Residue Findings of Melamine and Cyanuric Acid in Food

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Introduction
Melamine residues were on everyone’s lips a few years ago (2008). Extremely high quantities of up to 2500 mg/kg were found in infant milk, milk products and pet food from China [1]. In the latter case melamine was illegally used to give the false impression of a higher quantity of protein. This caused kidney damage and even death to infants and pets [2].

Residues of melamine and its hydrolysis product cyanuric acid (CA) in crops can also occur following the application of PPPs containing cyromazine.

Another possible source of contamination in the fields is the use of fertilizers containing cyanamide (known to trimerize to melamine, which further degrades to CA) or fertilizers containing melamine and CA as by-products. Further entry paths may include irrigating or washing with chlorinated water containing CA as a chlorine stabilizer and/or algicide, and contact with melamine-based residues.

Analytical method
Analysis was accomplished using the QuPPe method, developed by the EURL-SRM. This involves methanol extraction, filtration, dilution and LC-MS/MS analysis. The Hypercarb™ column (CA) is used in the ESI neg. mode and the Acquity® BEH Amide column (melamine, cyromazine) is used in the ESI pos. mode.

Results
From July 2013 to May 2016 more than 5,400 plant products of different commodity types were analyzed for residues of cyromazine, melamine and CA. Residues of melamine and CA were found in a wide variety of fruits and vegetables, as well as in processed food. Overall, 15 % of all the analyzed samples contained CA residues ≥ 0.01 mg/kg. Melamine residues ≥ 0.01 mg/kg were found in 12 % of the samples, whereas cyromazine exceeded this level in only 0.4 %.

In most cases residues of CA and melamine did not correlate with residues of cyromazine. There was also no visible correlation between high levels of melamine or CA and high levels of chlorate residues.

Residue situation

<table>
<thead>
<tr>
<th>Residue</th>
<th>All samples</th>
<th>Conventional</th>
<th>Organic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n ≥ 0.01 mg/kg</td>
<td>Average level of positives (mg/kg)</td>
<td>n ≥ 0.01 mg/kg</td>
</tr>
<tr>
<td>Cyromazine</td>
<td>5418 0.5 %</td>
<td>0.022 4668 0.5 %</td>
<td>0.022 750 0 %</td>
</tr>
<tr>
<td>Melamine</td>
<td>5375 12 %</td>
<td>0.11 4631 14 %</td>
<td>0.11 744 7 %</td>
</tr>
<tr>
<td>Cyanuric acid</td>
<td>5376 15 %</td>
<td>0.085 4639 15 %</td>
<td>0.094 741 19 %</td>
</tr>
</tbody>
</table>

- Findings in fertilizers
The analysis of 19 different fertilizers revealed in some cases high amounts of both substances up to 7.3 mg/kg (melamine) and 41 mg/kg (CA). In the case of cyanamide fertilizers additional melamine and subsequent cyanuric acid may be generated in treated fields. Cyanamide fertilizers are not permitted in organic agriculture but the reported high persistency of melamine in soil and its transformation to CA could be an explanation for the frequent findings of melamine and CA in organic products.

Summary
Melamine and CA are frequently found both in conventional and organic products. Among the many possible paths of contamination the use of fertilizers seems to be the most relevant. Risk assessment of the highest levels found appears to be inevitable.

References: