HorizonScan Occasional Articles

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Checking the Scope of your Pesticides Multi-Residue Analysis

Introduction

More than 1000 pesticide active ingredients have been authorised at some point over the past 50 years. The number of residues that could potentially be present in a food - through either direct use (approved or unapproved), cross-contamination, or environmental legacy - is enormous. This presents a challenge for analytical laboratories.

Different active ingredients have different chemical properties, and many legal residue definitions include metabolites which, by their very nature, are chemically different to their parent pesticide. The analytical conditions needed to measure different chemical classes of residue often depend upon the type of food. It is impossible to design a single test method to measure all potential residues in all types of food.

Laboratories base their test suites on a multi-residue method (or, often, complementary pair of methods) that cover the bulk of potential residues. They may then supplement this with bespoke methods for specific pesticides not covered by their multi-residue test; pesticides either specified by their customer, or suggested by the laboratory as "likely candidates" in that particular food.

The exact scope of the multi-residue test is dependent upon analytical extraction and clean-up conditions, measurement technique, and nature of the sample. Thus, although laboratories will typically list 300+ residues covered, the list varies from laboratory to laboratory. Even within one laboratory their standard list will not apply to every food type. It is therefore important to challenge whether your laboratory's scope includes the residue/crop combinations of most interest to you, based upon knowledge of likely agronomy and pesticide use. This list of your own priority residues can come from Proposed Pesticide Use records, if you have access to them, but can also come from datamining sources such as Horizonscan for residues previously found in produce from the country of interest or in the crop of interest.

Multi-Residue Test Methods: Scope and Validation

Most multi-residue detection methods are based upon chromatographic separation of components within a mixture, followed by mass spectrometry (MS). The separation mechanism can either be gas chromatography (GC) or liquid chromatography (LC).

- LC-MS can cover over 90% of residues of interest. Multi-residue configurations are less suited for measuring non-polar residues at very low concentrations (*e.g.* as required to monitor organochlorine insecticides) or distinguishing between related isomers (*e.g.* as required to discriminate residues of agricultural from veterinary cypermethrin). Depending on configuration, some residues may need bespoke LC-MS conditions (*e.g*. glyphosate, chlorpropham, captan).
- GC-MS can cover over 80% of residues of interest. It is generally suited to those residues not amenable to LC-MS. It is not suited to polar residues (*e.g.* carbendazim, glyphosate, 2,4-D) or to non-volatile residues.

Some laboratories will use both LC and GC-MS in a complementary manner to provide a wider scope.

Irrespective of detection method, the residues first must be extracted from the food and presented to the instrument. Extraction conditions are necessarily designed to be generic and can never be optimum for all residues. Different conditions have different strengths and weaknesses in terms of their scope. This, in turn, is highly dependent upon the sample type. Some residue methods (*e.g.* dithiocarbamates) require derivatisation steps, and therefore always need a bespoke test.

It is impractical for a laboratory to validate their multi-residue method for every residue in every sample type. Typical validation protocols require the extraction recovery of each residue in the 300+ list to be demonstrated in a selection of representative food types (*e.g.* "high water content", "high acid and high water content", "high oil content and intermediate water content"). On a day-to-day basis, laboratories may then choose a representative subset of these residues to demonstrate recovery in the specific food they are testing.

If you have your own priority list of residues, it is therefore reasonable to challenge your laboratory that

i) The validated scope of the multi-residue method includes these residues.
ii) These residues are included in the subset chosen to demonstrate day-to-day extraction recovery in your own sample type.

If this is not the case then you should consider supplementing the testing suite with a bespoke method.

