PESTICIDES : RESIDUES AND REGULATIONS

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Summary

The means by which national and international agencies establish pesticide residue tolerances on food are described. Pesticide regulations are an important aspect of the export of New Zealand horticultural crops, many of which are not widely grown in importing countries. This leads to problems in getting tolerances set for the pesticides needed to provide the high degree of pest and disease control demanded. Methods of residue analysis are described together with their application to research programmes into pesticide efficacy, spray programmes, tolerance levels and general monitoring. Factors influencing residue levels include application rate and method, type of fruit and persistence of the pesticide.

INTRODUCTION

As a seller of horticultural products to over 50 countries, New Zealand must meet the buyer's requirements, which call for pest and disease-free food. This involves the use by growers of pesticides which inevitably leave residues on the crop, the levels of which are also subject to regulation by importing countries.

A residue limit or tolerance is defined as the maximum amount of a pesticide chemical that should not be exceeded in or on food at a specific stage of food production, processing or marketing. The establishment of a tolerance for a pesticide involves evaluation of the mammalian toxicology and the field behaviour on various crops. Each country has its own procedures, but in recent years there has been a move to the setting of international standards.

In 1961, a meeting of both WHO and FAO experts decided to evaluate the possible hazards to man arising from the occurrence of pesticides in food. The WHO Expert Committee on Pesticide Residues examines the detailed toxicology of pesticides. The FAO Working Group of Experts on Pesticide Residues examines the levels and types of residues on agricultural produce. Since 1966, joint meetings of these two groups have been held to establish scientific recommendations for residue tolerances. These recommendations form a basis for inter-governmental action.

Codex Alimentarius Commission

Under the Joint FAO/WHO Food Standards Programme, the Codex Alimentarius Commission was established in 1963 to promote co-ordination of all food standards work undertaken by international governmental and non-governmental organisations and to publish a set of accepted standards in a Codex Alimentarius. In 1966, a specialist committee, the Codex Committee on Pesticide Residues was established and meets annually under the chairmanship of the Netherlands Government. The aims of this inter-governmental committee are to establish priorities for the determination of international tolerances and to consider recommendations for tolerances. It also provides a forum where member governments may discuss matters of public health concern and difficulties in international trade in foodstuffs resulting from the presence of chemical residues. Many recommendations for Codex tolerances have either been accepted or are being considered by member governments. New Zealand actively supports the setting of international tolerances and we have sent delegates to all 12 meetings.

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The setting of tolerance levels

The procedures used to set tolerance levels are basically similar whether by national or international body. The detailed toxicology of the pesticide is first assessed using the following types of information. For a new pesticide these are generally supplied by the manufacturer.

Acute toxicity, short term tests, mutagenicity, carcinogenicity, reproduction, teratogenicity, biochemical aspects, metabolism, long term studies and observations in man.

From this data, an acceptable daily intake (ADI) is established for man. The ADI is defined as the amount of chemical that might be ingested daily, even over a lifetime, without appreciable risk to the consumer. The figure is expressed in milligrams per kilogram of bodyweight and contains a large safety factor over the toxicological no-effect levels. However, the ADI is not an absolute guarantee of safety as the experts' decision can only be made on the basis of the information available at the time. The plant metabolites of the pesticide are included in its ADI as long as they are similar to those formed in animals. Where they are different, a separate ADI for the metabolite has to be established. Some examples of an ADI are azinphos-methyl 0.0025, captan 0.1 and aldrin 0.0001 mg/kg (FAO/WHO, 1973).

To produce a tolerance, the ADI is then combined with data relating to the crop itself of the following type:

Use of pattern of the pesticide (good agricultural practise); Consumption pattern of the crop (proportion of diet); Residue levels in supervised trials; Fate of residues in animals and plants; Methods of residue analysis; National legal tolerances.

Data for this phase of the procedure is again generally provided by the manufacturer but governmental agencies and pesticide distributors often contribute also. The WHO/FAO joint meeting has a policy that no tolerance will be recommended until an ADI has been established.

National tolerance levels

Most countries set their own levels of pesticide residues in food but in some cases are now adapting these levels to meet the Codex proposals. Some countries specify limits under the broad groupings of fruit and vegetables, while others have limits established for specified fruits and vegetables. The Ministry of Agriculture and Fisheries (MAF) has an up to date list of tolerances applicable in the countries to which we sell the major part of our exports. Table 1 lists the current tolerances established for kiwifruit in several countries.

