Residue

Risk reduction of chemical residues in soils and crops:
impact due to wastewater used for irrigation

Research on the environmental fate of organic chemicals using ^{14}C-radiolabelling

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PRIMA PARTNERSHIP FOR RESEARCH AND INNOVATION IN THE MEDITERRANEAN AREA | Fraunhofer IME | Freie Universität Berlin | CSIC Consejo Superior de Investigaciones Científicas | PHYTOR | Consorzio Italbiotec | האוניברסיטה העברית בירושלים THE HEBREW UNIVERSITY OF JERUSALEM

Carbon-14 / ^{14}C

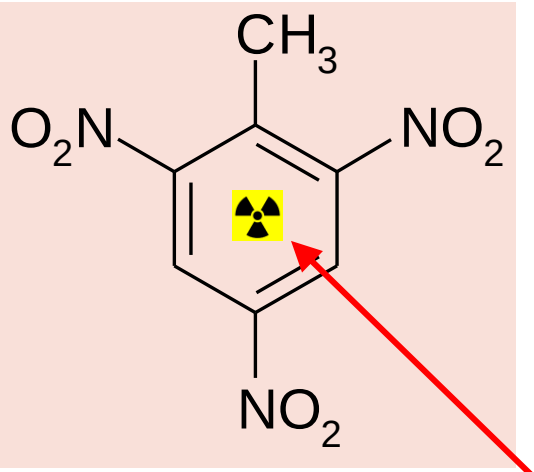
- Carbon-14, C-14, ^{14}C or radiocarbon
- Radioactive isotope
- Unstable with a half life of about 5700 years,
  ^{14}C decays into nitrogen-14 (^{14}N) through beta decay
- Sources: cosmic ray action on nitrogen in the atmosphere (cosmogenic nuclide),
  open air nuclear testing (1955-1980)

Carbon-12	Carbon-13	Carbon-14 
6 Electrons 6 Protons 6 Neutrons	6 Electrons 6 Protons 7 Neutrons	6 Electrons 6 Protons 8 Neutrons
Nuclear/mass number 6+6= 12	Nuclear/mass number 6+7= 13	Nuclear/mass number 6+8= 14
99% of all carbon	up to 1% of all carbon	trace amounts (ca. 1 per 10^{12} atoms)

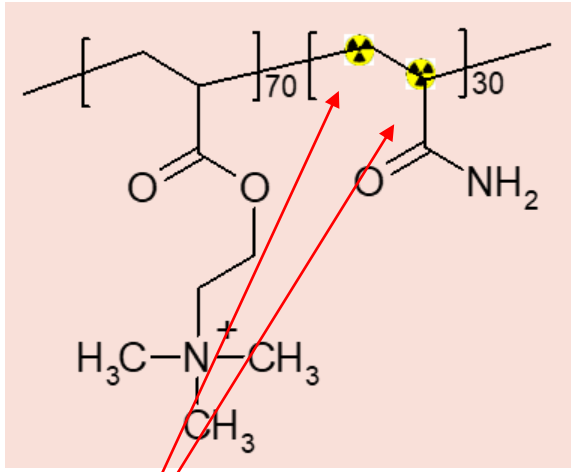
Residue

^{14}C-Labelling

2,4,6-TNT
(explosive)



Polyacrylamide
(polymere)



- Radioactivity
- Unit: Bequerel (**Bq**), an older unit is Curie (**Cu**)
- Labelling in the aromatic ring (U-label) or at specific positions in the molecule

One or more ^{12}C-atoms replaced by ^{14}C-atoms

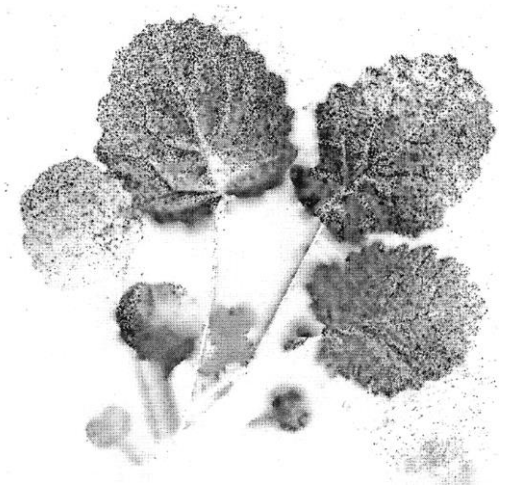
Residue

^{14}C-Labelling

- **Radiation protection: License for ^{14}C necessary**
- **Handling of ^{14}C-labelled test substances only in supervised or controlled areas (laboratories or outdoor facilities)**

Residue

Measuring radioactivity

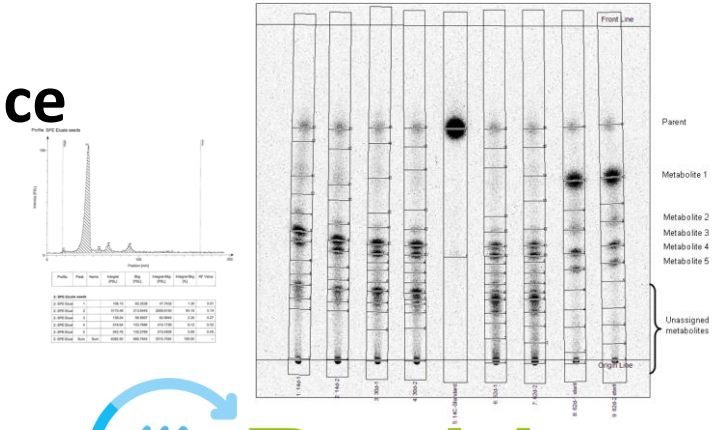


Detection of radioactivity (non-specific)

- Monitors measuring radioactivity on surfaces
- Liquid Scintillation Counting (LSC): Quantification of radioactivity in liquids
- Oxidizer: Combustion of solids followed by quantification of radioactivity ba Liquid Scintillation Counting (LSC)

Chromatographic measurements – What kind of substance (still including the radiolabel) is it? (specific)

- Radio-HPLC: HPLC equipped with an radiodetector
- Radio-TLC: TLC plates exposed to imaging plates sensitive to radioactive radiation



Residue

Aim and advantages of radiolabelling

- Conventional analytical method (e.g. residue analytical method) for environmental matrices like soil, sediment, plant tissue etc.:
  You need to know for which substance your are looking for!

