Opportunities and Risks Related to the Use of Biobased Fertilizers (BBFs) to Close Nutrient Loops

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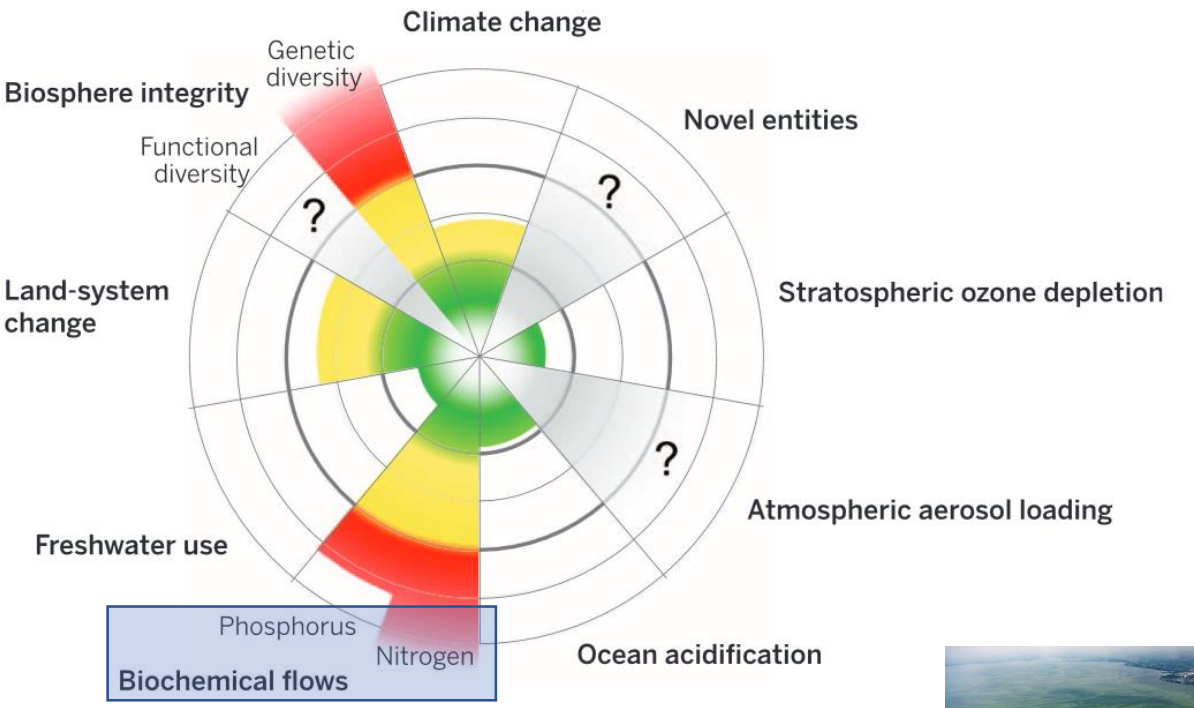
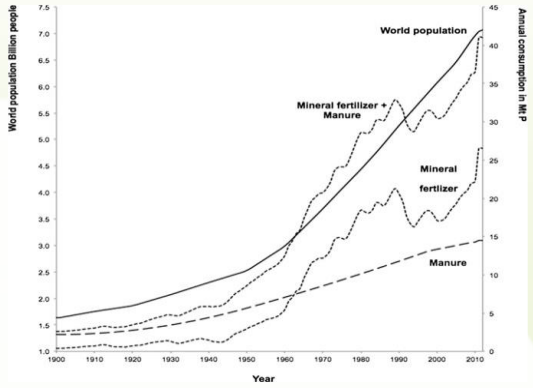
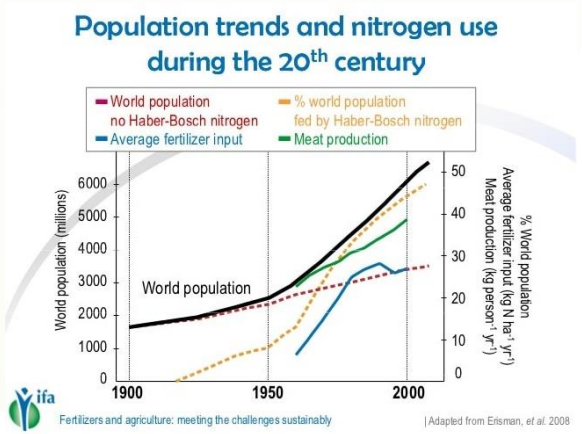
State of our nutrient cycles







Linear use..

