\text{Cond} = 12 \ \mu\text{mhos} \cdot \text{cm}^{-1}$ | |
| | Glyphosate (IPA salt) | 96 h | M, S | $LC_{50} = 11 \text{ mg} \cdot L^{-1}$ | (5.7-18 mg·L ⁻¹), 10-12°C, pH = 7.6, Hard = 85 mg·L ⁻¹ , Cond = 132 μmhos·cm ⁻¹ | |
| | Glyphosate (IPA salt) | 96 h. | M, S | $LC_{50} = 7.4 \text{ mg} \cdot L^{-1}$ | (5.7-10 mg·L ⁻¹), 10-12°C, pH = 7.7, Hard = 81 mg·L ⁻¹ , Cond = 132 \(\nu\)mhos·cm ⁻¹ | |
| Chinook salmon (Oncorhynchus tshawytscha) | Roundup ^R | 96 h | M, S | LC ₅₀ = 20 mg·L ⁻¹ | (17-27 mg·L ⁻¹), 10-12°C, pH = 6.1, Hard = 4.5 mg·L ⁻¹ , Cond = 12 μ mhos·cm ⁻¹ | |
| | Glyphosate (IPA salt) | 96 h | M, s | LC ₅₀ = 9.6 mg·L ⁻¹ | (7.9-13 mg·L ⁻¹), 10-12°C, pH = 6.1, Hard = 4.5 mg·L ⁻¹ , Cond = 12 \(\nu\)mhos·cm ⁻¹ | |



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