Bull. Environ. Contam. Toxicol. (1994) 53:543–547


Environmental Contamination and Toxicology

# Residues of Glyphosate and Its Principle Metabolite in Certain Cereals, Oilseeds, and Pulses Grown in Canada, 1990–1992

Y. Y. Wigfield, F. Deneault, J. Fillion

Laboratory Services Division, Food Production and Inspection Branch, Agriculture Canada, Ottawa, Ontario, K1A 0C6, Canada

Received: 8 September 1993/Accepted: 1 March 1994

Glyphosate, sold under the trade names of Roundup$^R$ (for ground application) and Vision$^R$ (for forestry use), is a non-selective herbicide which is absorbed through the leaves and translocated throughout the whole plant. The herbicide, when applied close to harvest for late season weed control and possible harvest management benefits, can result in the presence of residues throughout the whole plant including the seed coat. In Canada, glyphosate is registered for pre-plant and post-harvest uses and until June 1991, it was not registered for direct application on crops. Diquat, a fast acting herbicide, is registered for desiccation of canola, mustard, field peas, flax, soybeans, and lentils. While diquat is effective as desiccant, it is not particularly effective in controlling perennial weeds and it is not registered for use on cereals. In June 1991, a temporary registration was granted for pre-harvest application on flax for control of quackgrass, season-long control of Canada thistle and perennial sow thistle and harvest management by drying down the crops. In June 1992, the same registration was granted for application on certain cereals (wheat and barley), oilseeds (canola/rapeseeds and soybeans) and pulses (peas and lentils), and in June, 1993 it was granted for malting barley. The pre-harvest use may also provide soil conservation benefits by reducing the use of cultivation as a means of weed control. The maximum residue limit (MRL) (Doliner and Stewart, 1991a) when crops are treated with the proposed label directions (single application at the rate of 0.89 kg/ha glyphosate and the time of 7-14 days before harvest) are shown in Table 1. Registration for use on beans has not been granted due to insufficient residue data.

However, because glyphosate is effective as herbicide and provides harvest management benefits, in 1990 questions were raised from Agriculture Canada field inspection staff regarding the potential misuse of the herbicide which at that time was not registered for pre-harvest use on crops. Thus a post-harvest survey was conducted to monitor glyphosate residues in these cereals, oilseeds and pulses grown during 1990-1992 period to check if the registration uses of glyphosate were being followed. This paper presents the 3-year monitoring results comprising 459 samples of 8 different crops grown in 7 different provinces in Canada.

*Correspondence to:* Y. Y. Wigfield

**Table 1. Maximum Residue Limits (MRLs)[a] of glyphosate for Pre-harvest Application on Crops**

| Crop | MRL (ppm) |
|---|---|
| Wheat[b] | 5 |
| Barley | 10 |
| Wheat & barley milling fractions excluding flour | 15 |
| Soybean | 6 |
| Soybean oil | <0.1[c] |
| Pea | 5 |
| Lentil | 4 |
| Rapeseed (canola) | --[d] |
| Rapeseed (canola) oil | <0.1[e] |
| Flax[f] | 1.0 |

[a]Residues falling within these MRLs are not considered to pose a health hazard to consumers. [b]Including flour. [c]This level will not be listed but may be covered by the proposed 6 ppm MRL on soybeans. [d]No MRL for rapeseed needed because the whole seed is not consumed as such in significant quantities as a food; residues up to 5 ppm in whole seed may result from the proposed use. [e]This level will be covered under general regulation (Anonymous, 1992). [f]Including flax oil.

## MATERIALS AND METHOD

During the fall of 1990, the survey was conducted on 180 samples of wheat, barley or lentils grown in randomly selected farms in the Provinces of Alberta, Manitoba and Saskatchewan. The next year, the program was extended to include the Province of Ontario and Atlantic Region (mainly, the Provinces of New Brunswick and Prince Edward Island) and 152 samples of oilseeds (canola/rapeseeds and soybeans) and pulses (peas and white beans) were obtained. In the third year, since temporary registration was not granted for application on beans, it was directed to 27 samples of white beans grown in randomly selected farms in the Province of Ontario only.