- ^{14}C-labelling:
  The substance is carrying a label so all metabolites until $^{14}CO_2$ can be tracked, i.e. the fate of the substance can be traced back by the radioactivity

  Any radioactivity detected must be derived from the parent compound!

Where is it?

Is it parent compound?

Degradation to CO_2?

Are there metabolites detectable? Which ones?

Is there adsorption to soil or plant matrix?

Is something volatile formed?

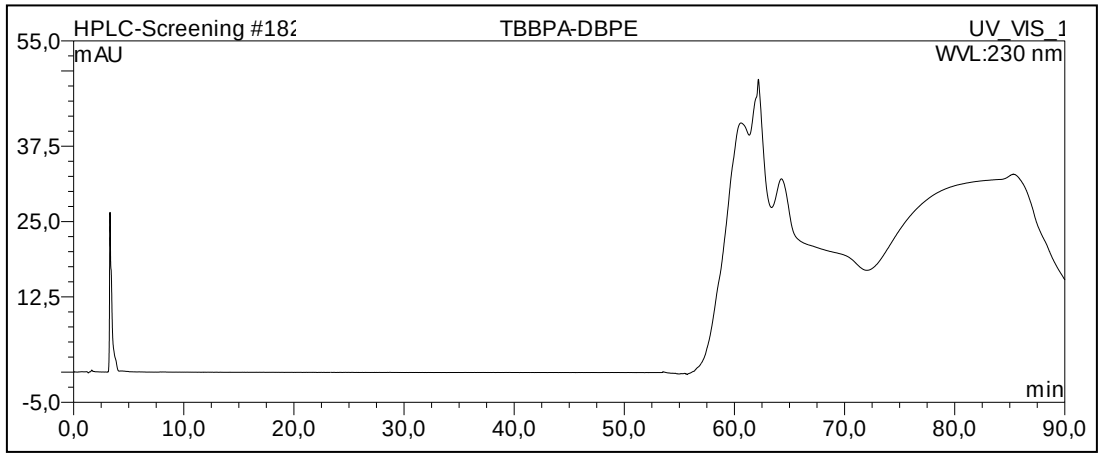
Natural matrices like soil, plant material, sediment etc. are very complex and contain thousands of different organic substances.

To find a definite substance is like looking for a needle in a haystack

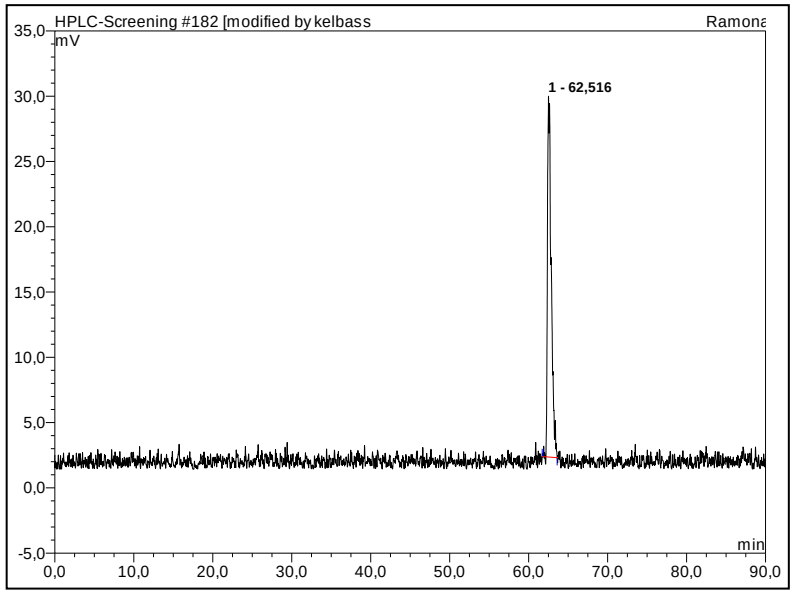
Residue

Aim and advantages of radiolabelling

HPLC analysis:
UV-detection



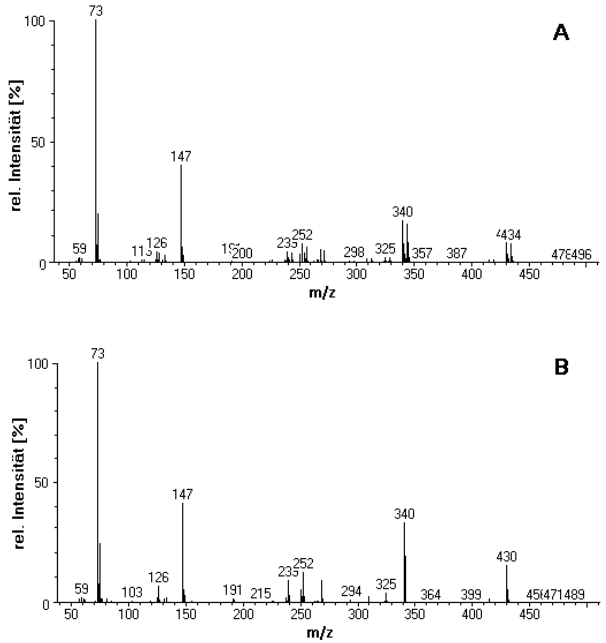
HPLC analysis:
radiodetection



Residue

Aim and advantages of radiolabelling

- Metabolites can be traced back to the parent compound definitely
- Identification of the metabolites is possible by LC-HRMS and radiodetection and/or the characteristic exact masses

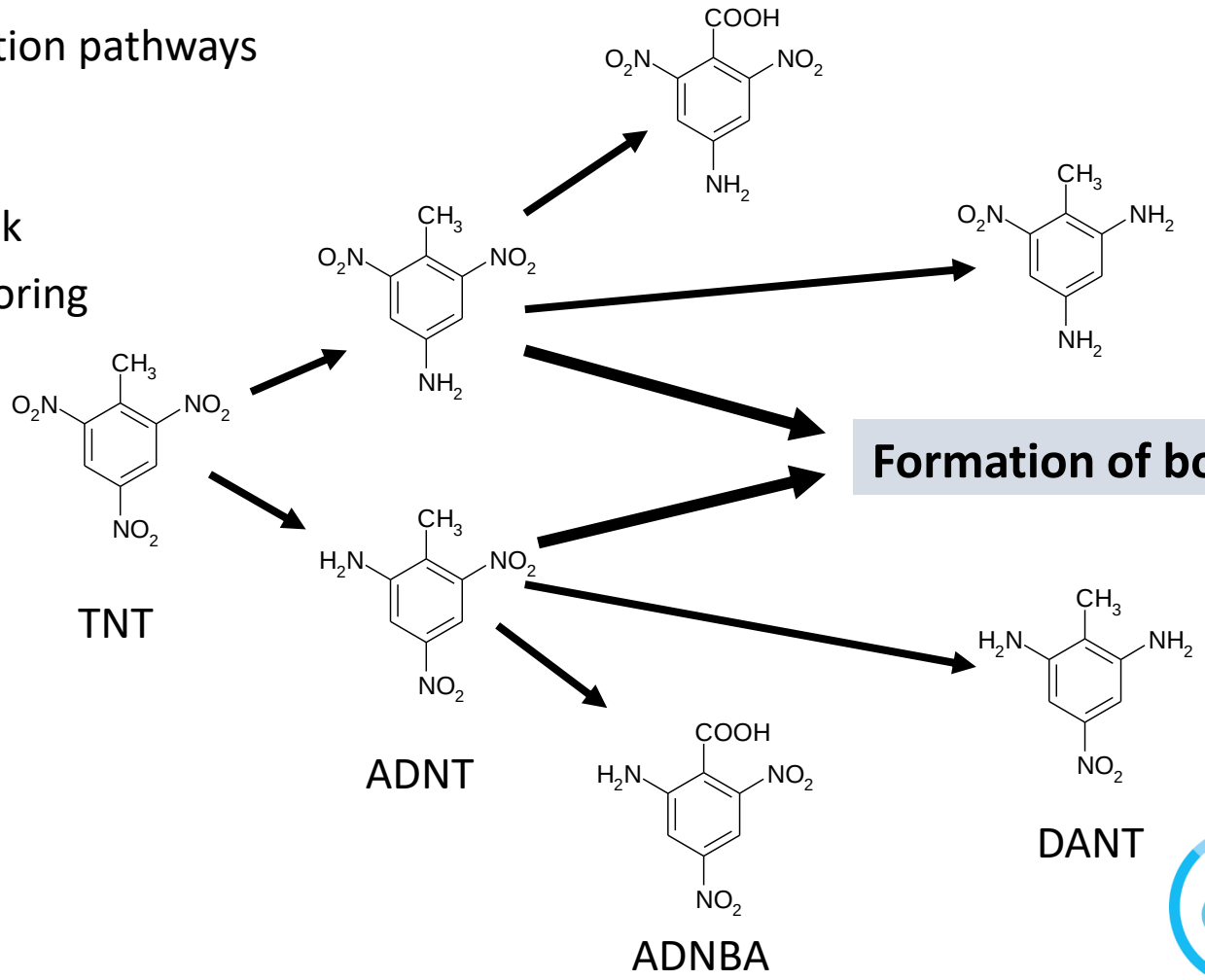


Mass spectrum of a BaP metabolite of radiolabelled (A) or non-labelled (B) test sets

Residue

Aim and advantages of radiolabelling

- Elucidation of degradation pathways (route of degradation)
- Basic knowledge for risk assessment and monitoring

