Verification of Product Quality: Agrochemical Residues

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Defining quality specifications for viticultural products with respect to agrochemical residues on export markets is straightforward. That is, the level of chemical residue remaining in the final product, whether it be harvested grapes, wine or dried fruit, must never exceed the level specified by the importing country. How we can ensure that acceptable levels of chemical residues are achieved is less straightforward. This paper describes how the issue of agrochemical residues in Australian grape products has acquired increasing importance during the last decade, and summarises actions that have resulted as a consequence. A reason requiring continued activity, research, negotiation and vigilance are also discussed.

Two terms frequently associated with agrochemical use and chemical residues are withholding period (WHP) and maximum residue limit (MRL). A WHP is defined as the number of days that must elapse between the final spray application on a crop and the harvesting of that crop, an interval that should enable spray residues to degrade prior to harvest. A MRL is defined as the maximum amount of specific chemical residue permitted on a particular crop at harvest. MRLs are expressed as mg of residue per kg of product (mg/kg).

In Australia, WHPs are specified on every agrochemical label, and are relevant to meeting Australian MRLs. However, a significant proportion of the Australian grape crop is exported as fresh grapes, wine or dried fruit, and to each country to which we export may determine their own MRL for any given chemical. When an export market has a lower MRL for a given chemical than Australia, the Australian withholding period cannot be assumed adequate to ensure compliance with the MRL. Sometimes a country has not set a MRL for a chemical that we use in Australia, which may mean that the default MRL is "no detectable residue".

The increasing significance of agrochemical residues as a trade issue for Australian Viticulture

Since the mid 1980s the Australian dried fruit and wine industries have been under increasing pressure to examine the chemical residue status of grapes, wine and dried fruit. By 1992, export markets, particularly the United Kingdom, requested assurance that products imported from Australia would not exceed their own MRLs. Increasingly through the 1990s we face the risk of residues being used as a non-tariff trade barrier to exclude Australian products from overseas markets.

The responses of the grape industries to requests for verification of residue status have been swift. A screening program undertaken by the Australian Dried Fruits Association since 1988 tests the fruit of every dried fruit grower for a range of pesticides. In 1992, the Australian Wine Research Institute (AWRI) published a table of agrochemicals used in Australian viticulture and their MRLs in major overseas markets, so that target MRLs for each chemical could be clearly understood by wineries. This document is updated each year. At the same time, the Australian Wine and Brandy Corporation began screening wines from supermarket shelves for residues that would exceed Australian or overseas MRLs.

By 1993, the AWRI developed the capacity to offer a commercial residue screening service to wineries for a select range of chemicals. By 1996 the range of chemicals that may be tested for by the AWRI has increased to cover those registered for use in Australian viticulture as well as other unregistered compounds.

The major wineries introduced spray diaries in 1993, for their growers to record all spray applications. This addressed the pressure for accountability from overseas buyers, and was a step for the wineries towards meeting the requirements of the international quality standards outlined in the ISO 9000 series. The spray diaries included Extended Withholding Periods. At ensuring residues would be able to degrade to meet the lowest target overseas MRLs. Extended Withholding Periods were not generally based on data, as little suitable degradation data existed at that stage, but were based on relative MRLs and extreme caution. Spray diaries were distributed by the larger wineries to some growers, but many other growers and smaller wineries were not made aware of Extended Withholding Periods.

A quality assurance process, these activities were all limited by major gaps in the availability of information. It was of primary importance to:

- identify which chemicals require residue testing
- determine which withholding periods on Australian agrochemical labels were insufficient to meet overseas MRLs, and
- determine which chemicals would persist through the winemaking or drying processes.

A research program to look at the degradation of pesticides in grapes, wine and dried fruit

From 1991 to 1995, the Dried Fruits Research and Development Council, the Grape and Wine Research and Development Corporation and the Cooperative Research Centre for Viticulture provided funding for a research program to investigate the degradation of pesticides used in viticulture, and the persistence of residues through the drying process and winemaking.

