



GLYPHOSATE IN TARGETED FOODS

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Barbara Thomson

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GLYPHOSATE IN TARGETED FOODS

Dr Fiona Thomson-Carter
Acting Food Safety Programme Manager

Barbara Thomson
Project Leader

Peter Cressey
Peer Reviewer

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SUMMARY

Glyphosate, commonly known as Roundup, is a systemic herbicide and will reach potato tubers if used preharvest, so it is possible that residues may remain at harvest. The purpose of the project was to ascertain whether glyphosate is being used on potatoes for preharvest weed control or as a desiccant to enhance the drying off of leafy tops before harvest, in a manner inconsistent with its conditions of registration.

A total of 56 samples were purchased in November 2003 and March 2004 from the main potato growing regions in New Zealand, namely, Pukekohe (28), Manawatu (18) and Canterbury (10). Aqueous potato extracts were derivatised and analysed by gas chromatography with mass selective detection. Recovery of glyphosate and the breakdown product aminomethylphosphonic acid (AMPA) from samples spiked at 0.05 mg/kg ranged from 43-169% and 26-165% respectively.

None of the 56 samples analysed were found to contain glyphosate or AMPA above the level of quantitation (0.05 mg/kg).

There is no evidence from this survey of off label, preharvest use of glyphosate on New Zealand grown potatoes.

1 INTRODUCTION

Glyphosate (Figure 1), commonly known as Roundup, is a broad-spectrum post emergence herbicide used for the control of broad-leafed weeds and grasses. It readily translocates from treated foliage to other parts of the plant. Residues from treated weeds passing into the soil are not taken up by other plants. Potato tubers have been found not to take up glyphosate from treated soil but to absorb very small amounts of the major breakdown product aminomethylphosphonic acid (AMPA). (FAO/WHO, 1986). Glyphosate acts by binding to and inhibiting the enzyme 5-enolpyruvoyl-shikimate-3-phosphate synthase (EPSPS), in this way preventing the plant from producing the aromatic amino acids essential for protein synthesis and growth. EPSPS is present in all plants, bacteria and fungi, but not in animals. (FAO/WHO, 1997).

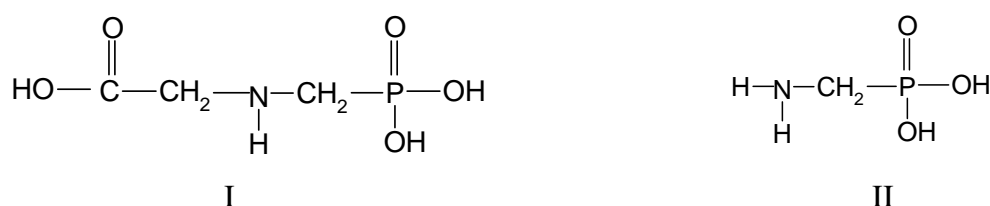


Figure 1: Glyphosate (I) and breakdown product, aminomethylphosphonic acid (AMPA) (II)

Glyphosate is chemically stable in water and is not subject to photochemical degradation. Glyphosate is metabolised very little by plants, the major metabolite, AMPA, is produced mainly by bacteria. A second degradation route via splitting of the C-P bond can also occur.

Glyphosate may be used to spray weeds prior to planting of commercial crops (pre-planting) or for in-crop spot treatment using recirculating sprayers, shielded applicators or wiper applicators. Glyphosate is used in some countries for pre-harvest application to commercial crops (cereals and ilseeds) for the purpose of pre-harvest weed control (FAO/WHO, 1986). Glyphosate is registered for many uses in New Zealand, including use as a desiccant. It is registered for preharvest use on cereals but not for preharvest use on potatoes where it may conceivably be used either for weed control or to enhance drying off of leafy tops to facilitate harvesting. Glyphosate is systemic and will reach potato tubers if used preharvest on potato top growth, so it is possible that residues may remain at harvest.

“Off-label” use is only permitted in New Zealand under the ACVM Act 1997 if residues meet the New Zealand domestic MRLs. Since no MRLs have been set for potatoes, the default MRL of 0.1 mg/kg for residues in primary plant products applies.

Glyphosate has not been included in the list of pesticides screened for in New Zealand Total Diet Surveys (1997/98 and 2003/04) because it is not amendable to the multi-residue, dithiocarbamate and acid herbicide methodologies used by those surveys (Cressey *et al.*, 2000, Vannoort 2003). The analysis of glyphosate requires a specialised analytical method.

1.2 Project Aim

The purpose of the project was to ascertain whether glyphosate is being used in potatoes in a manner inconsistent with its conditions of registration (off label).

2 MATERIALS AND METHODS

2.1 Sampling

Since glyphosate usage is a grower choice, the sampling plan incorporated samples from as many growers as possible.

The main growing regions of potatoes for the New Zealand domestic market, in decreasing order of production, are Pukekohe, Manawatu then Canterbury (Ron Gall, VegFed, personal communication, July 2003). Therefore samples were purchased from these three regions in a 3:2:1 ratio.

Based on seed potato demand and retail outlet enquiries, popular potato varieties include Rua, Ilam Hardy, Nadine, Desiree, Vanrosa, Chippawa, Maris Anchor, Red Rascal, Rocket and Desiree. So as to reduce the variation due to potato variety, and for consistency with the Multi Residue Survey, it was planned to limit potato varieties to Rua, Ilam Hardy and Nadine.

