Part I: Non-Extractable Residues (NER) in Soil – Review and Definitions

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Background & History

- First published information on pesticide NER in 1964 [1]
- First official definition in 1975 by the American Institute of Biological Sciences – Environmental Task Group
- Quantification possible with ^{14}C-labelled test substance only following combustion and liquid scintillation counting
- Process leading to reduced compound (bio)availability and decelerated degradability
- Transient stabilisation which may lead to subsequent slow release

Current Definition

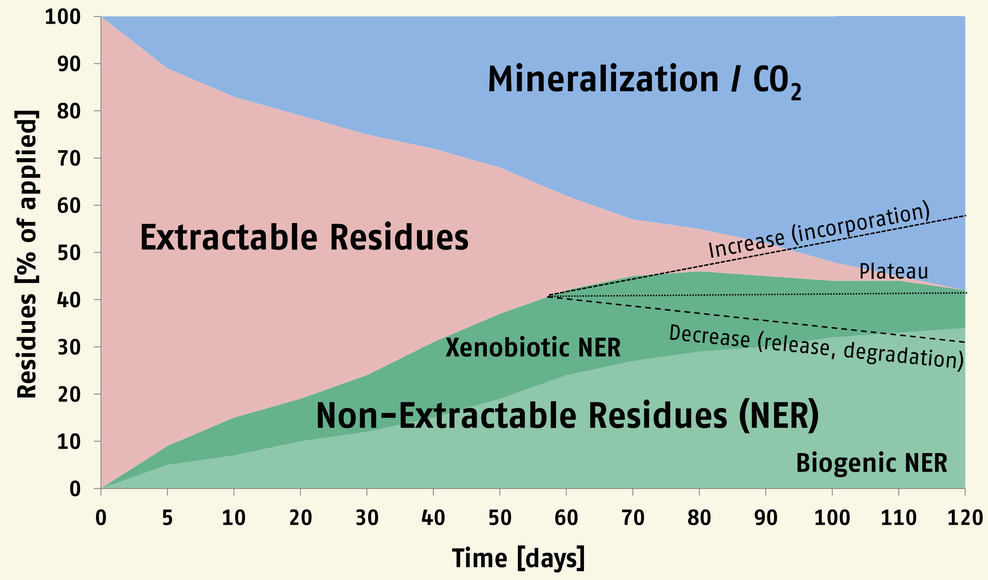
According to European Commission (Regulation No. 283/2013) and following IUPAC definition [2], non-extractable residues (NER) in plants and soil are defined as:

- Chemical species originating from **plant protection products (PPP)** used according to good agricultural practice
- **Cannot** be **extracted** by methods which do **not** significantly **change** the **chemical nature** of these residues or the matrix
- Do not include fragments through metabolic pathways leading to natural products (→ bioNER)

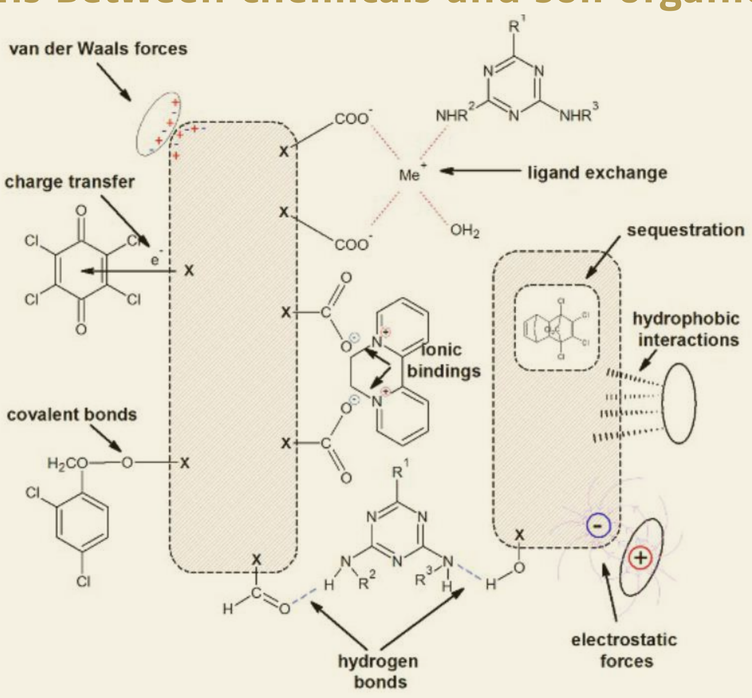
Difficulties

- Based on **methodical definition** (non-extractability)
- Composition and measured amount depending on **extraction method** (solvents and system used)
- Definition of acceptable **degree** of **matrix denaturation** for „exhaustive" extraction
- Extraction efficiency depends on PPP and soil properties