Eutrophication

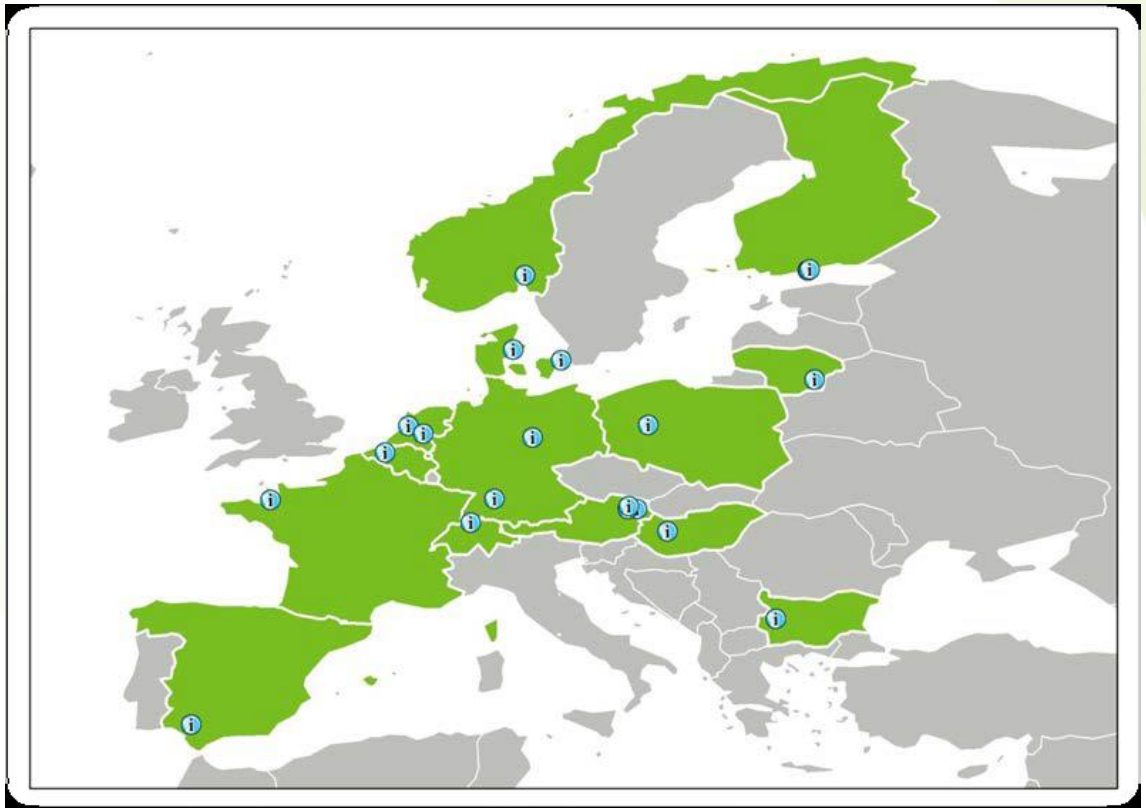
Steffen et al., *Science,* 2015,
Scholz et al., 2014, 10.1007/978-94-007-7250-2_1.
IFA, 2010.

The LEX4BIO project

- LEX4BIO provides the basis for closing the nutrient cycles at the European level
- LEX4BIO connects technology requirement for site specific fertilisers: producing efficient and safe BBFs regionally from nutrient-rich side-streams
- LEX4BIO provides a policy framework for optimizing the use of BBFs and evaluates socioeconomic impacts

LEX4BIO

- Total of 21 partners and 14 countries
- Project duration 1.6.2019 – 31.5.2024
- Budget 6 million €
- Consortium includes research institutions (6), Universities (8), SMEs (5) and industry partners (2)