Deriving Your Own Priority List

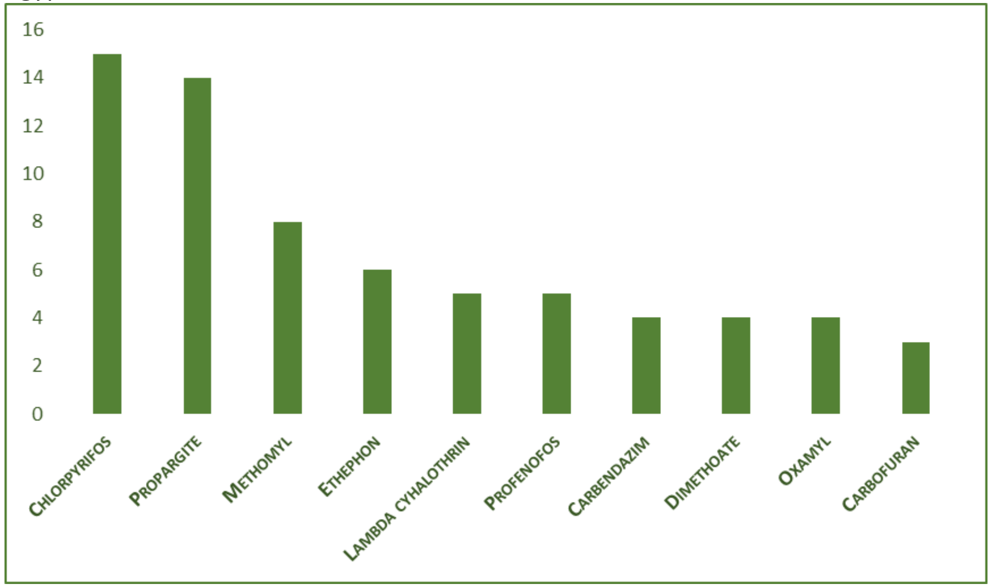
Pesticide residues are highly dependent upon local disease pressures and agronomy practice, local regulatory control of pesticides, and many other factors. If you have access to Proposed Pesticide Use records then these are the best basis for prioritisation. But if not, or if you are also concerned about cross-contamination or undeclared use, then looking at what residues have been reported in the past (either from the country of interest, or in the crop of interest) can provide some insight.

The following "Top 10" examples of were drawn from Horizonscan, using data from January 2016 – December 2018, choosing countries of origin where there were enough data points (50+) to provide a representative distribution.

