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

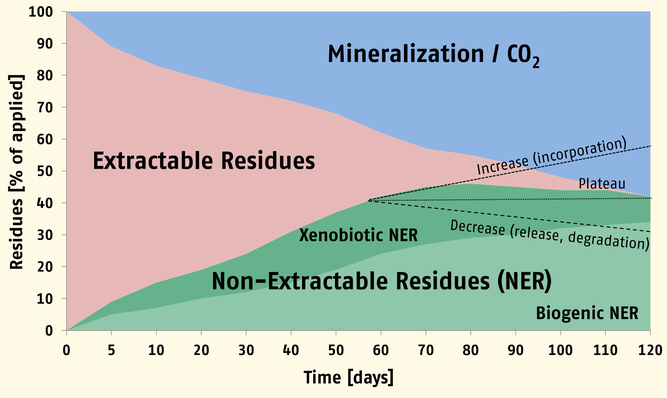
- Chemical species originating from **pesticides** used according to good agricultural practice
- **Cannot** be **extracted** by methods which do **not** significantly **change** the **chemical nature** of these residues
- Do not include fragments through metabolic pathways leading to natural products

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



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**

Regulatory View & Implementation in Risk Assessment

General

- 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 components 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

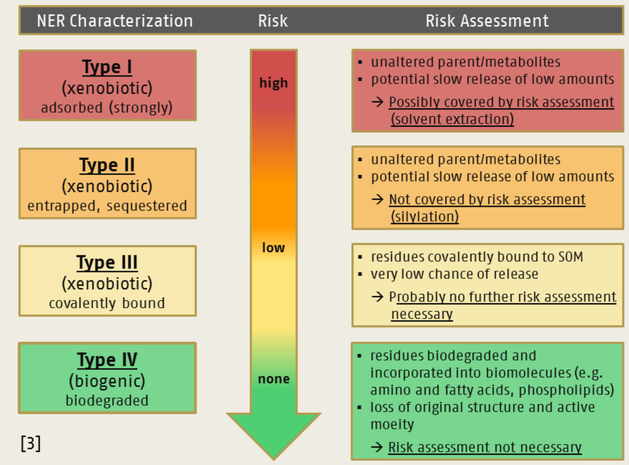
US

- 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 DT_{50} values including and excluding NER should be used.

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.

Type Model & Risk



[3]

Regulatory Challenges

- Lack of knowledge about **chemical nature** of NER
- Formation and occurrence not linked to **bioavailability** and **bioaccessability**
- Qualitatively and quantitatively not linked with **potential effects**

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 NER in the environment
- **Evaluation** of significance regarding ecotox **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 CO_2 and microbial growth used [5]
- **Assessment** of **toxicity**: Determination of bioavailable concentration using TENAX in bio-assays [6]

[1] Roberts T.R. (1984): Non-extractable pesticide residues in soils and plants. Pure and Applied Chemistry; 56: 945-956.
[2] EPA (2014): https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/guidance-addressing-unextracted-pesticide-residues.
[3] Eschenbach A (2013): Characterization of non extractable residues for their risk assessment in soil with special regards to pharmaceuticals. International Workshop Pharmaceuticals in Soil, Sludge and Slurry, Dessau.
[4] Kaestner M., Nowak K.M., Miltner A., Trapp S., Schaeffer A. (2014): Classification and Modelling of Nonextractable Residue (NER) Formation of Xenobiotics in Soil – A Synthesis. Critical Reviews in Environmental Science and Technology; 44: 2107-2171.
[5] Trapp S., Brock A.L., Nowak K., Kästner M. (2018): Prediction of the formation of biogenic non-extractable residues during degradation of environmental chemicals from biomass yields. Environmental Science & Technology; 16: 663-672.
[6] Harmsen J., Hennecke D., Hund-Rinke K., Lahr J., Deneer J. (2017): Advances in the development of procedures to establish the toxicity of non-extractable residues (NER) in soil. SETAC Europe 27th Annual Meeting.