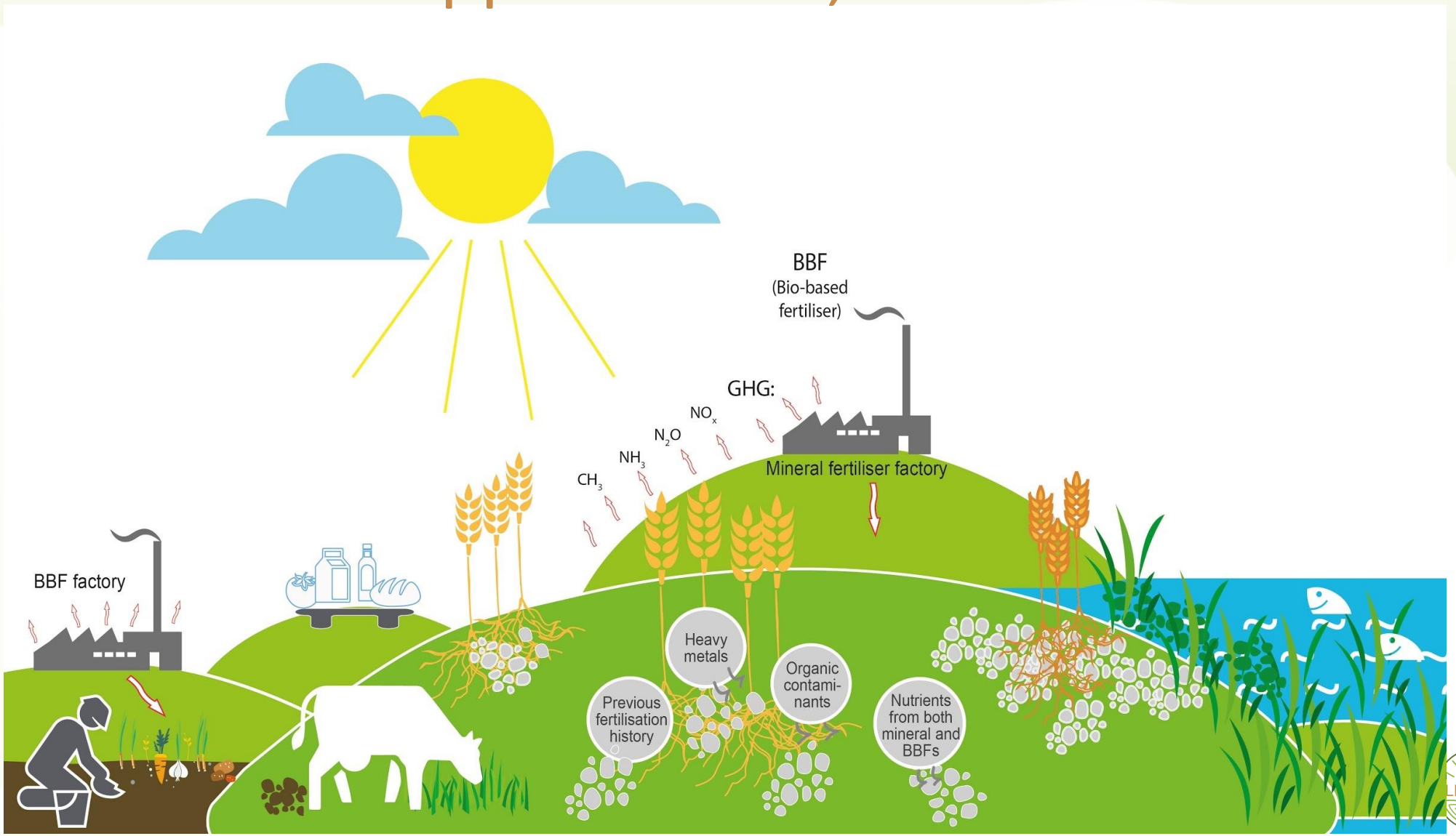
More details:
https://www.lex4bio.eu/

LEX4BIO

LEX4BIO consists of ten WPs

- WP1: Assessment of NRSS in the EU and their use as BBFs (lead JKI)
- WP2: General effects of BBFs on soil quality/functioning and plant growth (UHOH)
- WP3: Agronomic efficiency of BBFs as P source for crops (FiBL)
- WP4: Agronomic efficiency of BBFs as N source for crops (UCPH)
- WP5: Risk assessment of the application of BBFs (UvA)
- WP6: Life Cycle Assessment (LCA) (PM)
- WP7: Coherent policy framework and socioeconomic impacts for the use of BBFs (PAS)
- WP8: Dissemination and communication (EP)
- WP9: Project management (Luke)
- WP10: Ethics requirements (Luke)

BBFs: Great opportunities, but also risks…

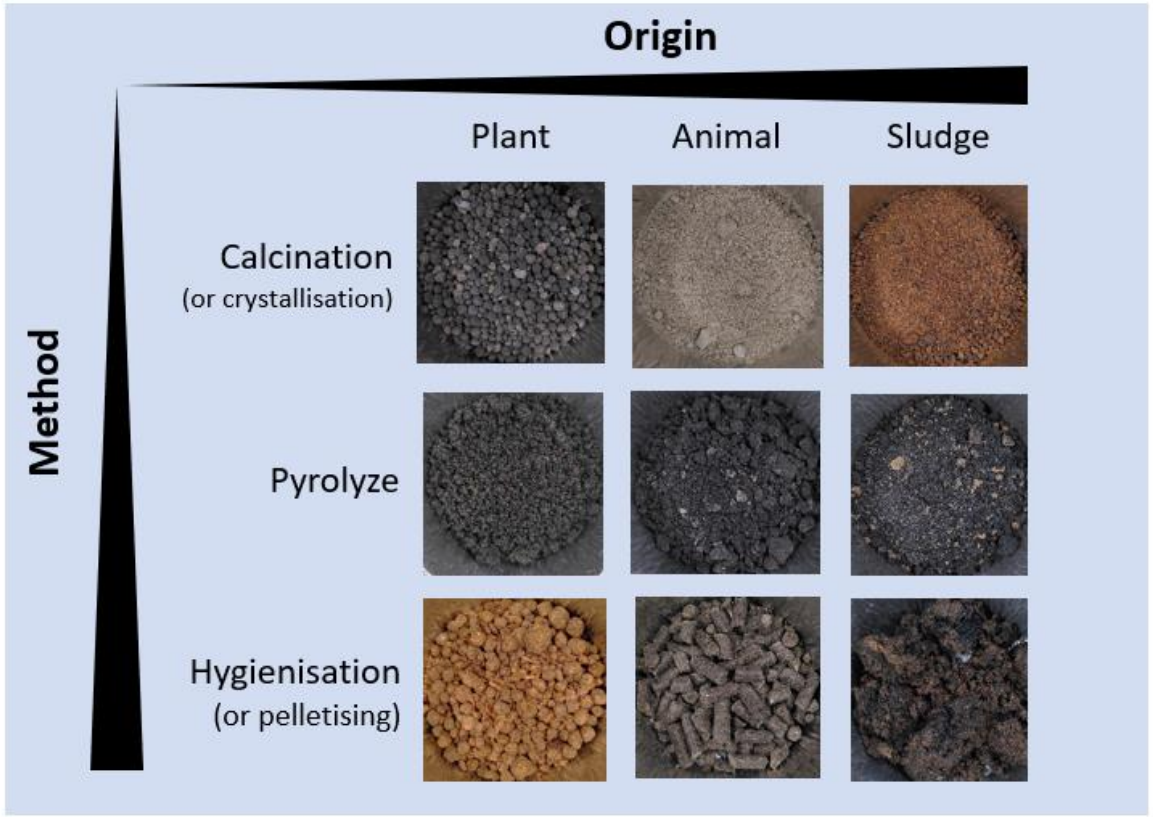


Case studies for today's presentation

- Screening of **13 low-risk commercial BBFs** for pollutants
- Screening of **two field-trail soils** for pollution after BBF application
- Results of a **persistency study of pollutants in soil**, and the influence of the (type of) BBF thereon