The chemical industry and National Registration Authority (NRA) seemed likely sources of relevant residue data, and in 1991, the chemical companies and NRA were asked for access to residue data relevant to grapes, wine and dried fruit. Some information was provided by chemical companies, supporting derivation of Australian MRLs. Very little data could be made available showing persistence of residues through winemaking or the drying process, as the NRA had never required that such data be collected for registration purposes.

As existing data was inadequate to meet the needs of the grape industries, it was necessary to conduct residue trials on a range of chemicals. Twenty one pesticides were included in degradation trials, during 4 seasons, at both South Australian and Victorian sites. Degradation was measured in fresh grapes...
after spraying, and the persistence of residues through winemaking and grape drying was assessed. Trials also included comparisons of the effect of using different types of spray equipment on residues at harvest, degradation rates after spraying grapes at different maturities, the effects on residues of the spray dilutions and volumes applied, and the effect on residues at harvest of multiple applications.

Persistence of residues through winemaking or grape drying
Some chemicals degraded through winemaking to much lower levels than had been present in the grapes at harvest. However, other chemicals did not degrade at all, or degraded only a small amount during winemaking. There was no apparent relationship between chemicals of similar chemical types in regard to persistence through winemaking. Therefore, assumptions should not be made about the persistence of untested compounds that are similar to tested compounds.

During the drying process, some pesticides were concentrated as berries dehydrated, resulting in higher residues in dried fruit than had been measured in fresh grapes. Other pesticides were degraded by the alkaline dipping and exposure to high temperatures and ultraviolet light during drying. The persistence or degradation of chemicals through the drying process was specific to each chemical.

Varying water volumes applied, or dilution rates mixed, influences residues
Chemical application rates are recommended in both mL/100L and/or mL/ha. When sprays were applied at the mL/100L rate in various volumes, or at the mL/ha rate in various volumes, residues varied at harvest. High residues can result from applications at the rate/hectare to a small canopy. Some labels recommend a range in application rates, and trial data showed that the length of time required for residue to degrade to the MRL increased as the application rate increased. These results further confound our attempts to determine appropriate extended withholding periods to meet export MRLs.

Variations in coverage, expressed as residue in bunches, occurred as a consequence of varying the spray volume applied to the vine canopy, even within the range that would be considered by visual assessment as “spraying to run-off”. Unfortunately there is no method currently able to assess optimum spray volumes for a grapevine canopy, and methods used in other perennial fruit crops cannot be applied to grapes because vine canopies vary so greatly in their architecture and with seasonal growth.

The efficiency of the spray equipment used influences residues
Comparisons between equipment types and equipment settings indicated that spray coverage of bunches varied greatly according to the type of sprayer used and the way the sprayer was set up. While commercial equipment clearly can achieve good coverage when properly configured and calibrated, in practice many commercial sprayers do not achieve adequate spray coverage. In one trial, bunch coverage after spraying with a commercial sprayer was much lower than coverage achieved with the hand held equipment used by chemical companies in their residue and efficacy trials. However, in a second trial, a commercial axial fan airblast sprayer was able to provide the same coverage of bunches as the hand held equipment, resulting in relatively high residue levels at harvest.

Canopy type influenced coverage: a constant volume of spray applied to three sizes of canopy resulted in relatively high coverage in the smallest canopy but decreasing coverage as canopy size increased. To achieve efficient coverage, spray equipment must be calibrated and modified according to canopy size and architecture.

While it is very likely that poor set-up of commercial spray equipment is currently limiting the efficacy of sprays applied to grapevines, poor coverage probably also keeps residues well below levels that could occur if coverage improved to the levels gained in trial work. A focus shift towards improving efficiency of commercial spray equipment, residues measured in commercial grape crops may also increase accordingly.

Berry size at spraying influenced initial residues, and growth of berries after spraying influenced the apparent degradation of residues. Initial residues after spraying were higher on smaller berries, due to their higher ratio of surface area to berry volume.

When berries were sprayed early in the season, residues degraded more quickly than when berries were sprayed after veraison. The difference in degradation rate was partly accounted for by dilution as berries grew. Physiological changes in the berry surface after veraison may also be responsible for causing residues to degrade more slowly after spraying mature berries, but the reasons for slower degradation on mature berries have not been determined.

