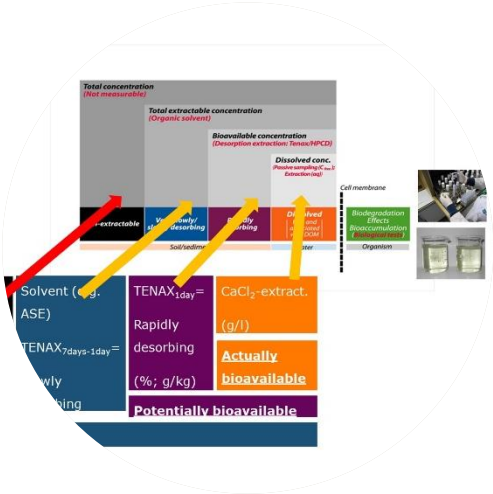
The development of procedures to establish the toxicity of non-extractable residues (NER) in soil

Joop Harmsen, Dieter Hennecke, Kerstin Hund-Rinke, Joost Lahr, John Deneer



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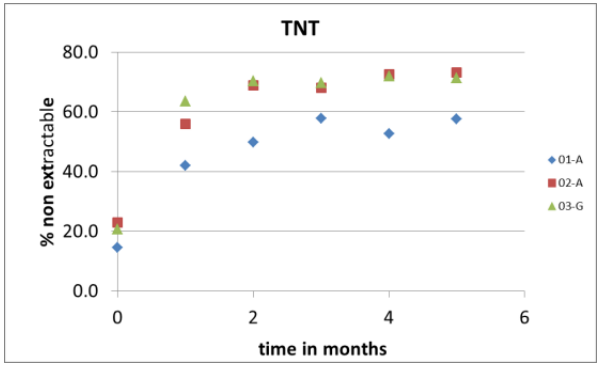
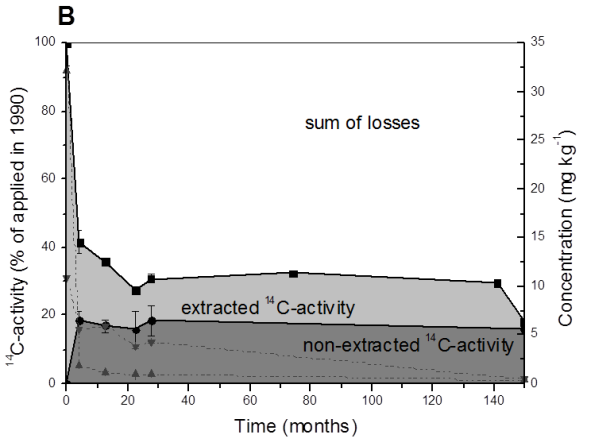
NER - detoxification process?
- or is it a hidden hazard?