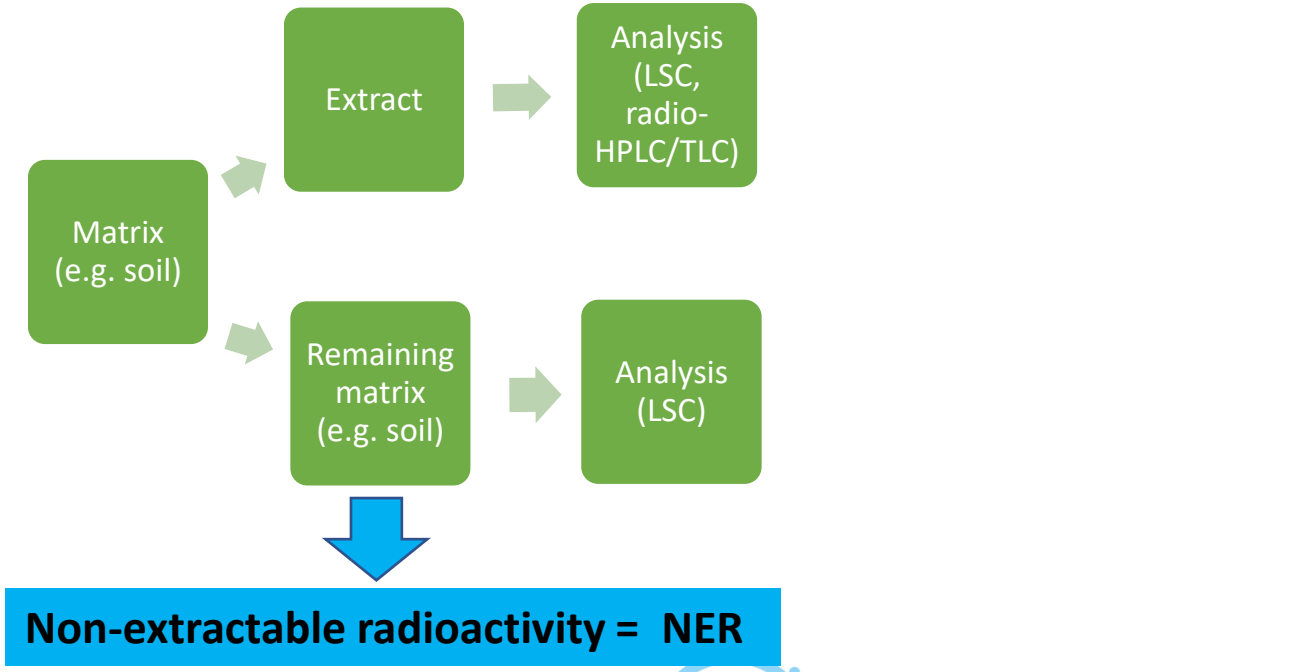


Residue

Non-extractable Radioactivity (NER)

Using non-labelled chemicals

Using ^{14}C-labelled chemicals



Residue

Mass balances

- Mass balances based on radioactivity recovered in the different compartments are possible

Radioactivity detected in extract(s) [% of applied radioactivity]	Radioactivity detected in the matrix after extraction NER [% of applied radioactivity]	Radioactivity detected in traps for $^{14}CO_2$ [% of applied radioactivity]	Radioactivity detected in traps for organic volatiles [% of applied radioactivity]	Total recovery [% of applied radioactivity]	
90	5	2	n.d.	97	√
5	3	10	60	78	

Residue

Test systems

- Test systems for environmental simulation studies in a lab scale - for research or regulatory approval

Investigating the fate of an organic substance

Hydrolysis, Photolysis (OECD 111,

Adsorption/Desorption (OECD 106)

Transformation in Soil (OECD 307)

Transformation in Water/Sediment Systems (OECD 308)

Transformation in Surface Water (OECD 309)

Degradation in Sewage Treatment Plants (OECD 314)

Metabolism in Plants (OECD 501)

Metabolism in Rotational Crops (OECD 502)

Lysimeter Studies

Residue

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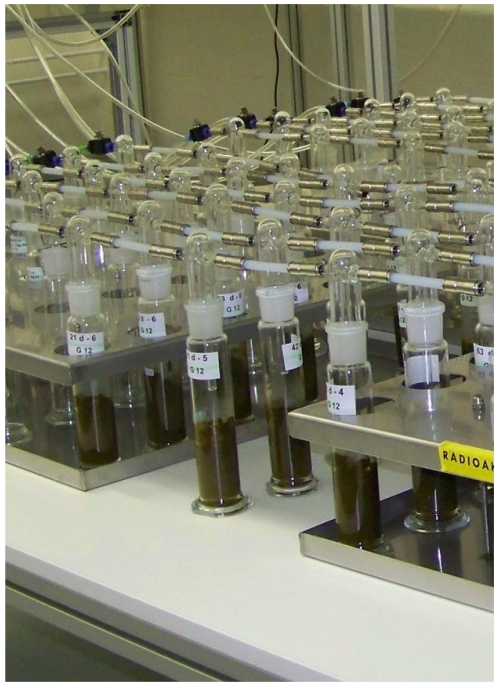

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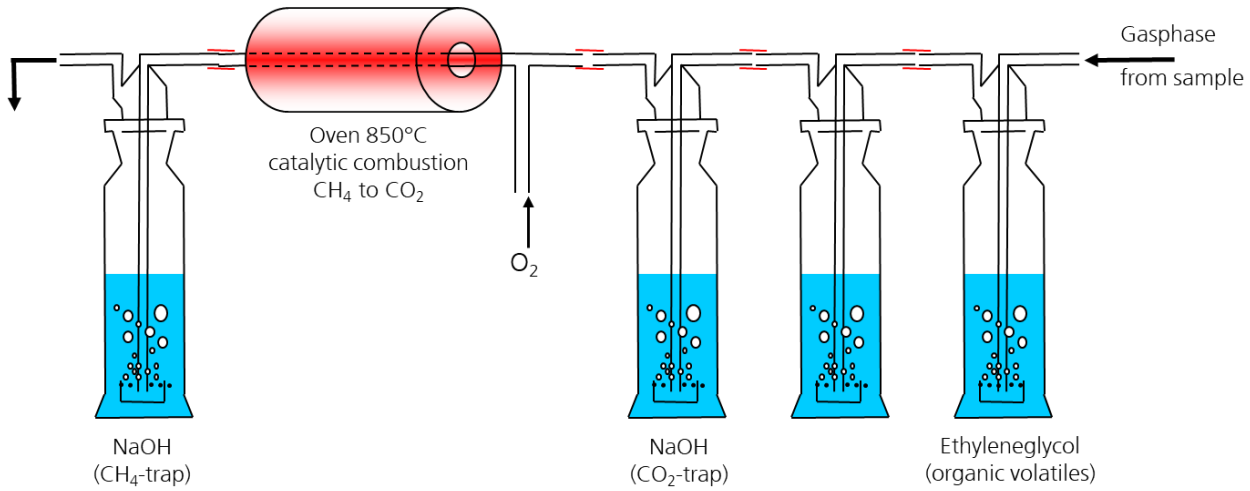
Scheme of gas traps (anaerobic)