Potatoes are grown year round but because climatic conditions change with season it is possible that herbicide management practices might differ with season. Sampling at different times has two benefits. Firstly, there is the opportunity of detecting seasonal usage of glyphosate and secondly, there is the opportunity of selecting different potatoes from the same grower to provide information on frequency of use by a grower.

With consideration of these factors, the following sampling plan was followed.

Table 1: Sampling plan for glyphosate in potatoes

	Pukekohe	Manawatu	Canterbury
Sites/growers	7	6	5
Seasons	2	2	2
Varieties collected	2	2	2
Total to be analysed (56)	28	18	10

Samples were purchased in November 2003 (Season 1) and March 2004 (Season 2) by Health Protection Officers and sent to Christchurch for analysis.

A total of 56 samples were analysed giving a 95% probability of detecting glyphosate if 6% of all potatoes contain glyphosate (Codex, 1999).

2.2 Analytical Methods

Glyphosate analysis:

The polar and non-volatile properties of glyphosate that contribute to its effectiveness as a herbicide mean that the determination of its residues, and those of the breakdown product (AMPA) is difficult. There are no reports in the open literature of glyphosate residues in potatoes. The analysis used for potato samples in the current survey was a simplification of methodology published by Alferness and Wiebe (2001) for the analysis of glyphosate and AMPA in corn grain, soya forage and walnut nutmeal.

Aqueous potato extracts were derivatised by direct addition of an aqueous extract into a mixture of heptafluorobutanol and trifluoroacetic anhydride. The derivatised analytes were then quantitated by capillary gas chromatography with mass selective detection in single ion monitoring mode on the following ions: glyphosate $m/z = 611,584,460$; AMPA $m/z = 372,446,502$. Neither solvent extraction nor cation exchange cleanup was used. Standards were linear over the concentration range 0-0.225 mg/kg. This methodology allowed quantitation of glyphosate in potatoes to 0.05 mg/kg that is below the MRL (0.1mg/kg).

Quality assurance:

A duplicate of each sample was spiked with glyphosate and AMPA at 0.05 mg/kg. This confirmed that there were no sample specific factors that would prevent detection of the target compounds at this concentration

3 RESULTS AND DISCUSSION

The varieties of potato sampled were restricted by availability. Actual samples achieved from the three regions are shown in Table 2.

Table 2: Potato varieties sampled and analysed.

Variety	Auckland		Manawatu		Canterbury	
	Season 1	Season 2	Season 1	Season 2	Season 1	Season 2
Rua	4	0	5	0	1	0
Ilam Hardy	2	0	5	2	2	0
Nadine	3	4	2	4	1	2
Other	3	8	0	0	1	3
Not specified	2	2	0	0	0	0
Total	14	14	12	6	5	5

The ranges for the recovery of glyphosate and AMPA from spiked potato samples are shown in Table 3.

Table 3: Range of recoveries of glyphosate and AMPA from spiked potatoes (%).

	Glyphosate	AMPA
Season 1 (n=28)	43-169%	26-138%
Season 2 (n=28)	57-165%	57-165%

None of the fifty six samples analysed was found to contain glyphosate or AMPA, with the exception of one sample that may have contained a trace amount of AMPA. However, this was below the level of quantitation (0.05 mg/kg) and may be indicative of herbicide drift (Duke et al., 2003).

There is no evidence from this survey that glyphosate is being used for preharvest weed control or dessication of potato crops in New Zealand.

4 REFERENCES

Alferness P, & Wiebe L. (2001) Determination of glyphosate and aminophosphonic acid in crops by capillary gas chromatography with mass-selective detection: collaborative study, *Journal of AOAC International*; 84(3):823-846.

Codex (1999) Report of the thirty-first session of the Codex Committee on Pesticide Residues, The Hague, 12-17 April, Alinorm 99/24A.

Cressey P, Vannoort R, Silvers K and Thomson. (2000) 1997/98 New Zealand Total Diet Survey. Part 1: Pesticide residues. Wellington:Ministry of Health. Available at:<http://www.moh.govt.nz>

Duke SO, Rimando AM, Pace PF, Reddy KN, Smeda RJ. (2003) Isoflavone, glyphosate, and aminomethylphosphonic acid levels in seeds of glyphosate-treated, glyphosate-resistant soybean. *Journal of Agricultural Chemistry*; 51: 340-344.

FAO/WHO (1986) Pesticide residues in food-1986. Evaluations 1986, Part 1-Residues. Joint meeting of the FAO Panel of Experts on Pesticide Residues in Food and the Environment and the WHO Expert Group on Pesticide Residues, Rome, 29 September-8 October 1986. FAO Plant Production and Protection paper 78/1. Rome: Food and Agriculture Organization of the United Nations.

FAO/WHO (1997) Pesticide residues in food-evaluations 1997. Part II- Toxicology. Joint meeting of the FAO Panel of Experts on Pesticide Residues in Food and the Environment and the WHO Core Assessment Group, Lyon, 22 September – 1 October 1997. WHO/PCS/98.6. Geneva: WHO.

Vannoort R. (2003) 2003/04 Total Diet Survey. Procedures Manual. ESR Client Report FW03/47. Christchurch: ESR Ltd.