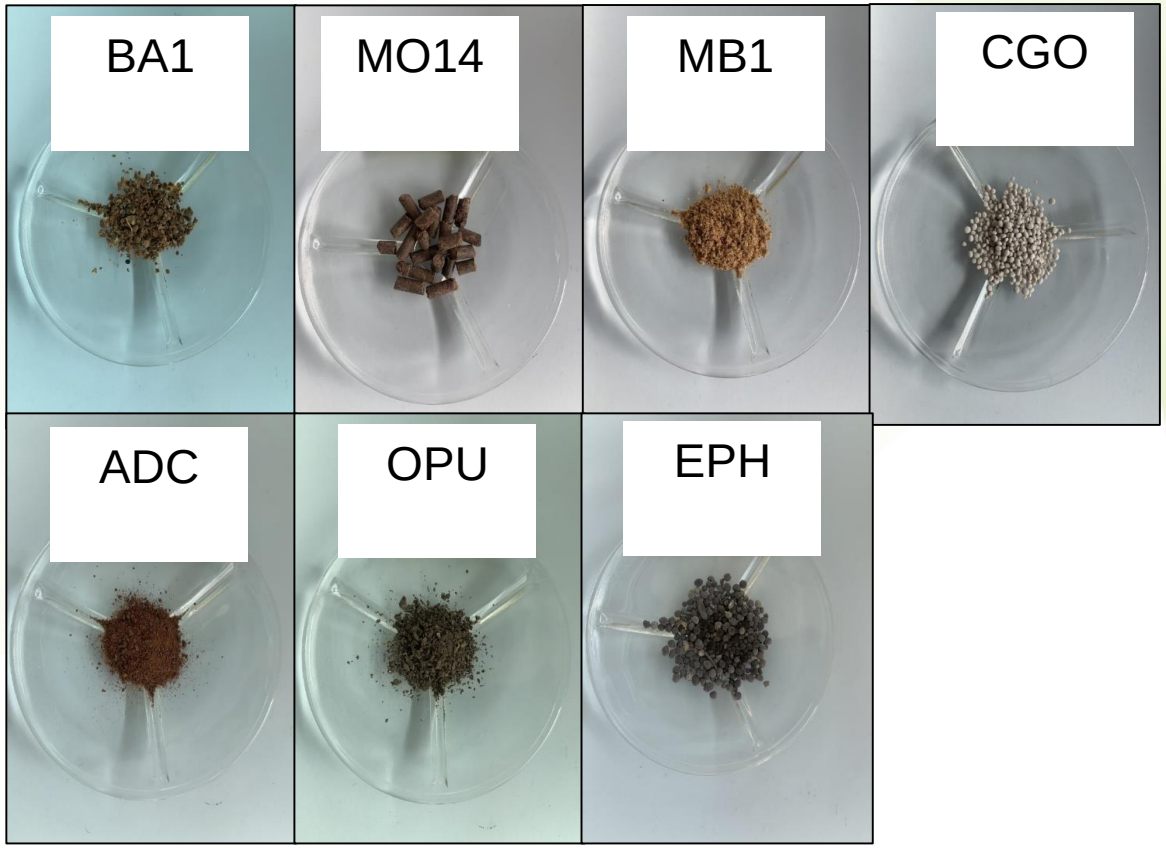
Various sources = various potential pollutants for soil and crops