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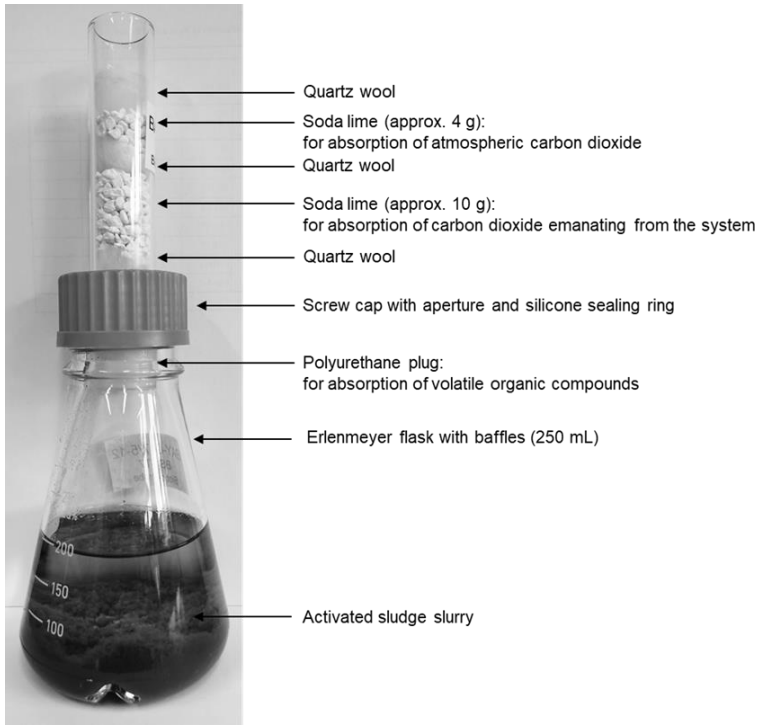

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Lysimeter Studies

Residue

Test systems

- Outdoor studies in a bigger scale

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Lysimeter Studies

Residue

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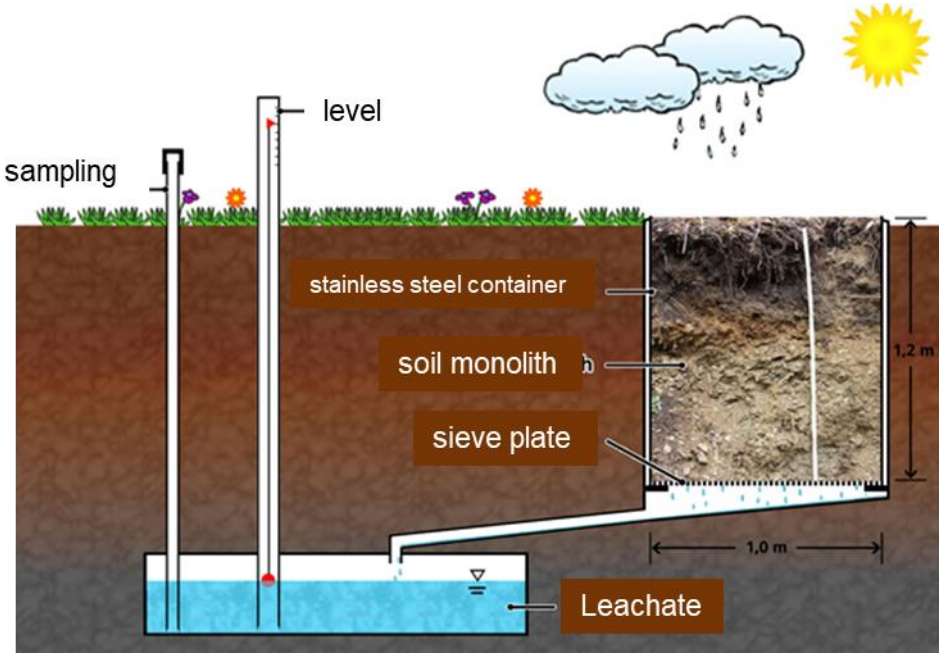

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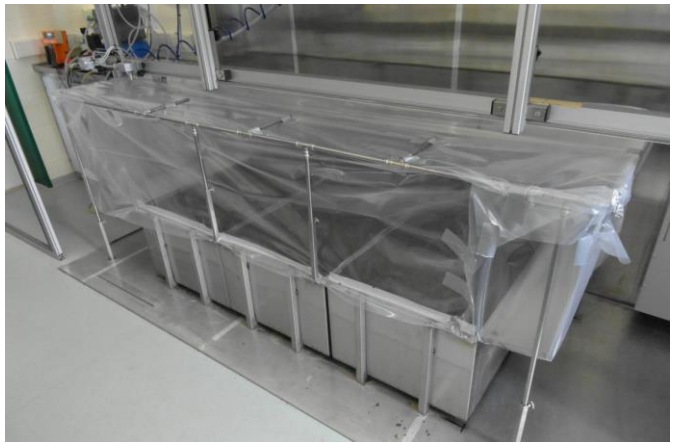
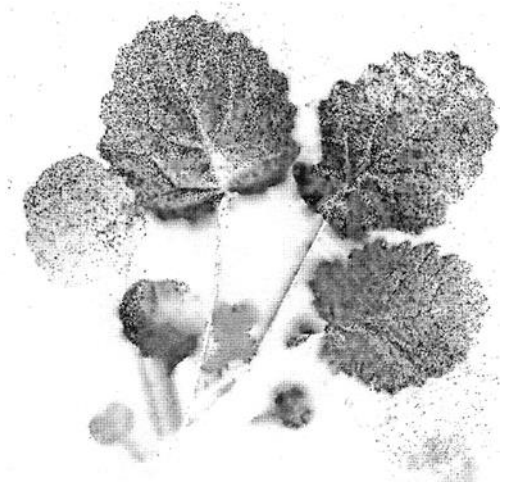
Lysimeter Studies