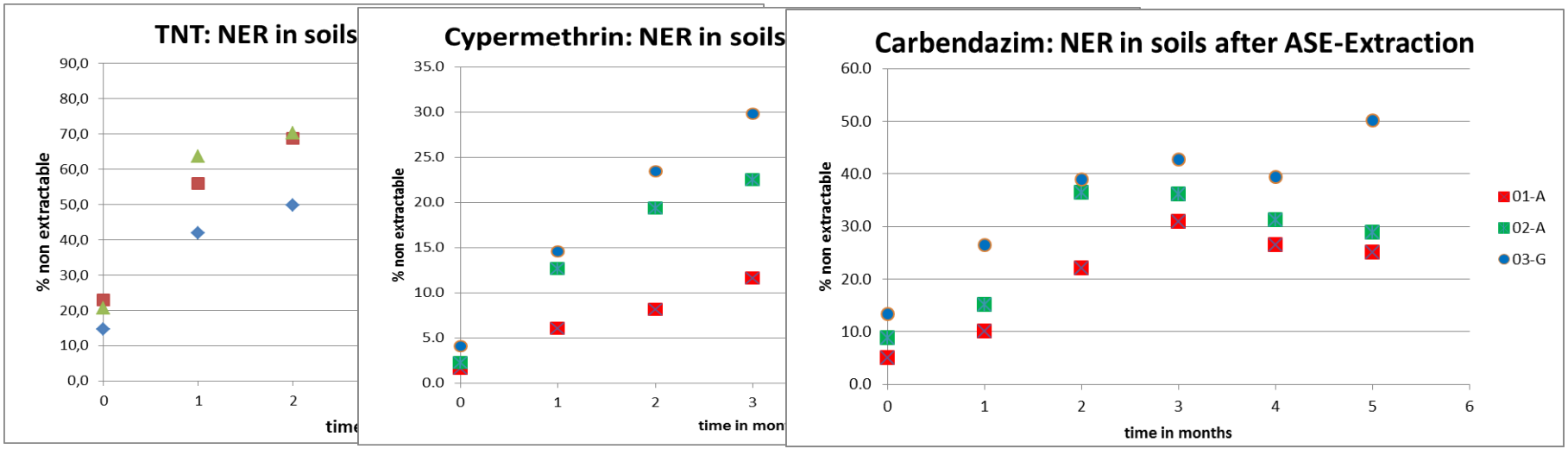
- Formation and presence
  - Association of the parent chemical or product with mineral and/or organic matter
  - incorporation into biomass
- NER can only be established using ^{14}C-radiolabelled/^{13}C compounds
- **Not detectable** in real life but should be **understandable and measurable**





Semple et al.

NER-formation, ^{14}C-experiment. Three selected chemicals



TNT	High NER-formation 60-75%
Cypermethrin	Low NER-formation 15-30%
Carbendazim	Intermediate 25-50%

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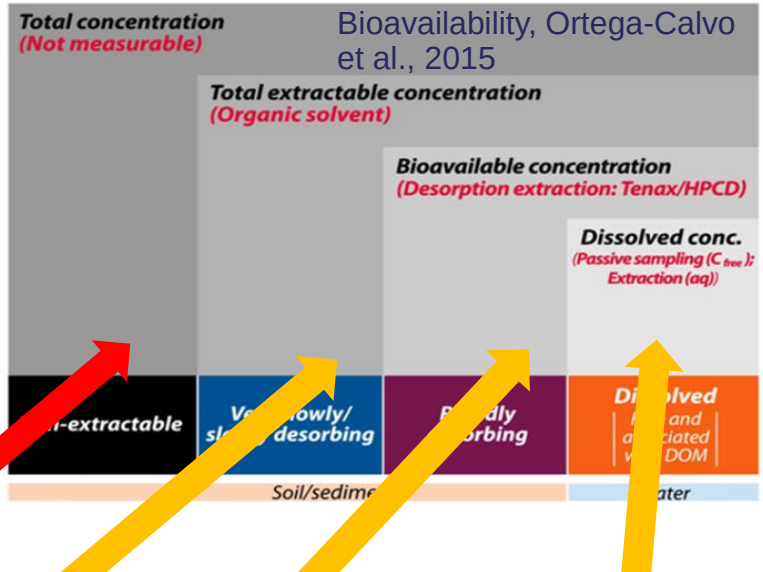
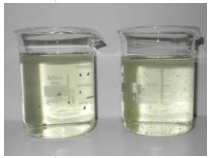
Make it measurable



Chemical Methods

Ecotoxicological Methods



^{14}C-study

(%)

^{12}C = not measurable

Acetonitri

ISO 11916.

ASE.

$TENAX_{20}$

ISO/TS 16751

(%; g/kg)

$CaCl_2$-extract.

(g/l)

Actually bioavailable

Potentially bioavailable

TOTAL

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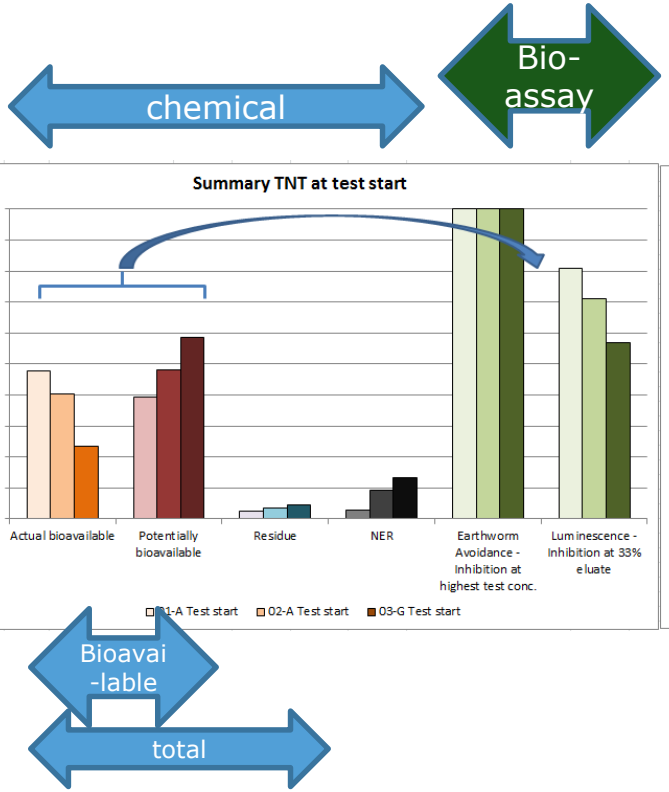
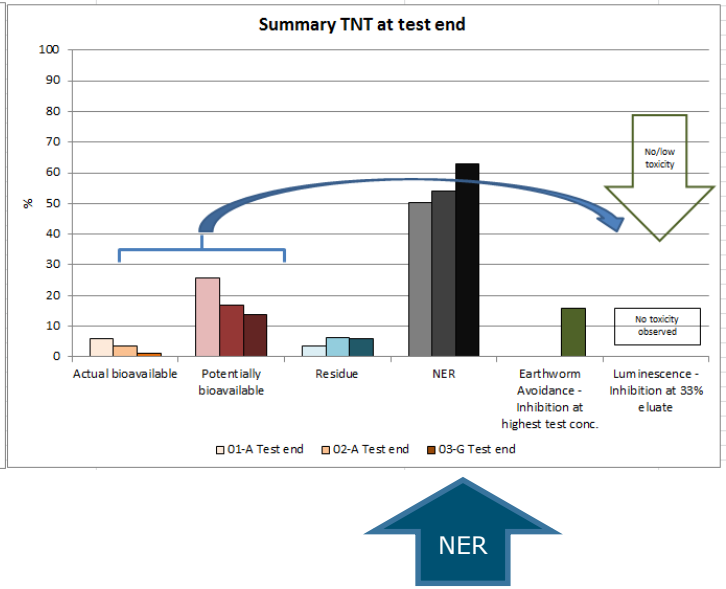
Method development TNT (^{14}C)

- TNT has a high water solubility
- High NER-formation during aging
- Aging reduces bioavailability and toxicity
- Easily explainable (continuous NER formation)