- pesticides
- pharmaceuticals
- PCBs
- PAHs
- Dioxins
- Furans
- PFASs



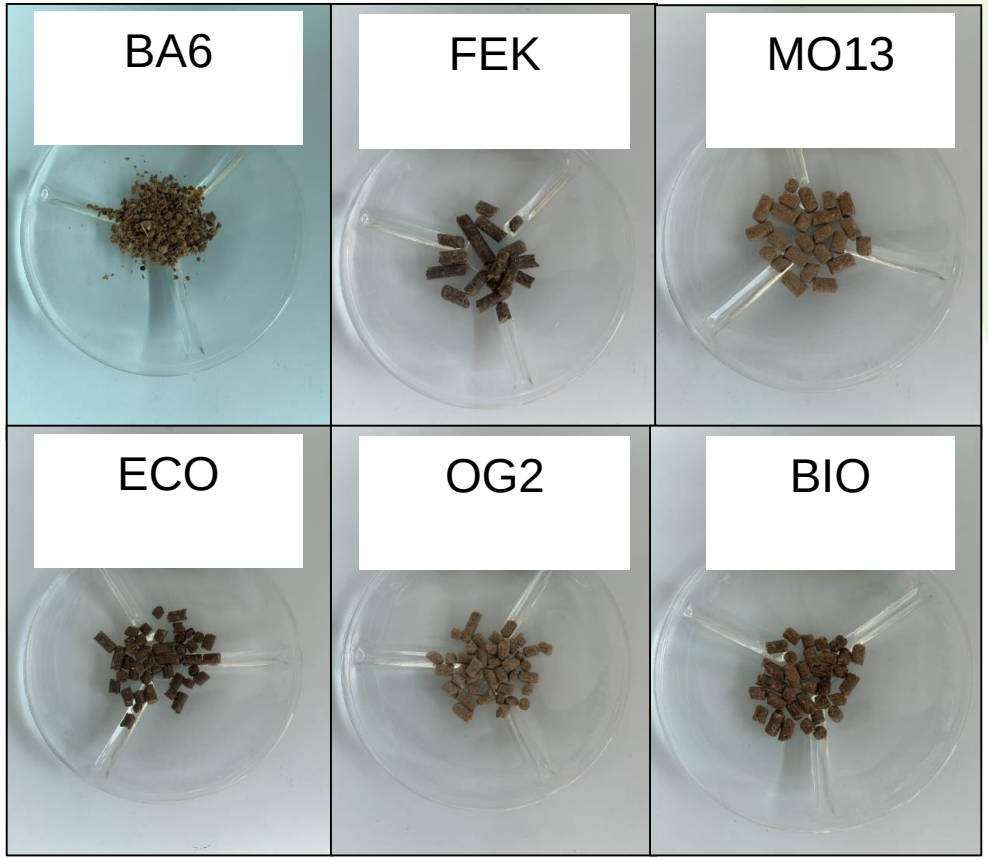
Bio-based phosphorus fertilizers

Name of BBF	Source	Group
BA1	Plant based organic (90%) NPK	Agriculture/Plant-based
MO14	Organic (45%) NPK	Agriculture/Plant-based
MB1	Meat Bone Meal	Veterinary/Poultry
CGO	Struvite	Sludge
ADC	Calcinated phosphate from sewage sludge ash	Sludge
OPU	Chicken manure pellets	Veterinary/Poultry
EPH	Sunflower husk ash	Agriculture/Plant-based



Bio-based nitrogen fertilizers

Name of BBF	Source	Group
BA6	Plant based organic (90%) NPK	Agriculture/Plant-based
FEK	Chicken manure	Veterinary/Poultry
MO13	Feather meal	Veterinary/Poultry
ECO	Blood meal, animal by-products	Veterinary/Poultry
OG2	Hornmeal	Veterinary/Poultry
BIO	Meat bone meal, vinasse, chicken manure and potassium sulphate	Veterinary/Poultry



Soils from LEX4BIO field trials in Spain and Finland

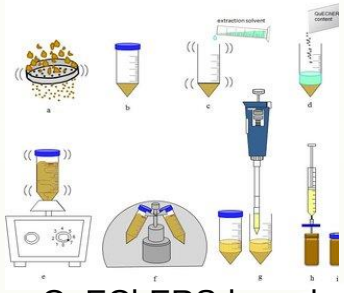
Barley and wheat crop rotation

Characteristics	Soil A: Spain	Soil B: Finland
% clay	61.7	48.8
% silt	25.9	26.1
% sand	10.6	20.4
Organic matter %	1.9	4.8
pH	7.66	5.74

Steps of analyzing pharmaceuticals and pesticides in BBFs and soil

Soil/BBFs

Step 1: Sample pre-treatment



QuEChERS-based

Step 2: Sample extraction

Liquid chromatography

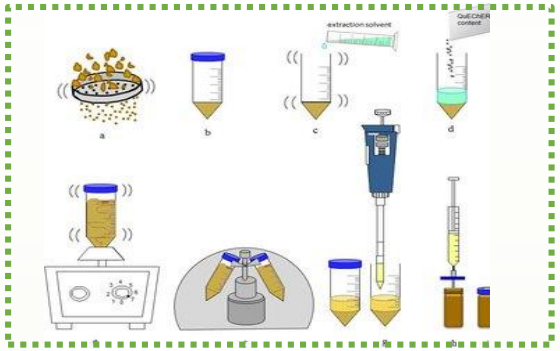
UHPLC-QTOF-MS/MS

Step 3: Sample analysis

Step 4: Data processing

Method development for BBFs (target analysis)

Spiked with **78** pesticides and **18** pharmaceuticals



Improved QuEChERS

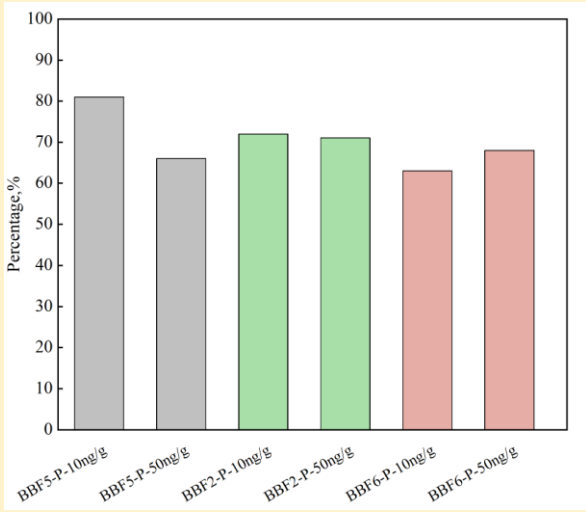


Figure: Percentage of compounds in the range of 70-120% at 10 ng/g and 50 ng/g concentration levels from BBFs

