Tolerances not clearly listed for metabolites and degradates which are also active ingredients

Lessons learned, and can anything be done to improve the system?

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SFIREG / POM Working Committee
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Oregon is a Minor Crops Export State

- More than 250 diverse products grown and processed in Oregon. Only California has a higher number of commodities in the United States.

- 80% of Oregon’s agricultural products are sent out of the state, with about 50% that amount exported to foreign countries.

- Ranks 4th nationally in exports of fresh and processed fruits, and tree nuts.

- Value of international exports –2.3 billion dollars
• Grower had a red currant berry crop intended for export to an Asian country.

• Crops are routinely analyzed for pesticides by private labs prior to harvest/shipment.

• Private laboratory found the presence of two labeled fungicides that grower used; and also two insecticides (thiamethoxam and clothianidin).

• Private laboratory informed the grower and exporting company that there was not a tolerance for clothianidin in 40 CFR 180.586 on currants, or a crop group which contained currants.

• Grower claimed he did not apply clothianidin.
§180.586 Clothianidin; tolerances for residues.

(a) General. (1) Tolerances are established for residues of the insecticide clothianidin, including its metabolites and degradates.

Compliance with the tolerance levels specified below is to be determined by measuring only clothianidin, in or on the following raw agricultural commodities:

(E)-N- [(2-Chloro-5-thiazolyl) methyl]-N’-methyl-N”- nitroguanidine

One crop group listed is: “Berry, low-growing, subgroup 13-07H, except strawberry” - but this group does not contain currants.
Grower contacted ODA

- ODA collected various samples and analyzed them for the presence of clothianidin.

Samples were from:
- Currants (in field)
- Four different types of nearby crops, and
- Three pesticides used: two fungicides and the insecticide Actara (a.i. thiamethoxam).

Only the currants were positive for clothianidin.
ODA’s response to the state verified presence of clothianidin?

EPA Headquarters was contacted and asked a basic question without being provided background regarding products use.

- ODA Question: Is there a tolerance for clothianidin on currant berries?
- EPA Response: “No … See 40 CFR180.568 for a full listing of the clothianidin tolerances”.

ODA issued a Notice of Detainment and the crop was lost in the field.
Several Lessons were learned

Lesson No. 1 - More fully explain the situation to EPA when asking for verification, including providing a list of pesticides used.

ODA Enforcement learned months post crop detainment that clothianidin is a metabolite of thiamethoxam.

Lesson No. 2 – It isn’t readily apparent to most people that clothianidin is a major metabolite of thiamethoxam.

- Tolerances are not cross-referenced, and different IUPAC nomenclature is used.

This situation is potentially problematic for a number of reasons. Increase in domestic & international sampling.
Is the currant berry situation unique?
No, there is not cross-references of tolerances

<table>
<thead>
<tr>
<th>Crops</th>
<th>Thiamethoxam (includes metabolite Clothianidin) 40 CFR 180.565</th>
<th>Clothianidin 40 CFR 180.586</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bean, succulent</td>
<td>0.02</td>
<td>Silent</td>
</tr>
<tr>
<td>Berry, low growing, subgroup 13-07G, except cranberry</td>
<td>0.30</td>
<td>Silent</td>
</tr>
<tr>
<td>Brassica, head and stem, subgroup 5-A</td>
<td>4.50</td>
<td>Silent</td>
</tr>
<tr>
<td>Alfalfa hay</td>
<td>0.12</td>
<td>Silent</td>
</tr>
</tbody>
</table>
§180.565 Thiamethoxam; tolerances for residues.

_General._ Tolerances are established for residues of the insecticide thiamethoxam, including its metabolites and degradates, in or on the following commodities.

Compliance with the tolerance levels specified below is to be determined by measuring only thiamethoxam 3-[(2-chloro-5-thiazolyl)methyl]tetrahydro-5-methyl-N-nitro-4H-1,3,5-oxadiazin-4-imine and its metabolite CGA-322704 N-[(2-chloro-thiazol-5-yl)methyl]-N’-methyl-N”-nitro-guanidine, calculated as the stoichiometric equivalent of thiamethoxam, in or on the following commodities:

- It is not indicated in 40 CFR 180.565 that CGA-322704 is also known as clothianidin, a registered pesticide.
- The clothianidin tolerance doesn’t mention thiamethoxam, 40 CFR 180.586.
What about IUPAC nomenclature?

- In the thiamethoxam tolerance (§180.565), clothianidin isn’t called clothianidin, but it is referred to as:
  - CGA-322704 N-[(2-chloro-thiazol-5-yl)methyl]-N’-methyl-N’’-nitro-guanidine

- However under the clothianidin tolerance (§180.586), there is different nomenclature used and clothianidin is written as:
  - \((E)\)-N- [(2-Chloro-5-thiazolyl)methyl]-N’-methyl-N’’-nitroguanidine

Note - if you went to EPA’s ChemSearch, there would be another variation.

How are most people who aren’t chemists suppose to know these are the same structure?
Side Story – Currants

- If you query the Global MRL Database for “Currant, red, white” it would indicate that there is not a MRL for clothianidin. This is a widely used database.

- Codex/European Union: If you look at Crop Group FB 0018, there is a MRL on “Berries and other small fruit” for clothianidin (0.07 ppm) and thiamethoxam* (0.5 ppm), these are listed as separate tolerances.
  - ODA is trying to determine if currants are in FB 0018. In any case, levels detected in Oregon currants are well above the Codex MRL for currants.

- Harmonization Issue - Thiamethoxam:
  - MRL for currants at 0.01 ppm in the EU
  - Tolerance for currants at 0.20 ppm in the US
Possible Remedies

- Cross reference tolerances in 40 CRF 180, for metabolites and degradates that are also registered pesticides.
- For metabolites and degradates that are also registered pesticides, clearly indicate the chemical names.
- Consistently use the same IUPAC nomenclature.
- Have an EPA web page which lists pesticides and their degradates/metabolites which are also pesticides.
  - Provide 40 CFR 180 citations.

Possible Alternatives

**Assign separate tolerances.** In the case of thiamethoxam and clothianidin, they are split up by Codex Alimentarius; or

Consider the metabolites and degradates that are also registered as pesticides, as **indirect or inadvertent residues** (although these are not included in global databases).