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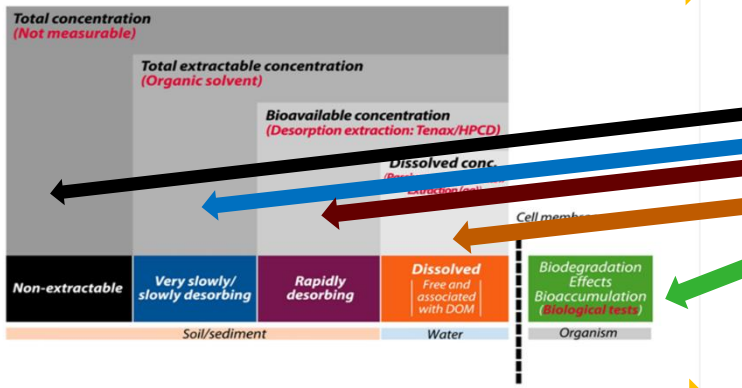
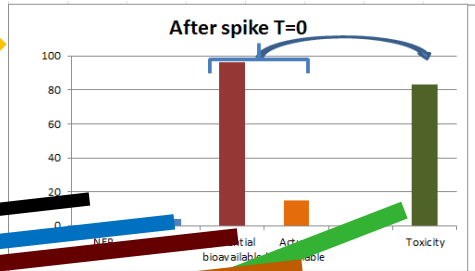
TNT, test ready for non-labelled application

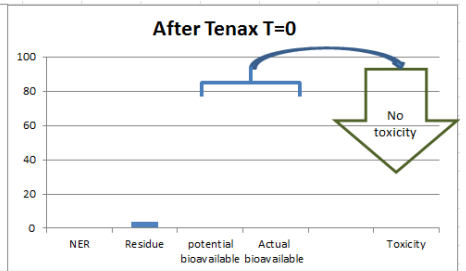
All fractions in soil

Bioavailable part removed with TENAX

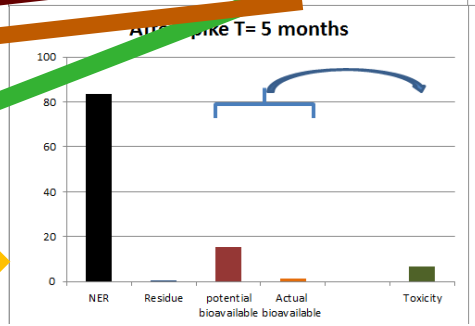
Spiked

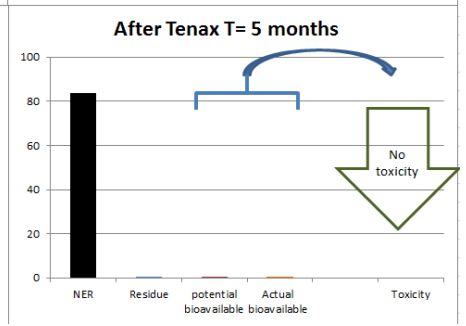






Aged





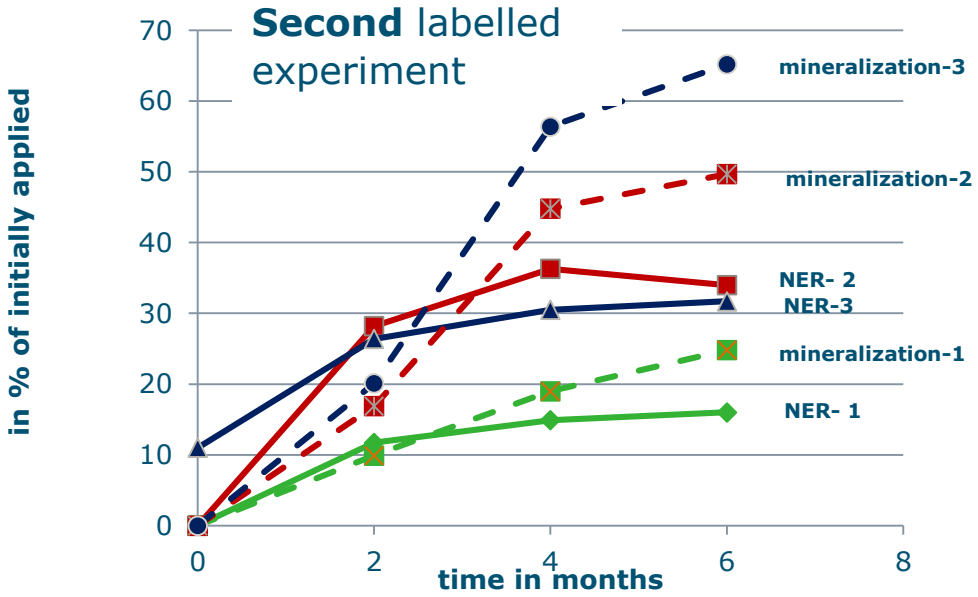
Conclusion:
Bioavailable part explains toxicity