- **63-82%** of compounds were in the acceptable range of 70-120%
- Pharmaceuticals and pesticides were **co-extracted**

Original QuEChERS

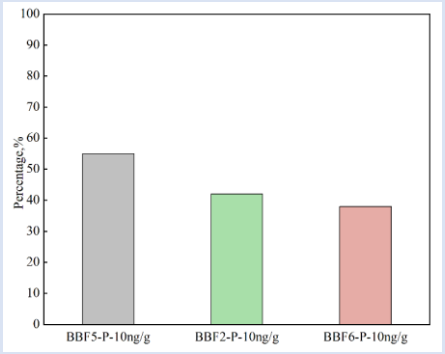


Figure: Percentage of compounds in the range of 70-120% at 10 ng/g concentration levels from BBFs

- **38-52%** of compounds were in the acceptable range of 70-120%
- Pharmaceuticals and pesticides were **co-extracted**

Dong et al. (2023), *Journal of Hazardous materials*

Result: organic pollutants in BBFs (target analysis)

- Most BBFs contain low levels of pharmaceuticals, and sometimes pesticides
- **Ibuprofen** and **1-hydroxyibuprofen** were frequently detected in 9 out of 13 BBFs

Concentrations in BBFs, ng/g

	Pharmaceuticals									Pesticides		
Samples	Ibuprofen	1-Hydroxyibuproxen	Atenolol	Antipyrine	Climbazole	Lincomycin	Sotalol	Gemfibrozil	Lenacil	Methylpirimifos	Fenuron	atrazine
BA1	102.0	7.3	ND	a	ND	ND	ND	ND	a	a	ND	ND
MO14	181.0	8.1	ND	5	a	ND	ND	ND	ND	ND	a	a
MB1	ND	2.4	a	a	ND	ND	ND	ND	ND	ND	ND	ND
CGO	a	3.1	ND	ND	a	ND	a	ND	ND	ND	ND	ND
ADC	ND	3.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
OPU	12.5	2.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
EPH	ND	a	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BA6	102.0	7.3	ND	a	ND	ND	ND	ND	a	a	ND	ND
FEK	109.0	7.5	ND	ND	ND	46.4	ND	a	ND	a	50	ND
MO13	4.1	a	13.3	a	ND	ND	ND	ND	ND	ND	ND	ND
ECO	a	a	ND	a	ND	ND	ND	ND	ND	ND	ND	ND
OG2	8.2	a	ND	a	ND	ND	ND	ND	ND	ND	ND	ND
BIO	a	ND	a	ND	a	ND	ND	ND	ND	ND	ND	ND

ND: concentration was less than LOD

a: concentration was between LOD and LOQ

Dong et al., (2023) *Journal of Hazardous materials*

Method performance for soil (target analysis)

Method performance evaluated for 2 soils from the LEX4BIO field trials:
Soil A (Spain) and **Soil B (Finland):**

- The target list contained **35 compounds of interes**t, including pesticides, pharmaceuticals and transformation products.
- The method **co-extracted** both pesticides and pharmaceuticals
- Recoveries for Soil A and Soil B were within **60-130 %** for **74% of targeted compounds**