**Recommendations arising from the research program on residue persistence**

The wine and dried fruit industries now have access to more data on which to base extended withholding periods, and in some cases, where winemaking has been shown to degrade residues, the extended withholding periods set by wineries in their spray diaries may now be reduced. The extended withholding period recommended for a chemical may differ for winegrape or dried fruit production, because of different responses of the chemical to drying or wine making, and also because the industries target different export markets and the default MRLs vary accordingly.

In-house monitoring of wine and dried fruit by industry must continue, as there are many factors that influence the residue levels that may occur in grapes, but which cannot be regulated.

It is appropriate for the grape industries to focus on awareness and training to improve spray application, as this is a key factor influencing the success of early season disease and pest management, and consequently the need for late season sprays.

The grape industries must continue to liaise closely with the National Registration Authority and the chemical industry.

Research into methods for calculating spray-row-volume for various vine canopy types was commenced in 1995 under a newly funded project for the Grape and Wine Research and Development Corporation. Research is also required to determine the optimum spray coverage and droplet spectrums for various chemical types on vine leaves.

**Greater awareness and co-operation**

As the research project progressed, the NRA and the Chemical Industry became more interested in, and have accepted more responsibility for, the issue of meeting overseas MRLs in wine and dried fruit. In 1994 the NRA altered their charter to consider export implications when they register chemicals for use in Australia. In 1996 the NRA and AWC are participating in a review of protocols for the conduct of residue trials in grapevines, incorporating recommendations from the GW RDC/DFRDC pesticide project. The way rates and volumes are recommended on chemical labels is being reviewed by the Victorian and SA Departments of Agriculture and members of the chemical and the grape industries.

The GW RDC/DFRDC project on pesticide degradation was completed in 1995, but new programs have already com-
Wine and dried fruit are routinely monitored for the presence of pesticides, but this is expensive, and the number of samples tested is limited by available funds. New ELISA assays for pesticide detection in grapes and dried fruit (and in the longer term wine) will be cheap, rapid and able to be performed in the field or at a fruit receival point. The number of samples tested will therefore increase.

Residue data has been collected that supports Extended Withholding Periods, in wine and dried fruit production, for the fungicides and insecticides most commonly used in viticulture. However, some chemicals remain untested and these must be treated with caution if used on a crop that will be exported.

Spray diaries to record chemical use are maintained by many, but not all, growers.

Much progress has been made to ensure that residues in Australian grapes, wine and dried fruit meet the specifications for residues in overseas markets. However, long-term responsibility for the assurance of product quality with respect to chemical residues rests equally with all sectors of the viticultural industry; growers, wineries and packers, funding agencies, policy negotiators, extension staff and researchers.

The AWBC Act presently do not extend into the vineyard but, it is a subject under consideration—not in a way which would in any way prescribe viticultural practices but, only as a legal means of gaining entry to a vineyard to verify vintage, varietal and geographical indication claims made by grape growers and winemakers.

If legislation is introduced, it may mean, in the event of a label claim dispute, a visit to a vineyard to obtain vine samples for DNA identification, to verify any claims made.

There is already legislative provision in the AWBC Act to list the grape varieties (and any conditions for use) which may be used for the manufacture of wine in Australia. The list is still under discussion and it may be some time before it is finalised and placed in the register of protected names. The list will most likely contain varieties, including some hybrids, which are prohibited for export to the EU, but which may continue to be used in Australia.

A further aspect of wine legislation is your right to benefit from investment in wine intellectual property. What is intellectual property?

One definition is: intellectual property is property in the abstract creations of the human intellect.

The Macquarie Dictionary defines it as 'the rights of creative workers in literary, artistic, industrial and scientific fields which can be protected either by copyright or trademarks, patents, etc.' In other words it is a legal way of protecting a concept (e.g. plant variety rights are a form of protecting intellectual property).

The AWBC Act protects your intellectual property and gives you legal rights to protect use of your regional name, a traditional expression and any conditions of use of those names, whether in Australia, in the European Union or any other country which may have a wine agreement with Australia.

If your region has not yet been defined, it is in your interest to urge your local industry group to expedite a submission to the Geographical Indications Committee to protect in law your intellectual property. Further details of this process are available from the AWBC on 08 8364 2828.