NER, residue and potentially bioavailable in %
Actually bioavailable in mg/l
Toxicity (microtox) in $1/Ec_{20}$

Method development cypermethrin

- **First** labelled experiment. At 120 mg/kg only 2-4% mineralized in 6 months period
- 15-30% NER formation

- **Third** unlabelled experiment.
- 35% of added cypermethrin was not measured
- - NER-formation?
- - Mineralization?



Very high uncertainty on NER without ^{14}C-experiments

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Method development carbendazim

First labelled experiment

- 25-50% NER formation
- Proper mass balance

Second labelled experiment

- Total recovery radioactivity after 6 months 7% to 36% only,
- Most of radioactivity disappeared from system. Unexpected loss by volatile compound
- Degradation speed depends on soil, remaining radioactivity only partially due to parent

Very high uncertainty on NER without ^{14}C-experiments

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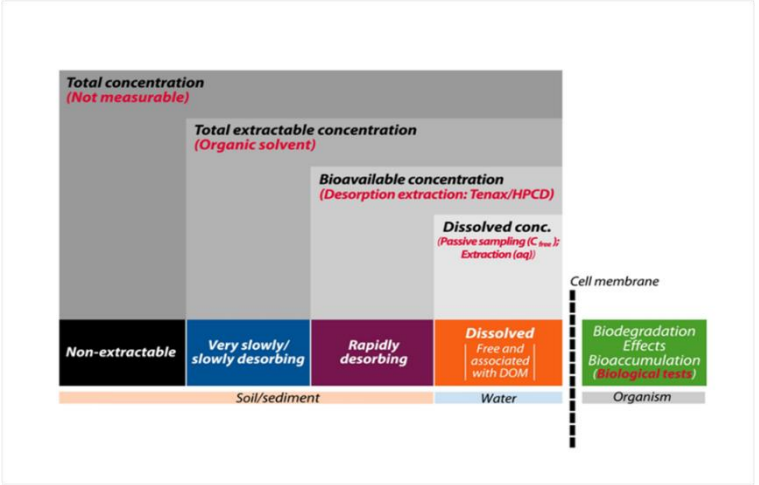
Conclusions (technical)

- If fate is known, a test with non-labelled chemical is available and results are well explainable (TNT);
  - Toxicity can be explained by the bioavailable chemical and not by NER;
- Uncertainties in fate (e.g. volatility, biodegradation) result in high uncertainty of NER.
  - Additional ^{14}C-experiments are necessary to eliminate uncertainties in a non-labelled test.



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Recommendations

9th Int. Workshop on Chemical Bioavailability in the Terrestrial Environment. Warsaw, November 2017

- If chemicals are non-extractable, they are strongly bound and will not cause risks
- In the past scientific communications and unclear definitions have caused uncertainty in regulatory context
- Present scientific "certainties" on bioavailability have to be communicated

This Project

- Make results of this project available for regulators
- Define shortcoming of current approaches (technical and regulatory)

Future work

- Eliminate uncertainties by using experiments including ^{14}C.
- Use generally accepted definitions

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Acknowledgement

This research is part of the Cefic-LRI program (ECO25)

We thank the monitoring group of ECO25, Bruno Hubesch (CEFIC-BE), Malyka Galay-Burgos and Lucy Wilmot (ECETOC), Charles Eadsforth and Joy Worden (Shell-GB), Chris Finnegan (Unilever-GB), Garry Roberts (GR Consulting-GB) and Gordon Sanders (Givaudan-CH) for their stimulating discussions.