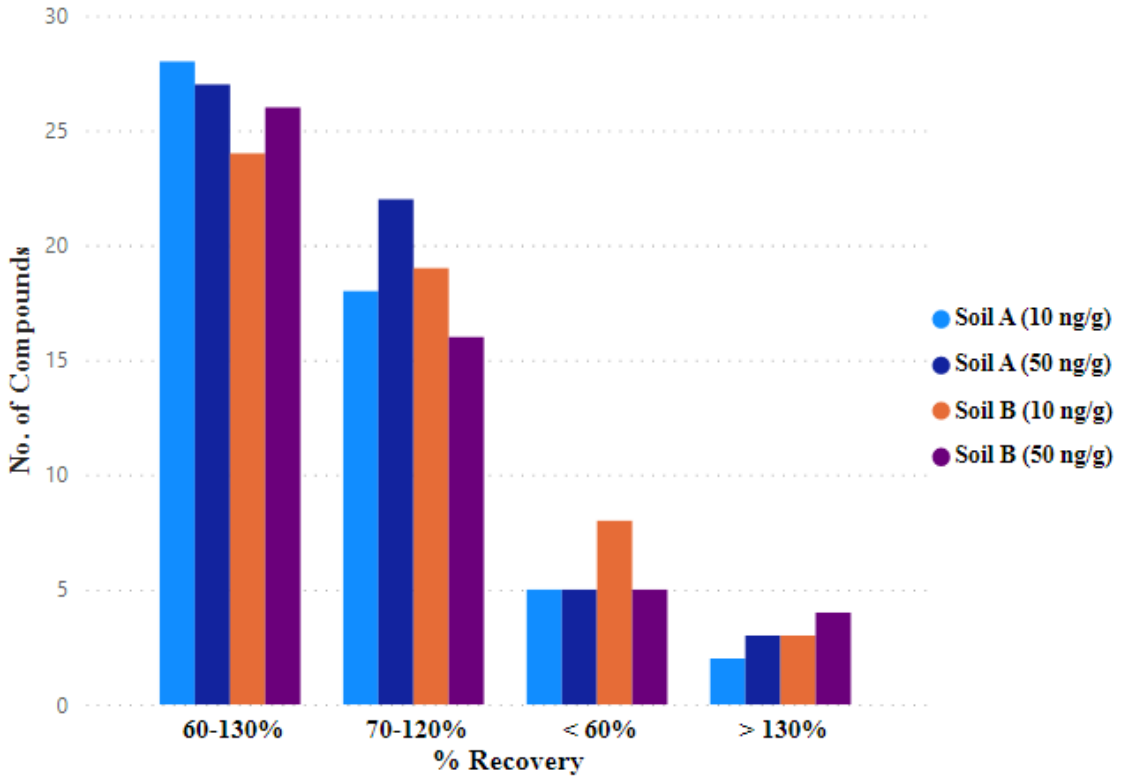


Figure: Method recovery rates for Soil A and Soil B at 10 ng $g^{-1}$and 50 ng g^{-1}concentration levels .

Das et al. (2023), *Chemosphere*

Screening soils from field trials before and after BBF treatment (N or P)

- **Before soil:** Only **ibuprofen** and **1-hydroxyibuprofen** detected in **Soil A** (Spain). No target pollutants detected in **Soil B** (Finland).

- **After soil: Ibuprofen** and **1-hydroxyibuprofen** detected in **Soil A** & **B. Lenacil** in **Soil B** only.

Concentrations in Soil samples, ng/g				
	After Soil A		After Soil B	
Samples	Ibuprofen	1-Hydroxyibuprofen	Ibuprofen	Lenacil
Before soil	a	a	ND	ND
BA6	a	a	a	**14.1**
PAL	ND	a	**2.2**	ND
FEK	a	a	a	ND
MO13	a	a	a	ND
ECO	a	a	a	ND
OG2	a	a	a	ND
BIO	a	a	a	ND

ND: concentration was less than LOD

a: concentration was between LOD and LOQ

Concentrations in Soil samples, ng/g				
	After Soil A		After Soil B	
Samples	Ibuprofen	1-Hydroxyibuprofen	Ibuprofen	Lenacil
Before soil	a	a	ND	ND
BA1	a	a	**1.6**	**28.7**
MO14	ND	a	**2**	ND
MB1	a	a	ND	ND
CGO	a	a	a	ND
ADC	a	a	a	ND
OPU	a	a	a	ND
EPH	a	a	ND	ND
PLA	a	a	ND	ND

ND: concentration was less than LOD

a: concentration was between LOD and LOQ

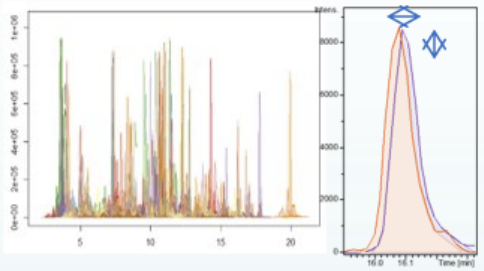
Das et al., (2023) *Chemosphere*

Suspect screening of BBFs and soil

HRMS analysis

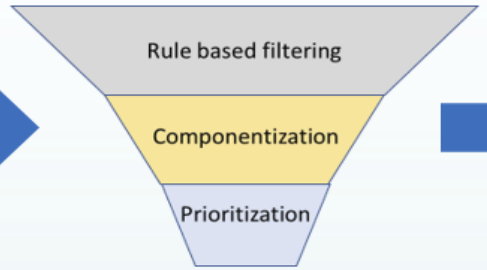
Generic screening

Features



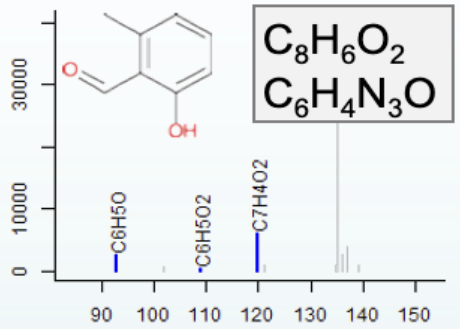
Automatic peak detection & analyses grouping

