Leaching of metabolite CGA108906 demonstrates a shortcoming in the EU pesticide authorization procedure

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Introduction
Metabolites of pesticides used in agricultural production are frequently detected in groundwater, often more frequently than pesticides. Evaluating the risk of groundwater contamination by metabolites is thus important. Within the European Community pesticide authorization procedure, leaching risk of a metabolite will only be assessed if one of the following conditions applies: i) the metabolite accounts for more than 10% of the amount of pesticide added in soil at any time during the laboratory soil degradation studies, ii) the metabolite accounts for more than 5% on a molar basis of the amount of pesticide added in soil in at least two sequential measurements during degradation studies, or iii) the maximum of formation of the product is not yet reached at the end of soil degradation studies. If none of these conditions applies, the metabolite will be considered as a degradation product of no concern (Sanco/221/2000, 2003), its relevance (e.g. genotoxicity and toxicity) will often not be evaluated, and hence there will be no restriction on the concentrations in the groundwater enforced by the Water Framework Directive.

We question whether the above mentioned conditions are suitable for identifying all metabolites posing a risk to groundwater under field conditions. When adding metalaxyl-M to the list of approved pesticides for use in the EU (Annex 1), CGA108906 was one of its metabolites considered of no concern, even though results of lysimeter studies indicated clear potential for leaching. Under field conditions, this study evaluates the EU pesticide authorization procedure regarding metalaxyl-M and examines transport of the compound as well as its two metabolites CGA108906 and CGA62826.

Material and methods
Leaching of metalaxyl-M and its degradation products CGA108906 and CGA62826 was studied in two sandy fields (Tylstrup and Jyndevad), both arable fields included in the Danish Pesticide Leaching Assessment Program (PLAP) (Brüsch et al., 2013).

Jyndevad consists of coarse sandy soil deposited rather homogeneously by meltwater, whereas Tylstrup consists of fine sandy soil deposited rather heterogeneously by salt water – an elevated sea bottom. The groundwater table is situated at 1-3 m depth at Jyndevad and at 2.5-4.5 m depth at Tylstrup. Both fields have been monitored continuously since 1999 to determine the water balance and study the leaching of pesticides and metabolites (e.g. Rosenbom et al., 2010).

The PLAP fields are cultivated in accordance with conventional agricultural practices within the local regions. Potatoes were sprayed with Ridomil Gold MZ Pepite (77.6 g metalaxyl-M ha⁻¹) late in the growing season against potato blight (*Phytophthora infestans*) (Tylstrup: 9 July 2010, BBCH 60; Jyndevad: 25 July 2010, BBCH 71).
Water was sampled from the variably-saturated and saturated soil media of the two fields. In the vadose zone water was collected monthly via suction cups installed at 1 m depth at Jyndevad and at 1 and 2 m depth at Tylstrup. In the groundwater zone water was sampled monthly or biannually from a number of screens in vertical monitoring wells (Brüsch et al., 2013).

The concentration of metalaxyl-M, CGA108906, and CGA62826 in the collected water samples was determined by a commercial laboratory accredited for pesticide analysis. Extra quality control was performed to assure the quality of the sample handling, transport, and storage procedures (Brüsch et al., 2013).

Results
In line with the findings of the lysimeter studies, which received low weight in the final assessment of metalaxyl-M, CGA108906 was detected in high concentrations in water samples collected from both the variably-saturated (VSZ) and the saturated zone (SZ), Table 1.

Table 1. CGA108906 detections in water samples collected from both the variably-saturated (VSZ) and saturated (SZ) zone at Jyndevad (25/7 2010 – 12/6 2012) and Tylstrup (9/7 2010 – 12/6 2012) after application of metalaxyl-M. Frequency of detection is indicated in brackets.

<table>
<thead>
<tr>
<th>SITE</th>
<th>Zone</th>
<th>Number of water samples analysed for CGA108906</th>
<th>Number of water samples with concentration of CGA108906 &gt; 0.1 µg L⁻¹</th>
<th>Number of water samples with concentration of CGA108906 ≤ 0.001; 0.1 µg L⁻¹</th>
<th>Maximum concentration of CGA108906 µg L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jyndevad</td>
<td>VSZ</td>
<td>46</td>
<td>37 (80%)</td>
<td>9 (20%)</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>SZ</td>
<td>120</td>
<td>54 (45%)</td>
<td>56 (47%)</td>
<td>2.7</td>
</tr>
<tr>
<td>Tylstrup</td>
<td>VSZ</td>
<td>62</td>
<td>25 (40%)</td>
<td>28 (45%)</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>SZ</td>
<td>118</td>
<td>40 (34%)</td>
<td>72 (61%)</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Annual average concentrations of CGA108906 in water sampled from 1 m depth exceeded 0.1 µg L⁻¹ at both sites. CGA108906 was detected in approximately 93% of the groundwater samples analysed, and 39% of the samples with concentrations exceeded 0.1 µg L⁻¹, which is the EU limit for relevant metabolites in ground water and drinking water. This limit can, however, not legally be enforced in connection with CGA108906, as the relevance of this metabolite was not fully assessed. These findings indicate a shortcoming in the decision tree for Determination of relevance of metabolites in groundwater within the EU pesticide authorization procedure (Sanco/221/2000, 2003) when evaluating degradation products to be of no concern based on degradation studies only. The procedure may therefore not always be suitable for assessing the leaching risks of metabolites under field conditions.

References