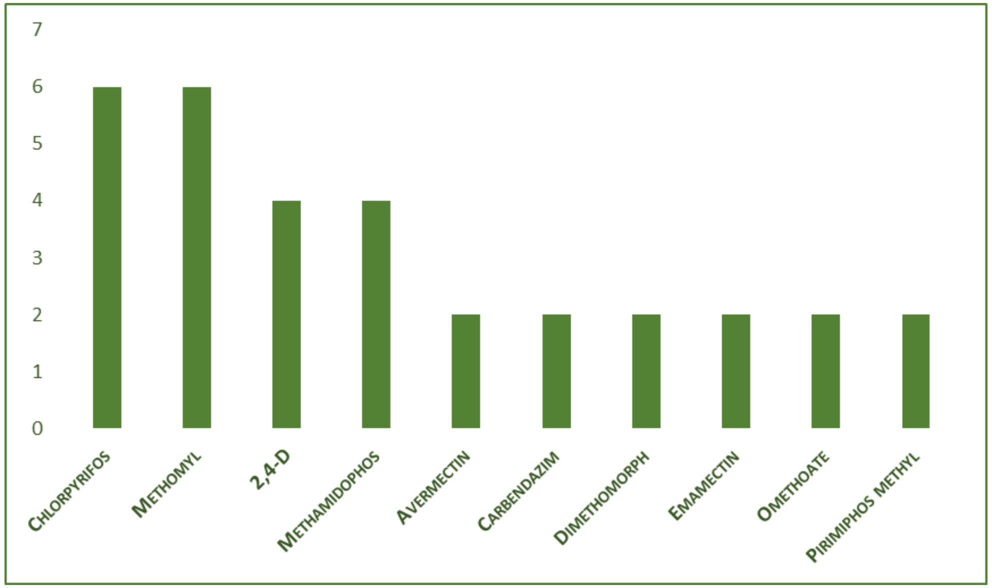
Comparison by Country of Origin

1. Two countries on different continents, both used for seasonal UK sourcing of fresh produce: Egypt vs Peru

Egypt: Count of Residues 2016-18



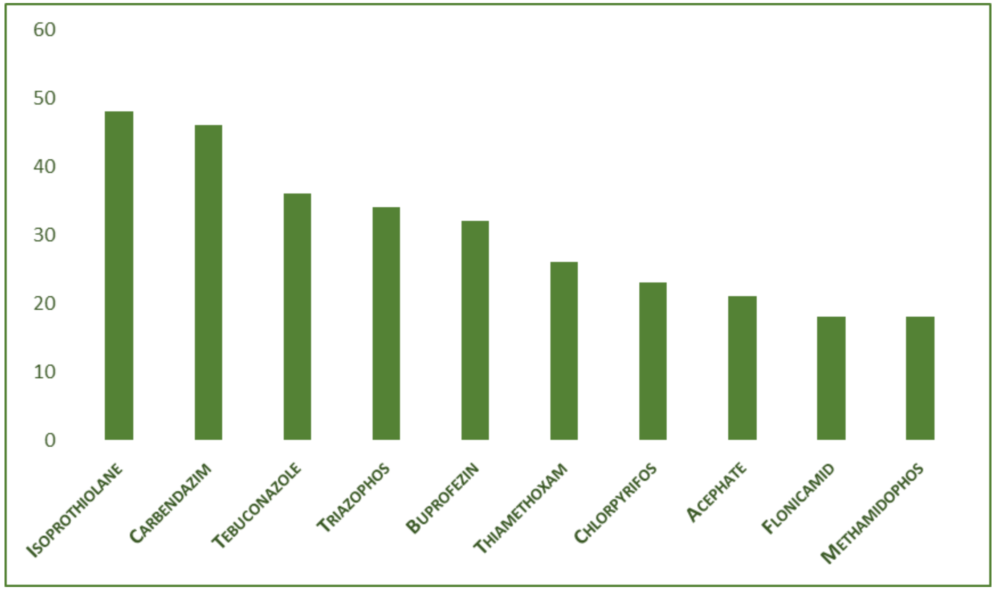
Peru: Count of Residues 2016-18



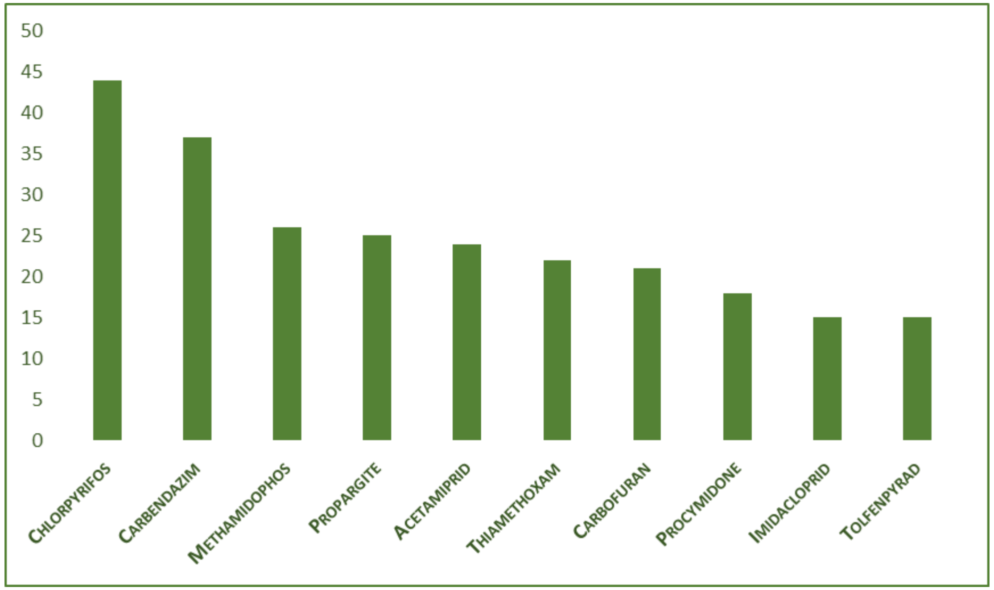
In this example, you might like to specify that your laboratory use an LC-MS, rather than GC-MS, multi-residue screen if you source from Peru. This is as at least 4 of the Top 10 (2,4-D, avermectin, carbendazim and emamectin) are not amenable to GC-MS. If sourcing from Egypt, it may be more cost-effective to run a traditional GC-MS screen supplemented by bespoke assays for carbendazim and oxamyl.

2. Two countries with similar range of climates and disease pressures, different agronomy and pesticide approval: India vs China

India: Count of Residues 2016-18



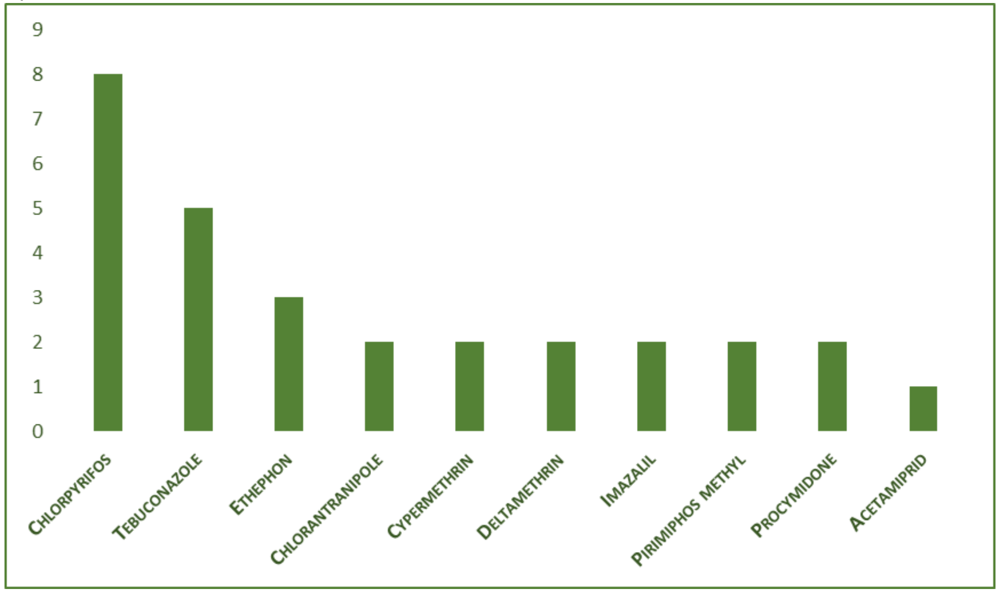
China: Count of Residues 2016-18



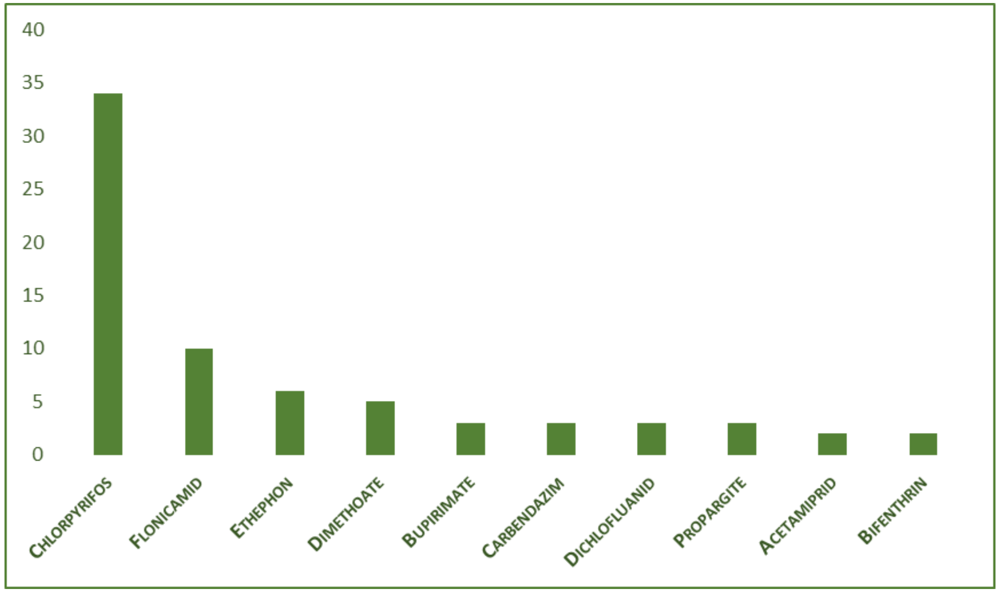
In this example, both residue Top 10's are similar in terms of their analytical requirements, with only carbendazim not fitting into a traditional GC-MS screen. Isoprothiolane is a specific issue in Indian rice, and so rice suppliers sourcing from India should consider specifying that their laboratory chooses isoprothiolane as one of the representative day-to-day extraction recovery checks.