A random sample was obtained from each farm. The samples (500 g) in cotton bags were shipped to the Pesticide Laboratory in Ottawa and, on arrival, were mixed thoroughly and ground up with a Hobart food chopper (Robot Coupe, Jackson, MS) and stored in 500-mL glass bottles at -18 $^0$C until analysis. The remainings of the samples were discarded.

The method of extraction, cleanup and analysis of samples for the residues of glyphosate and its major metabolite, (aminomethyl)phosphonic acid (AMPA) was as previously described (Wigfield and Lanouette, 1991). Briefly, it involved adding water (150 mL) and chloroform (50 mL) to the ground sample (6 g for all crops, 12 g for wheat) in a polypropylene centrifuge bottle (250-mL size) and shaking the mixture for 30 min using a horizontal shaker followed by centrifuging at 9000 rpm at 4 $^0$C for 30 min. The aqueous layer was decanted through glass wool into a 250 mL graduate cylinder and made to volume with rinses. An aliquot (125 mL) was transferred to a second centrifuge bottle to which HCl (1.5 mL, 0.5 M) and chloroform (50 mL) were added. The mixture was shaken for 15 min and centrifuged at 9000 rpm at 4 $^0$C for 30 min. The aqueous layer was filtered through glass wool and the filtrate was transferred quantitatively to a cation exchange column (disposable 75-mL size column reservoir from Baker, Toronto, ON or Analytichem, Harbor City, CA) packed with AG50W-X8 in hydrogen form (4 cm, analytical grade, 100-200 mesh from Bio-Rad, Richmond, CA) in between 2 layers of sand (2 cm each). The column was eluted with aqueous rinses (3 x 50 mL) and then water (50 mL). Sodium hydroxide solution (600 $\mu$L, 3 M) was added to the combined eluates (300 mL, pH 2) to change pH to 7-10. The basic solution was transferred to an anion exchange column (20-mL size Econo-Pac polypropylene column with a fritted end from Bio-Rad) packed with AG1-X8 in hydroxide form (6 mL, biotechnology grade, 100-200 mesh from Bio-Rad) under slight vacuum using Vac Elute SPS 24. The column was eluted under the same vacuum with aqueous rinses (3 x 100 mL) of the container and water (20 mL) and then vacuumed to dryness. All eluates were discarded and the column was eluted by gravity with HCl solution (40 mL, 0.3 M). The HCl eluate was collected and rotary evaporated to 1 mL at 40-60 $^0$C. The concentrated extract and the rinses were transferred to a volumetric flask (10-mL size) and diluted to volume with water. An aliquot of this solution was filtered through a syringeless filter (0.45-$\mu$m pore size) and injected (100 $\mu$L) into a liquid chromatograph (LC) equipped with a postcolumn fluorescence detector. Two postcolumn LC pumps were used, one to deliver the oxidizing solution (calcium hypochlorite) at 0.2 mL/min and another to deliver fluorogenic solution (o-phthalaldehyde and 2-mercaptoethanol) at 0.4 mL/min. The LC guard column and analytical columns (two 100-mm columns connected in series) and mobile phase were the same as described by Thompson et al. (1989).

Using the described method, the limits of detection (LODs), defined as 3 $\times$ the standard deviation (SD), and the limits of quantitation (LOQs), defined as 10 $\times$ SD, obtained from 0.54 ppm (0.27 ppm for wheat samples) fortification level are shown in Table 2 (Wigfield and Lanouette, 1991). The samples were processed as a set of 6 which consisted of 5 samples from the field and 1 fortified (at 0.5, 1.0 and 5.0 ppm in barley, lentil and wheat and 1.0 ppm in all other crops) sample which was a field sample previously analyzed and found to contain below the LODs of both analytes. The ranges of recovery of glyphosate and AMPA from these samples are shown in Table 2. Samples found to contain higher than LOQs of glyphosate and AMPA were confirmed by retention time comparison

with the standard solution. The presence of glyphosate residues was further confirmed by the absence of its LC peak when the oxidizing reagent was not added to the postcolumn LC run.