TABLE 1: Tolerance levels (mg/kg) for pesticides on kiwifruit

Country	diazinon	carbaryl	phosmet	azinphos-methyl	captan
Australia	0.03*	1*	1.5*	0.05*	-
Belgium	0.5	1.2	10†	0.4	15
Canada	0.1*	-	1.0*	0.4*	-
France	-	1.2	10	0.4	15
Germany	0.3	1.2	15‡	0.4	15
Japan	C	C	C	N	C
Netherlands	0.5	3	10	0.4	15
Sweden	0.5	10	10	0.4	15
U.S.A.	0.75	-	25	10	-
* edible portion	‡ agreed		C	cleared	
† applied for	N not cleared		-	no level set	

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Pesticide residue analysis

It is apparent that both the setting of tolerances and their enforcement are very dependent upon the results of chemical analysis. Residue analysis is also a useful tool to assist in determining the efficacy of pesticides and in designing spray programmes to minimise residues. The objectives of such analytical programmes within MAF include:

1. Efficacy testing - lifetime of activity, spray distribution;
2. Setting residue tolerances
 - a) decay curves - persistence after single spray;
 - b) spray programmes - multiple sprays under grower conditions;
 - c) terminal residues - metabolites, effects of processing and storage.
3. Monitoring farm output.
Survey of residues on fruit at harvest from export orchards (kiwifruit, apples, boysenberries).

Methods of residue analysis

This is a complex field of analytical chemistry due to the diversity of pesticides involved. There are over 300 chemicals registered for agricultural use in New Zealand and the list is constantly expanding. Normal orchard spray practice results in residues in the 0.1 to 20 milligram per kilogram range and analytical methods must be sensitive enough to measure these low levels. Most pesticides are organic compounds (based on a carbon skeleton) and the following schema gives an outline of the procedures that are normally used to measure their residues:

1. Subdivision of the crop sample to obtain a representative portion (20 - 250 g) for analysis;
2. Maceration and exhaustive extraction with organic solvent followed by evaporation of the solvent to produce a crude extract;
3. Purification and crude fractionation of the extract - removal of plant waxes and pigments - separation into pesticide classes (organochlorine, organophosphate, carbamate etc.);
4. Determination of pesticides in the purified fractions - generally by gas-chromatography which combines a further separation step with very sensitive and selective detectors that respond to halogen, nitrogen, phosphorus or sulphur containing compounds.

Regulatory authorities such as the Food and Drug Administration (FDA) in the U.S.A., spot check shipments of food imports using methods similar to the above. With care and suitable calibration these "multiresidue" methods can determine the levels of several of up to 50 or so pesticides in a single sample with detection limits of less than 0.1 mg/kg. Certain pesticides and crops require specialised procedures to eliminate losses or interferences at some of the steps.

The sample throughput of a pesticide residue laboratory is generally low due to the time consuming procedures. A skilled technician can handle about 25 routine determinations of a pesticide per week. New pesticides or crops require time consuming adaption and checking of procedures. Where low detection limits are required as in the determination of nanograms/kg (ppt) levels of dioxin (TCDD) in food, extremely specialised methods and sophisticated equipment must be used (Hummel 1977).

Factors affecting residues on fruit

1. Application rate and method: Low volume or high volume application at the same area rate should result in similar residue levels unless the high volume spray is applied past runoff point. In this case, the residue levels will be lowered by the proportion lost as drips. Too high spray pressure can also result in wastage due to drift away from the fruit.
2. Size and surface characteristics of fruit: The larger the fruit, the lower the residue expressed as mg/kg due to the $1/r$ relation between surface area and weight. For example, for the same spray application, the initial residue levels would be blueberries ►plums ►apples. Initial deposition will be more thorough and overall residues higher where wetting agent is used. Where the fruit surface is convoluted (raspberries), downy (peaches) or hairy (kiwifruit) high volume spray retention is greater than for an equivalent sized smooth fruit.