Residue

Application

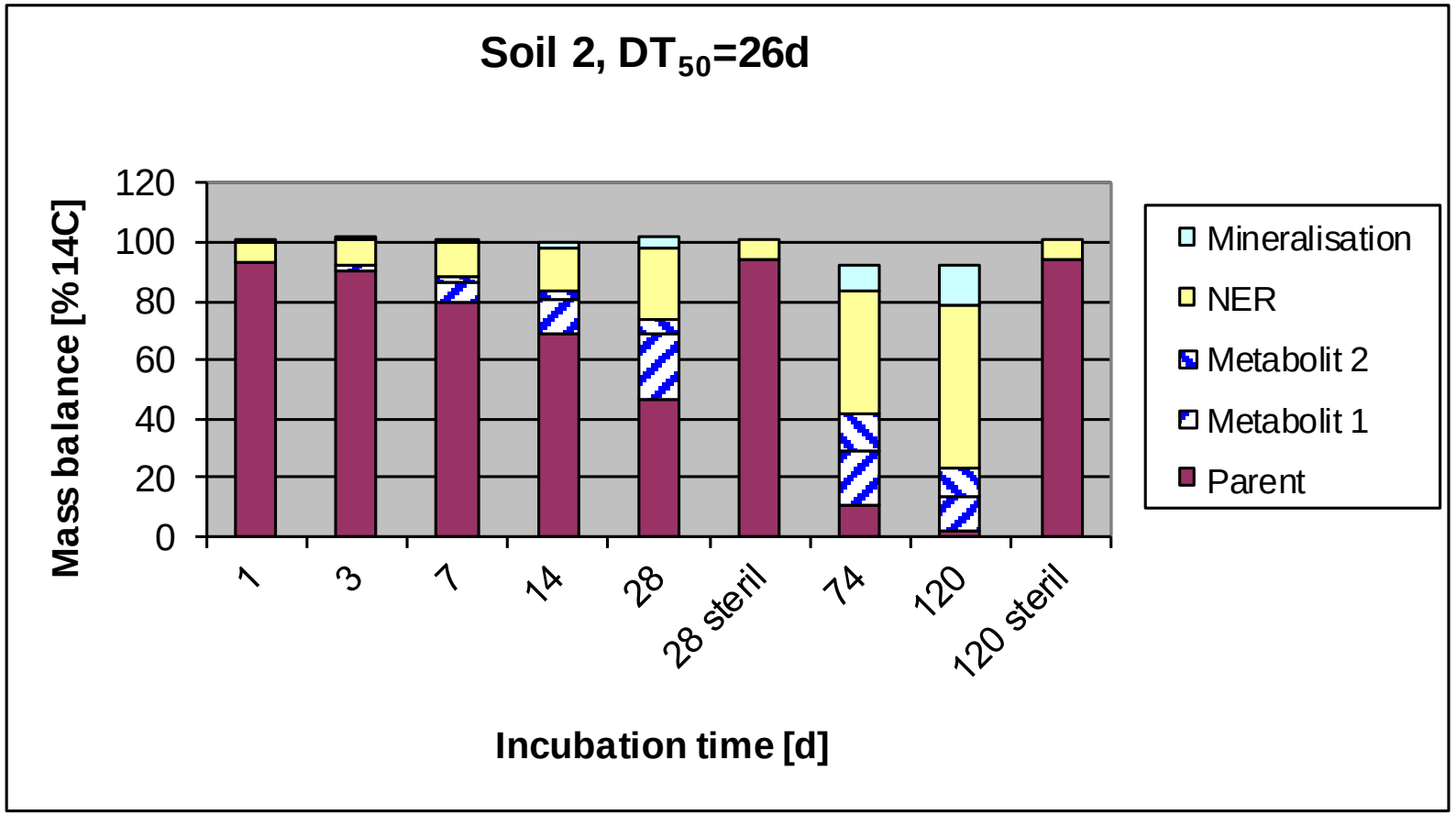




Residue

Degradation / Transformation in Soil

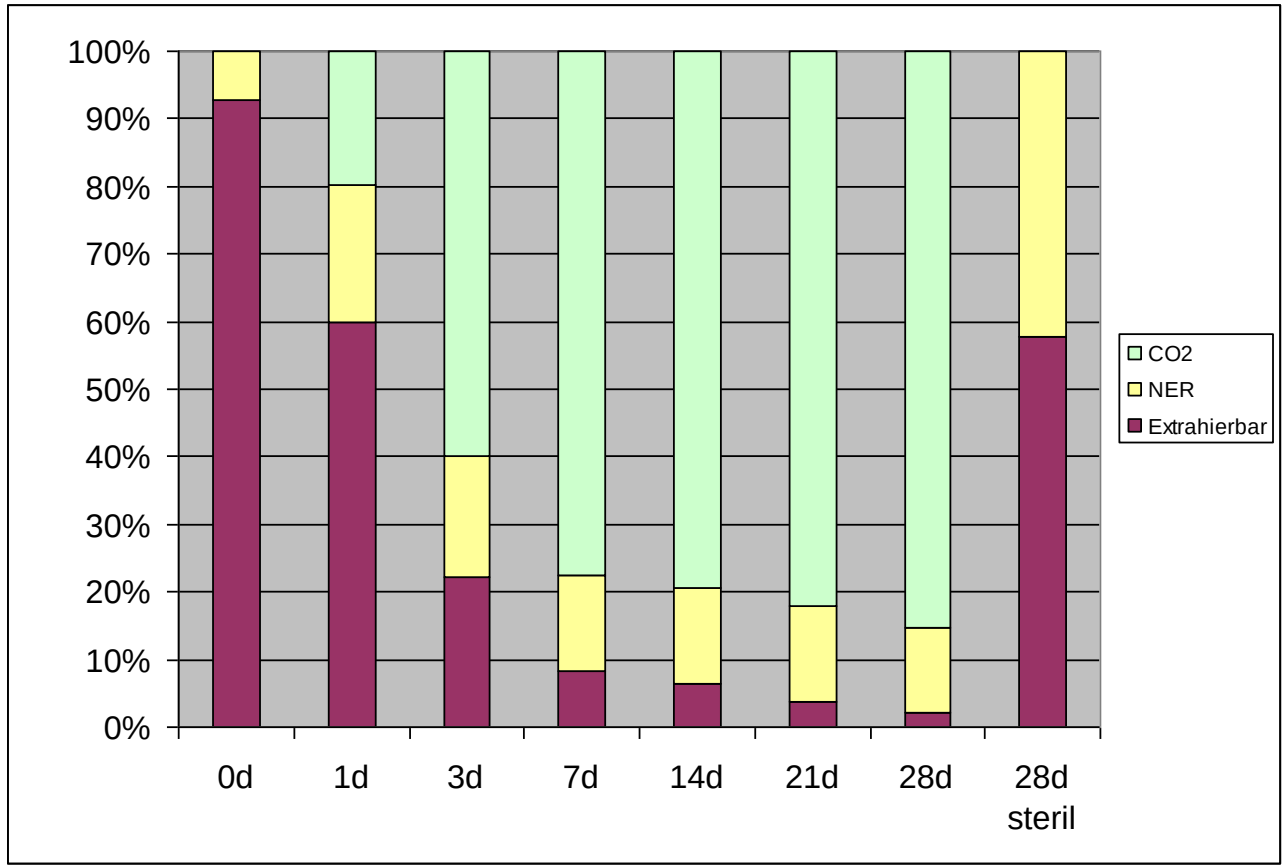
- Example 1: Degradation of a pesticide



- DT50 of parent compound was 26d, metabolites are formed
- Mineralisation is low
- NER-formation biotic

Degradation / Transformation in Soil

