Non-Extractable Residues of Agrochemicals in Soil in the Regulatory Context

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Definition
According to European Commission (Regulation No 283/2013) and following IUPAC definition [1], non-extractable residues (NER) in plants and soil are defined as follows
- Chemical species originating from pesticides used according to good agricultural practice
- Cannot be extracted by methods which do not significantly change the chemical nature of these residues
- Do not include fragments through metabolic pathways leading to natural products

Background & Relevance
- Process reducing pesticide availability and concurrently increasing persistence
- Transient pesticide stabilization which may lead to subsequent slow release
- Significant impact of formation in soil/sediment on behaviour in environment
- Kinetic process to be included in risk assessment
  - Important element of risk assessment

General Degradation of Xenobiotics & Formation of NER

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>40</th>
<th>80</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residues [% of applied]</td>
<td>0</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>60</td>
<td>80</td>
</tr>
</tbody>
</table>

- Mineralization / CO₂
- Extraction Efficiency
- Non-Extractable Residues (NER)
- Biogenic NER

Problems
- Composition and amount depending on extraction method (solvents and system used)
- Definition of acceptable degree of matrix denaturation for "exhaustive" extraction
- Extraction efficiency depends on pesticide and soil properties
- Different views of role of NER formation and their subsequent toxicity

US
- Guidance for Addressing Unextracted Pesticide Residues in Laboratory Studies [2]
- If NER >10% screening for adequate extraction methods:
  - use of polar and nonpolar solvent systems (range of dielectric constants) in order to:
    - quantify degradation of parent and
    - avoid double-counting sorption in exposure models
- If NER cannot be excluded from the residues of concern (assuming similar toxicity as parent): aquatic exposure modeling approaches with DT₅₀ values including and excluding NER should be used.

Regulatory View & Implementation in Risk Assessment
- NER usually accounted for in the description of dissipation kinetics
- Considered as degradation, sink and detoxification process
- Based on methodical definition (non-extractability)

EU
- Data requirements given by Regulation 283/2013 in the framework of Regulation 1107/2009
- NER in determination of fate and behavior in soil, water and sediment (7.1.1. route of degradation in soil, 7.2.2.2. aerobic mineralization in surface water and 7.2.2.3. water/sediment)
- Identify individual compounds present which at any time account for more than 10% of the amount of active substance added, including, if possible, non-extractable residues
- Authorization declined if NER >70% and Mineralization <5% after 100 days (Guidance Document on Persistence in Soil)
  - unless clause: scientific demonstration that there is no accumulation in soil under field conditions at such levels that:
    - unacceptable residues in succeeding crops occur
    - unacceptable phytotoxic effects on succeeding crops occur
    - unacceptable impact on the environment occur

Japan (JMAFF) and other countries
No specific guidance regarding NER in context of risk assessment. NER considered as sink and degradation resulting in detoxification of parent compound.

Future Requirements
- Additional information on the nature of NER
- Reliable methods and experimental or modeling tools to evaluate NER toxicity, environmental impact and residue carry-over
- Reliable models for predicting the long-term fate of residue in the environment
- Evaluation of significance regarding ecotoxic relevance as non-point source pollution of water bodies through slow release

Outlook / Scientific State of the Art
- Characterization / Identification: Determination of biogenic NER (for compounds showing rapid mineralization and a high formation rate of NER) [4]
- Prediction of biogenic NER formation: Relationships between microbial yield, released CO₂ and microbial growth used [5]
- Assessment of toxicity: Determination of bioavailable concentration using TENAX in bio-assays [6]