**Table 2. Limits of detection (LODs), limits of quantitation (LOQs) and recoveries of glyphosate and AMPA in cereals, oilseeds and pulses.**

| Crop | Glyphosate (ppm) | | | AMPA (ppm) | | |
|---|---|---|---|---|---|---|
| | LOD (ppm) | LOQ (ppm) | Rec'y (%) | LOD (ppm) | LOQ (ppm) | Rec'y (%) |
| Barley | 0.09 | 0.26 | 79-99 | 0.12 | 0.37 | 78-92 |
| Canola | 0.12 | 0.36 | 85-101 | 0.11 | 0.33 | 72-106 |
| Dry pea | 0.11 | 0.33 | 109 | 0.11 | 0.33 | 84 |
| Lentil | 0.08 | 0.24 | 73-102 | 0.10 | 0.29 | 76-125 |
| Soybean | 0.08 | 0.23 | 92-116 | 0.08 | 0.23 | 69-81 |
| White bean | 0.07 | 0.21 | 87-123 | 0.07 | 0.20 | 67-92 |
| Wheat | 0.11 | 0.32 | 73-92 | 0.05 | 0.16 | 71-91 |

Rec'y = Recovery

## RESULTS AND DISCUSSION

Field trial residue data provided by the applicant, Monsanto, (Doliner & Stewart, 1991b) clearly showed the presence of high levels of glyphosate in most samples of all grains harvested from treated plots with a minimum of 0.5-3.6 ppm and a maximum of 1.9-14.6 ppm depending on the timing of samples collected for a given crop. AMPA was detected at relatively low levels in some samples of wheat, barley, canola and soybeans but was undetected in samples of lentils and peas. Thus the absence of glyphosate residues suggested that it was not applied on these crops before harvest. At the time of analysis, because glyphosate was not registered for pre-harvest use on crops under the Food and Drug Regulations (Anonymous, 1992) residue should be below 0.1 ppm. The monitoring results of glyphosate residues in 459 samples of cereals, oilseeds and pulses shown in Table 3 indicate that during the period of 1990-1992, the compliance rate of farmers abiding with the registration use of glyphosate on most crops was in the range of 92-100% except on pea, it was 80%. However, the number of pea samples analyzed was not sufficiently large to be representative.

One sample of white beans was found to contain 15.9 ppm glyphosate. This level is indicative that glyphosate has been applied on this crop grown in this particular

farm. Since glyphosate has not been registered for pre-harvest use on beans, 10 samples of white beans are scheduled to be analyzed in 1993.

**Table 3. Monitoring results of 1990-1992 glyphosate analyses**

| Year | Crop | Total no. of samples analyzed | Total no. of samples detected | Glyphosate[a] | |
|---|---|---|---|---|---|
| | | | | Range | Average |
| 1990 | Wheat | 76 | 1 | 4.3 | 4.3 |
| | Barley | 55 | 1 | 4.7 | 4.7 |
| | Lentil | 49 | 4[b] | 0.9-13.1 | 5.2 |
| 1991 | Canola | 79 | --[c] | -- | -- |
| | Pea | 5 | 1 | 0.7 | 0.7 |
| | Soybean | 19 | -- | -- | -- |
| | Rapeseed | 14 | -- | -- | -- |
| | White bean | 35 | -- | -- | -- |
| 1992 | White bean | 27 | 1 | 15.9 | 15.9 |

[a]AMPA was below limit of detection in all but one sample (see note b). [b]One sample contained 5.92 ppm glyphosate and 0.4 ppm AMPA. [c]-- none.

## REFERENCES


Anonymous (September 1992) Food and Drug Act and Regulations B15.002(1). Food Directorate, Health and Welfare Canada, Ottawa, Canada, K1A 0L2.

Doliner, LH, Stewart, M (November 1991a) Discussion document: preharvest use of glyphosate herbicide, Canada **D91-01**, P. 65, Pesticide Directorate, Agriculture Canada, Ottawa, Canada, K1A 0C6.

Doliner, LH, Stewart, M (November 1991b) ibid P. 38.

Thompson, DG, Cowell, JE, Daniels, RJ, Staznik, B, MacDonald, LM (1989) An alternative method for the determination of glyphosate and AMPA residues in organic and mineral soils, stream sediments and hardwood foliage. J Assoc Off Anal Chem **72**: 355-360

Wigfield, YY, Lanouette, M (1991) Residue analysis of glyphosate and its principle metabolite in certain cereals, oilseeds and pulses by liquid chromatography and postcolumn fluorescence detection. J Assoc Off Anal Chem **74**: 842-847