- Example 2: Degradation of an antibiotic

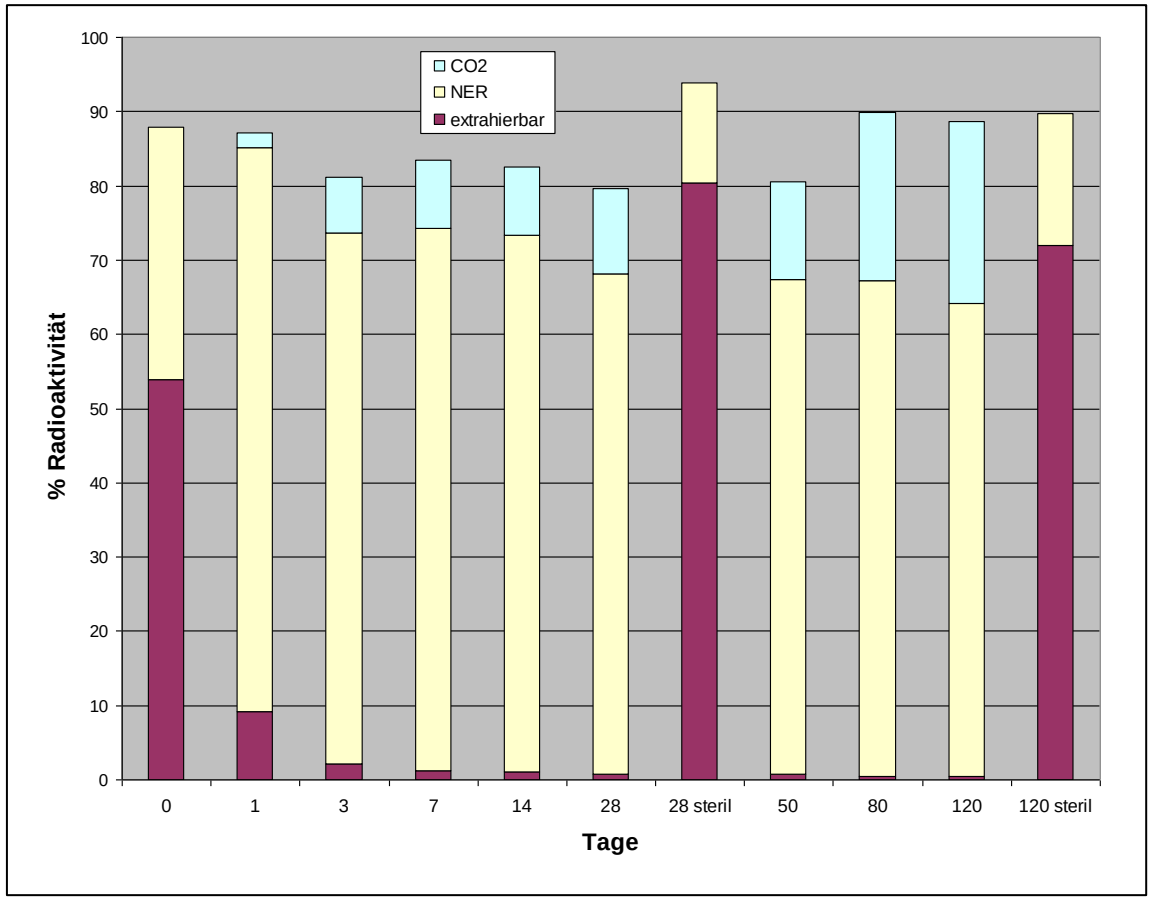


- Rapid mineralisition
- NER-formation abiotic
- Stopped at 28 d
  (90% Trigger reached)

Residue

Degradation / Transformation in Soil

- Example 3: Degradation of an another antibiotic compound



- Rapid NER-generation but:
- Nevertheless considerable mineralisation till study end!