General Degradation of Xenobiotics & Formation of NER



Interactions Between Chemicals and Soil Organic Matter [3]



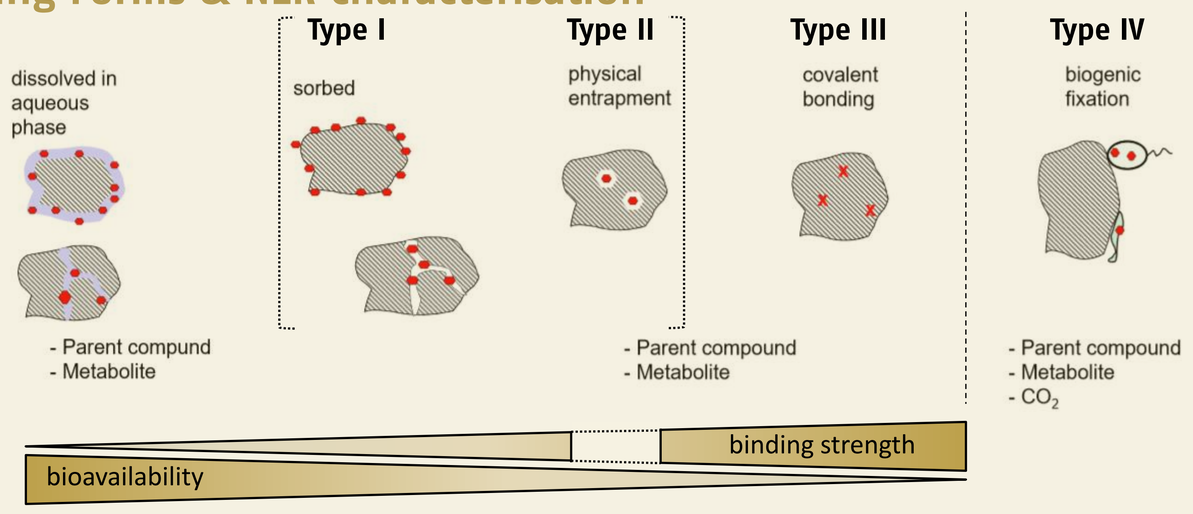
Commonly Used Extraction Methods

- Shaking at ambient temperature using organic solvents or buffer solutions
- Ultrasonication using organic solvents or buffer solutions
- Soxhlet extraction
- Accelerated solvent extraction (ASE)
- Microwave assisted extraction
- Supercritical fluid extraction

Binding Interactions & Binding Strength [3]

- **Type I**
  - Electrostatic (e.g. ionic, ligand exchange, charge transfer): <5 – 350 kJ/mol
  - Hydrogen bond: 4 – 120 kJ/mol
  - Hydrophobic: 5 – 10 kJ/mol
  - Van der Waals: 0.5 – 5 kJ/mol
- **Type II**
  - Physically entrapped
- **Type III**
  - Covalent binding: > 300 kJ/mol

Binding Forms & NER Characterisation [4]



Regulatory Positions

Different views of role on NER formation and their resulting **persistence/toxicity** (EFSA <-> ECHA)

- ECHA: NER regarded as non-degraded substance for **P/vP assessment** (industrial chemicals)
- EFSA:
  - Considered as **degradation**, **sink** and **detoxification** process (plant protection products)
  - NER usually accounted for in the description of **dissipation kinetics**
  - **Authorization declined** if **NER >70%** and **Mineralization <5%** after **100 days** (Guidance Document on Persistence in Soil), unless clause (see also associated Poster „Part II")

Challenges & Future Requirements

- In-depth knowledge about **chemical nature** of NER
- **Guidance** for determination & differentiation of NER
- Reliable **models** for predicting the long-term fate of NER in the environment

Outlook / Scientific State of the Art

- **Characterization / Identification**: Determination of biogenic NER (for compounds showing rapid mineralization and a high formation rate of NER) [5]
- **Prediction** of **biogenic NER** formation: Relationship between microbial yield, released CO_2 and microbial growth used [6]
- **Assessment** of **toxicity**: Determination of bioavailable concentration using TENAX in bio-assays [7]

[1] Bailey G.W., White J.L. (1964): Review of adsorption and desorption of organic pesticides by soil colloids, with implications concerning pesticide bioactivity. Journal of Agricultural and Food Chemistry; 12(4).
[2] Roberts T.R. (1984): Non-extractable pesticide residues in soils and plants. Pure and Applied Chemistry; 56: 945-956.
[3] Ecetoc Technical Report No. 117 (2013): Understanding the Relationship between Extraction Technique and Bioavailability.
[4] 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.
[5] 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.
[6] 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.
[7] 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.