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# Non-extractable residues (NER) from xenobiotics in soil: a new classification and relevance in the risk assessment

Karolina M. Nowak<sup>1</sup>, Matthias Kästner<sup>2</sup>, Anja Miltner<sup>2</sup>, Stefan Trapp<sup>3</sup>, Andreas Schäffer<sup>1</sup>

<sup>1</sup> RWTH Aachen University, Institute for Environmental Research, Worringerweg 1, 52074 Aachen, Germany,

<sup>2</sup> Dept. Environmental Biotechnology, Helmholtz-Centre for Environmental Research UFZ, Leipzig, Germany,

<sup>3</sup> Department of Environmental Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

E-mail contact: karolina.nowak@ufz.de

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## 1. Introduction

Anthropogenic organic chemicals are deliberately (e.g. pesticides) or unintentionally (e.g. polyaromatic hydrocarbons, chlorinated solvents, pharmaceuticals) released in major amounts to nearly all compartments of the environment. Soils and sediments as complex matrices provide a wide variety of binding sites and are the major sinks for these compounds [1]. Xenobiotics entering these complex systems may undergo various turnover processes. They can be degraded chemically (e.g. photolysis), biologically by microorganisms, volatilised, leached to the groundwater or taken up by living organisms or immobilised in the form of non-extractable residues (NER) [1]. Pesticides are of particular interest, since they are applied in considerable amounts to soils used for food crop production [2]. The term "non-extractable residues" (NER) according to a definition by IUPAC is reserved for the parent compound and its metabolites originating from pesticides, which are not extractable from soil with appropriate solvents that do not change the properties of the extracted matrix significantly [3]. The formation of NER from a pesticide or other xenobiotic in soil is generally considered to be based on various physical and chemical interactions between the parent xenobiotic or its xenobiotic metabolites and soil organic matter (SOM), clay minerals, and organo-clay complexes [4]. However, recent results showed that NER formed from degradation of xenobiotics can be also of biogenic origin [5, 6]. Therefore, the aim of this presentation is to provide a comprehensive overview about NER formation from xenobiotics and to distinguish between various types of NER and their relevance in human and environmental health.

## 2. Materials and methods

For a detailed understanding of the processes of NER formation from xenobiotics, a thorough review of the literature was performed and combined with recent results providing evidence for the formation of biogenic NER. In addition to available studies on NER formation, several experimental data from incubation of different classes of stable isotope labelled tracer compounds (e.g. <sup>13</sup>C<sub>6</sub>-2,4-D, <sup>13</sup>C<sub>6</sub>-ibuprofen, <sup>13</sup>C<sub>3</sub><sup>15</sup>N-glyphosate and <sup>13</sup>C<sub>10</sub><sup>15</sup>N-bentazone) will be also summarized.

## 3. Results and discussion

Depending on environmental conditions, xenobiotic structure, degradation kinetics, and sorption properties or concentration of the xenobiotic, different types of NER can be formed. The dissolved xenobiotic and/or its degradation products present in the environment may become either *sequestered (type I*, adsorbed or entrapped) within the soil matrix, e.g. in pores and voids of organo-clay complexes, in SOM aggregates, or *chemically bound (type II)* via covalent bonds to SOM ultimately forming NER. Therefore, NER formed during degradation of an organic contaminant in soil are commonly divided into these two binding modes [8, 9, 10, 3]. To date, the parent xenobiotic and its metabolites are believed to interact with SOM or clays forming NER [4] of either *type I* or *type II*, i.e. NER in strict sense according to the IUPAC definition [4]. Recent studies with readily biodegradable compounds (<sup>13</sup>C<sub>6</sub>-2,4-D, <sup>13</sup>C<sub>6</sub>-ibuprofen, <sup>13</sup>C<sub>3</sub><sup>15</sup>N-glyphosate) showed that the NER identified by isotope mass balance are of biogenic origin. Therefore, the actual NER classification needs to be extended to a new classification scheme in terms of compounds forming the NER: into *xenobiotic NER*, which are composed of sequestered or bound parent xenobiotic and / or xenobiotic metabolites (*type I* and *II*) and into *biogenic NER (type III, bioNER)* containing natural biomass compounds (see Figure 1).

BioNER should be clearly distinguished from the xenobiotic NER of type I and II, since the processes of abiotic NER formation and biodegradation resulting in biotic NER formations are competing processes. BioNER in soil are composed of mostly microbial biomass components, which are natural products and thus explicitly excluded from the IUPAC definition of NER [4]. Therefore, they are usually not analysed in terms of structural identification but are included in the NER pool. In <sup>14</sup>C-isotope studies the mass balance data thus

bias the risk assessment and lead to overestimation of the risk of NER. In particular for biodegradable xenobiotic compounds, bioNER formation in soil cannot be excluded, and their formation is strongly related to the presence of potential degraders. In contrast, xenobiotic NER are usually relevant for non-biodegradable or compounds toxic to microorganisms. A proper understanding of on-going processes in soil, e.g. bioavailability, degradability, toxicity dependence, and NER formation (including bioNER) is needed for complex soil systems and sediments.

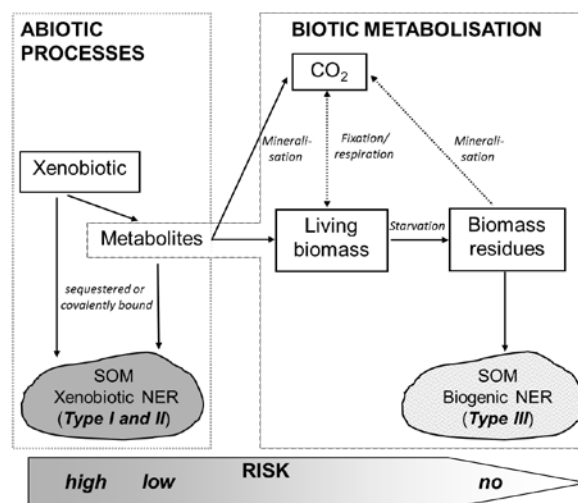


Figure 1. Scheme of abiotic and biotic NER formation including microbial degradation of organic compounds in soil: Type I (sequestered), Type II (covalently bound) and bioNER (type III).

#### 4. Conclusions and outlook

It is necessary to distinguish between the three types of NER [7] in order to access properly the respective xenobiotic degradation rate and to estimate its potential risks for human and environment. Low or no CO<sub>2</sub> indicates mainly the formation of xenobiotic NER (type I and II), whereas the major formation of bioNER is expected for xenobiotics displaying high mineralisation rate in a short time course. However, in case of more recalcitrant xenobiotics, but non-toxic to microorganisms like bentazone, the formation of bioNER cannot be completely excluded.

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