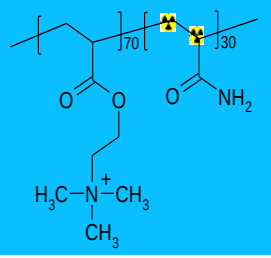
Main reason for NER: biotic processes!

Apparently bioavailability of NER

No release of parent substance!

Residue

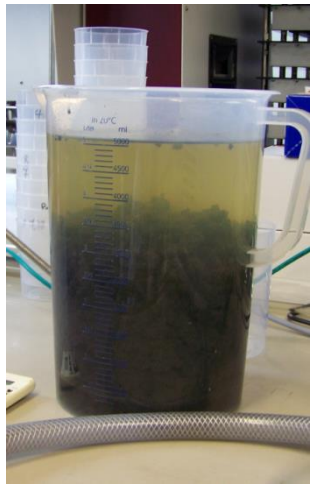
Degradation of Polymers



Fate testing of polymeric flocculants

- Synthesis of ^{14}C-polyacrylamide
  Average molecular weight: 6 Mio Da

Sewage sludge

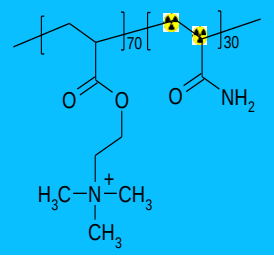


flocculation

dewatering

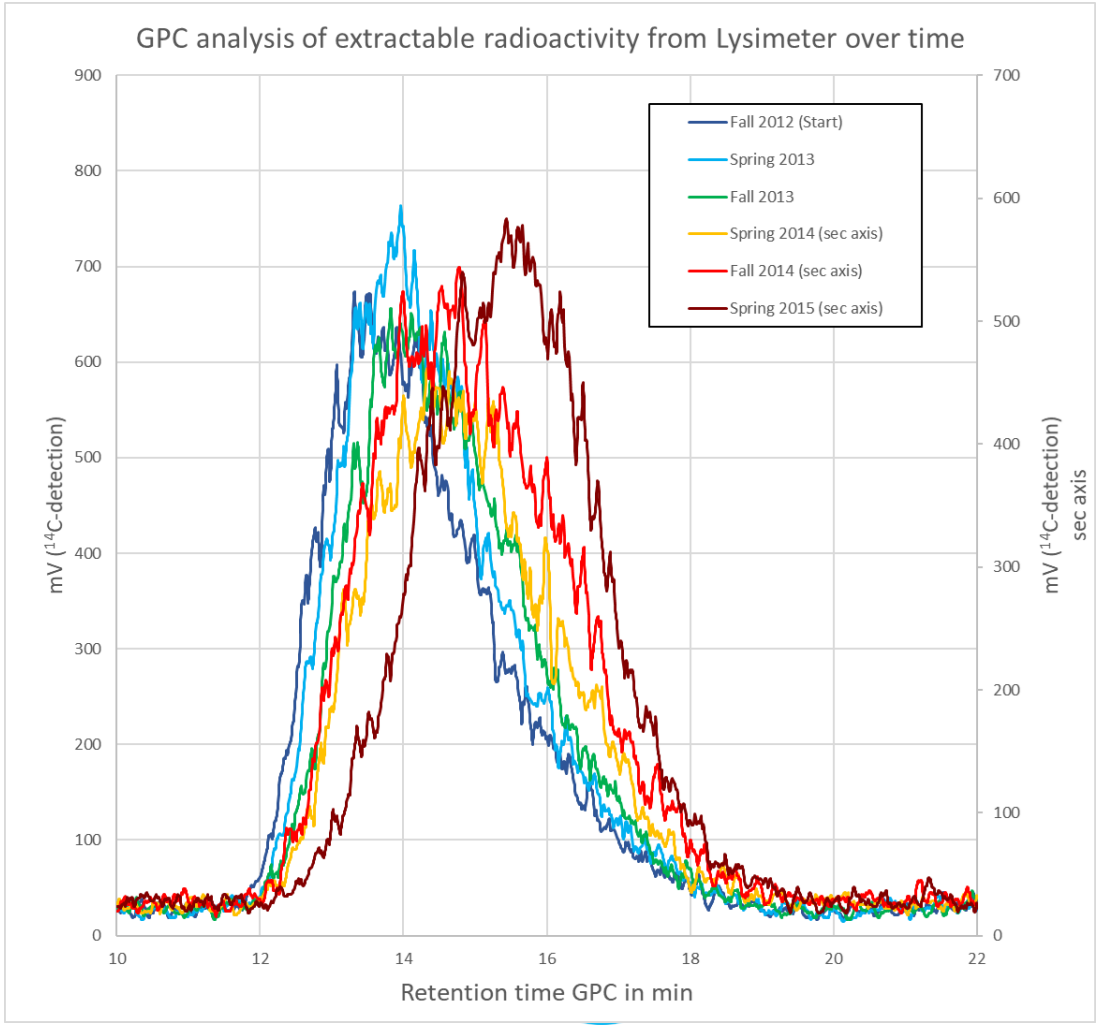
Application to outdoor soil lysimeter

Degradation of Polymers



Fate testing of polymeric flocculants

- GPC-analysis (separation by hydrodynamic volume of molecules, largest molecules elute first) coupled to ^{14}C-detection
- Over time the distribution of the molecular masses shifted to smaller sizes



RESIDUE

Irrigation of plants with (artificial) wastewater including ^{14}C-labelled Lamotrigine and Carbamazepine

Uptake of the radiolabel into the plants

Many thanks for your attention

Contact

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