Amitraz Residues in Pears - Detection via Metabolites in a Multi-Residue Scheme

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INTRODUCTION
In 2007 and 2008 CVUA Stuttgart had found high levels of amitraz residues in pears from Turkey. Thus, in 2009, 45 samples of pears from different origins were sampled and tested for amitraz residues.

ANALYSIS
Traditional methods of analysis for amitraz are very laborious and time-consuming, as they involve cleavage to 2,4-dimethylaniline (DMA) and a GC-determination following a derivatization step. Aiming to include amitraz analysis in a multi-residue scheme, the EU Reference Laboratory for Single Residue Methods (EURL-SRM) distributed a method targeting amitraz parent as well as its most important DMA-containing metabolites: N-2,4-Dimethylphenyl-N-methyl-formamidine (DMPF) and N-(2,4-Dimethyl-phenyl)-formamide (DMF), which are all analyzed individually depending on the pH.

DMF was detected only in negligible concentrations. Considering these facts, the analysis of amitraz parent alone would lead to a significant underestimation of the total amitraz as defined in the residue definition ("sum of amitraz including the metabolites containing the 2,4-aniline moiety, expressed as amitraz"). In our case total amitraz was calculated as the sum of amitraz parent plus DMPF expressed as amitraz.

INSTABILITY OF AMITRAZ IN PEAR EXTRACT
While DMPF is relatively stable amitraz degrades very fast in pear extract with pH-values lower than 5 (see Figure 1).

RESULTS
In 2009 CVUA Stuttgart analyzed 45 samples of pears from different countries for amitraz residues. Again, all of the 8 tested pear samples originating from Turkey contained amitraz residues above the MRL (0.05 mg/kg). The contents ranged from 0.2 to 15.7 mg/kg (see Table 1). The concentrations were even higher than in the previous years, resulting in massive ARID exceedances of up to 143 times the ARID (calculated for German toddlers; ARID 0.01 mg/kg bw). All 8 samples were considered “unsafe”, with 6 of them “injurious to health” and 2 samples “unfit for human consumption” according to Article 14 of Reg. (EC) No 178/2002. These results show that amitraz residues were mainly present as DMPF and demonstrate how important it is to test for amitraz residues, especially regarding pears.

Table 1 Amitraz findings in pears from Turkey (2009) in mg/kg

<table>
<thead>
<tr>
<th>Amitraz (parent)</th>
<th>DMPF</th>
<th>Amitraz (sum)</th>
<th>ARID Exceedance (%)</th>
<th>Unit for human consumption</th>
<th>Injurious to health</th>
</tr>
</thead>
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<tr>
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<td>4.7</td>
<td>9.8</td>
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<td>x</td>
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<tr>
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<td>3.3</td>
<td>6.0</td>
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<td>0.11</td>
<td>0.2</td>
<td>183</td>
<td>x</td>
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</table>

ANALYSIS OF AMITRAZ IN EU LABS – EURL-SRM SURVEY 2009
- 54 (40 %) of 135 official labs in the EU analyze for amitraz but 32 of these labs only check for the parent compound.
- 37 labs (27%) plan to analyze for amitraz in the near future.
- 6 labs detected amitraz in pears from Turkey in 2009.

SUMMARY
- The high rate of MRL- and ARID-exceedances underline the importance of analyzing for amitraz residues, especially regarding pears.
- Amitraz residues in pears were mainly present as the DMPF-metabolite. Only traces or lower concentrations (depending on the total amitraz concentration) of amitraz parent and DMF were found in pears treated with amitraz.
- If only the amitraz parent is targeted, the total amitraz residue is underestimated.
- Analysis by conversion to 2,4-DMA is troublesome.
- New approach: analysis of parent and main metabolites via MRM [1].

LITERATURE
[1] www.crv-pesticides.eu