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3. Persistence of the pesticide: Pesticide residues on fruit and foliage are lost by evaporation and washing off, and degraded by the action of sunlight and moisture. If adsorbed into the plant they are also subjected to biochemical degradation (metabolised). Residue levels generally decay in a roughly exponential manner and the persistence of a pesticide can be expressed in terms of a half life. The range behaviour observed in single spray trials on kiwifruit are illustrated by the following examples:

Shortlived chemicals such as dichlorvos have a half life of 1 - 2 days. Moderately persistent materials including captan, carbaryl and the synthetic pyrethroids such as permethrin have half lives of about 7 - 14 days. Persistent pesticides such as DDT have half lives greater than 30 days. Phosmet is persistent on kiwifruit. Consequently, its residues accumulate when used repeatedly in a monthly spray programme (Love *et al* 1978). The exact form of a degradation curve is very dependent upon the climatic conditions and degree of shelter for the fruit. Trials at several sites are required to assess the effect of these variables on persistence.

4. Residue location: Residues are generally concentrated on the skin of fruit. Some pesticides have systemic action and a proportion can move from the skin of the fruit into the flesh to kill sucking insects or pathogens. Thus, even if a fruit is peeled before eating or processing, some residues may remain. The tolerance regulations of importing countries often specify the whole fruit be analysed. In this case, even if the skin is normally discarded along with the bulk of the residues before consumption, this has no relevance as far as the residue level is concerned. Kiwifruit and avocado are in this category with regard to Codex and U.S.A. regulations (See Table 1).

Residue problems on New Zealand export

Monitoring data on New Zealand produce shows that pesticide residues are at levels below the national tolerances and are generally acceptable by overseas countries (Love *et al* 1974; Dick *et al* 1978). However, difficulties have been experienced with some of the newer export crops. Lack of tolerances in the importing country have led to some consignments of fruit being rejected when residues of particular pesticides have been detected.

Specific problems New Zealand has in getting tolerances set are:

1. No registered use of the pesticide in the importing country, The lack of a tolerance for any crop is a serious barrier as this generally means not even an ADI has been established. Several important new insecticides and fungicides of European origin are not yet registered in the U.S.A. It also applies to azinphos-methyl in Japan.
2. The use of the pesticide may markedly differ in New Zealand because of different pests, cultivation or climatic factors than those that exist in the importing country, i.e. good agricultural practices may differ.
3. The crop may not be widely grown in the importing country so that although a pesticide may be used on the other crops, no tolerance has been set for the particular New Zealand produce. The U.S.A. sets tolerances on a plant species basis and several of our subtropical fruits are rather unique.

Where cases 2 and 3 apply, New Zealand can provide residue data and attempt to get tolerances set. MAF has made submissions to Codex and to the major countries to which kiwifruit is exported. Generally, favourable responses have been received (Table 1) and other chemicals are under investigation. Similarly, data is being obtained for submissions on other crops for which export markets are being developed, for example black currants, blueberries, tamarillos and passion fruit. However, procedures in Codex are somewhat slow and even when limits are set, their acceptance by each country is not automatic. In the USA, the Environmental Protection Agency (EPA) is responsible for setting tolerances and their procedures are extremely rigorous and slow.

Monitoring of grower orchards

The MAF programme of surveying pesticide residue levels on kiwifruit samples is not designed to police individual growers. Rather the residue levels measured provide a tool for MAF and the industry to evaluate the recommended spray programme and its acceptance by growers. Where particular samples have residues well above average, there may be a need for the industry to provide advice to growers on their spray

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programmes and application techniques. In the 1979 season, the Chemistry Division, DSIR, determined the levels of five pesticides on samples from 100 kiwifruit orchards. The levels of azinphos-methyl and diazinon were below international tolerances (Table 1). However, some over-spraying with phosmet was indicated by 30% of samples having phosmet residues greater than 10 mg/kg although none exceeded 25 mg/kg. One third of the samples also had captan and carbaryl residues which, in some cases, led to problems on the U.S.A. market. Many growers apparently were not fully following MAF recommendations with regard to these chemicals. Residue levels in the 1980 harvest are being checked by MAF at present.

It is intended to extend this monitoring programme in the 1981 season to include apples and boysenberries.

CONCLUSIONS

The stringent quarantine and residue tolerance requirements for international trade in food commodities make imperative continued pesticide research on New Zealand horticultural crops. As improved methods of pest and disease control are developed, a closely linked pesticide residue programme must be used to ensure that new spray schedules can meet the residue requirements of importing countries.

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