3. Two countries with the same EU regulatory regime, different climates and disease pressures: Spain vs Poland

Spain: Count of Residues 2016-18



Poland: Count of Residues 2016-18

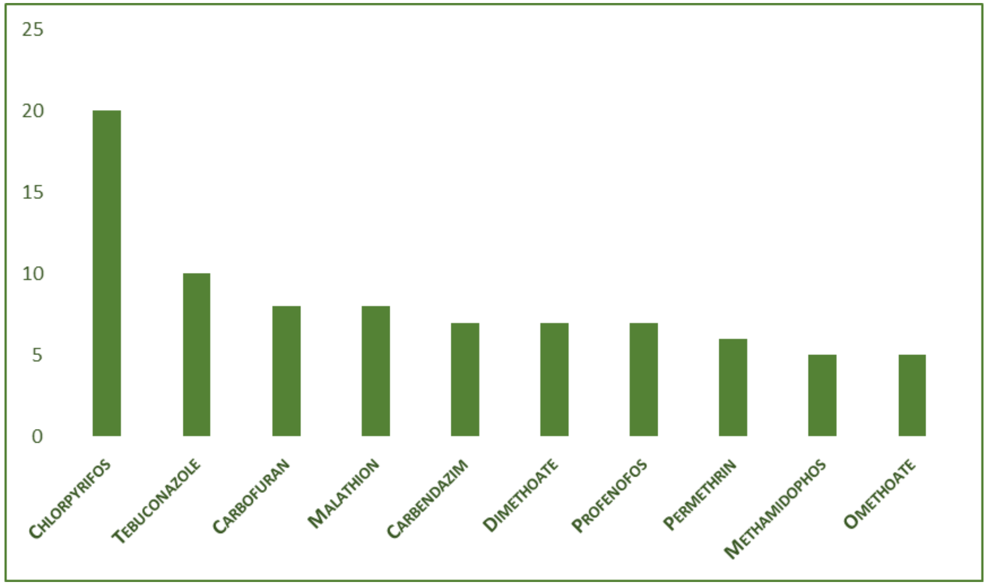


Given the relative predominance of chlorpyrifos residues in Polish origin food (driven by apples, but also across a wide range of different crops), it would be sensible if sourcing from Poland to specify that your laboratory includes chlorpyrifos as one of the day-to-day extraction recovery checks in every food type.

Comparison by Crop

Most crops mirror the example of fresh herbs; they can be grown in many different climates and different production systems, but there is no obvious bias to the residue profile by country. However, there are a few extreme examples such as cocoa, where climates and production systems tend to be similar wherever they are grown, and a small number of residues predominate irrespective of country of origin. In the case of cocoa, it would be essential to specify that your laboratory's scope included 2,4-D (not an automatic assumption, for laboratories using a GC-MS multi-residue screen).

Fresh Herbs: Count of Residues 2016-18



Cocoa: Count of Residues 2016-18