Pre-Processing & Prioritization



Chemistry, suspects, statistics, …

Annotation



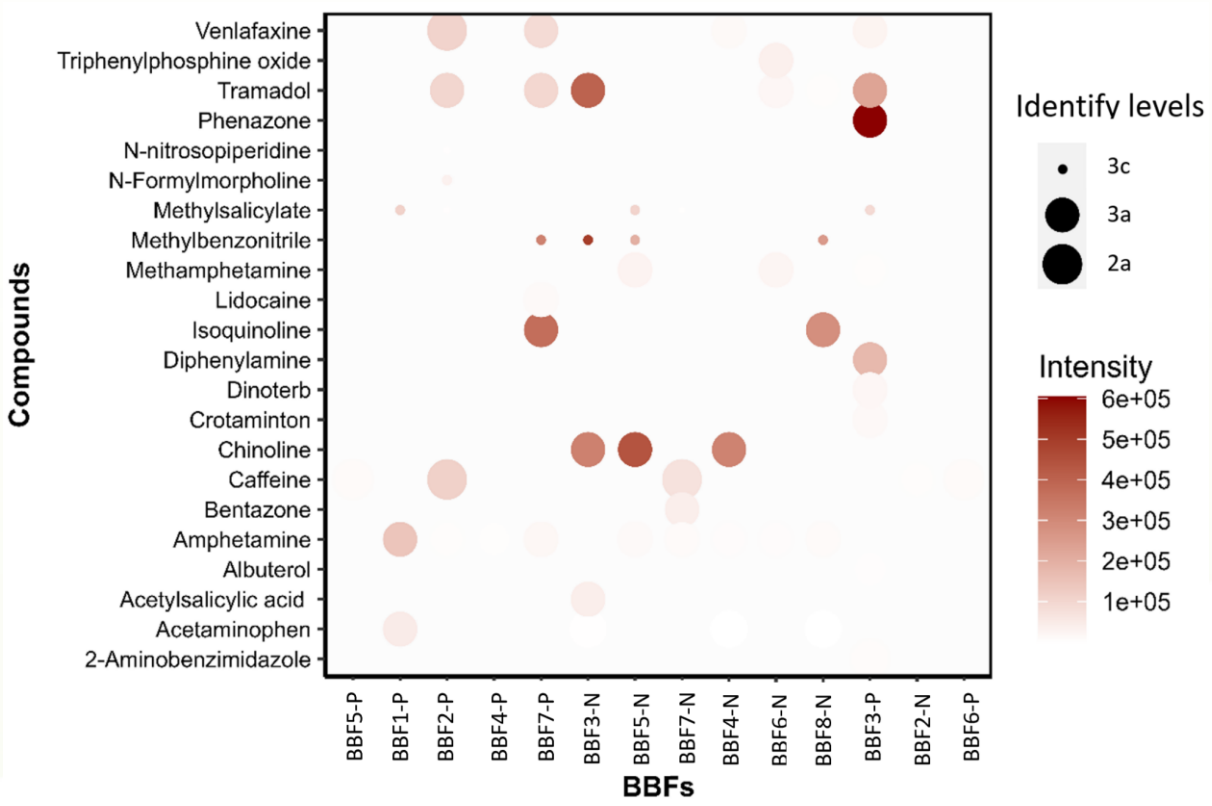
Automatic formula & structure search/prediction

Workflow source: Rick Helmus

patRoon, a comprehensive mass spectrometry based non-target analysis (NTA) workflows, was used for suspect screening against the **NORMAN Priority List** containing **>950 compounds of interest,** including pharmaceuticals and pesticides

Das et al., (2023) *Chemosphere*; Helmus et al.,(2021) *Journal of Cheminformatics*

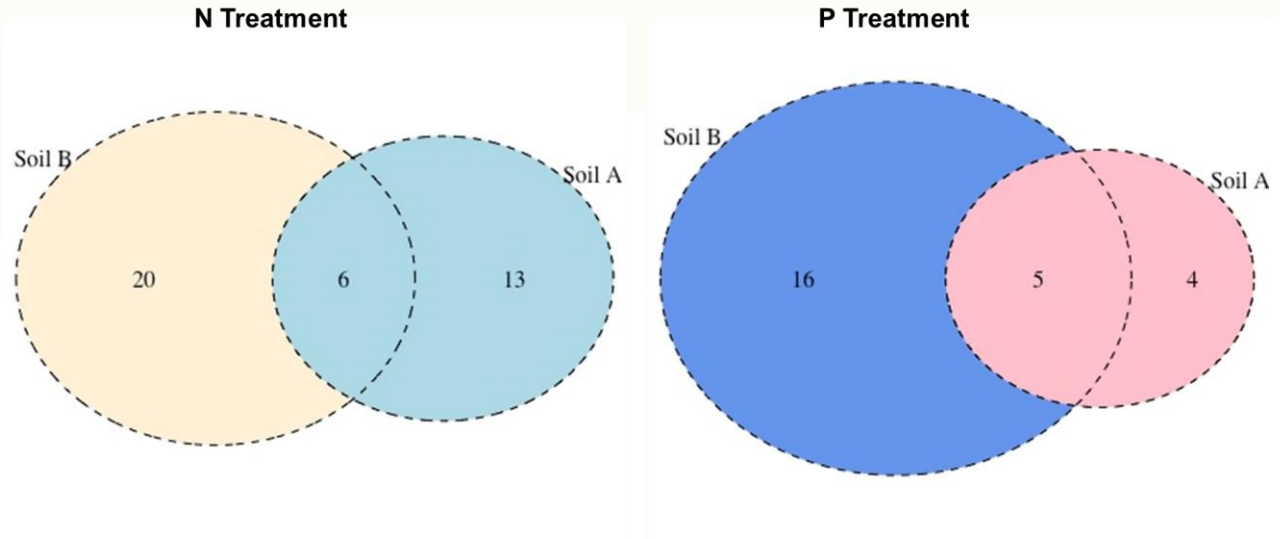
Suspect screening: tentatively identified compounds in BBFs



- Most BBFs contain **more than one pharmaceutical or pesticide**.
- The identified compounds included **caffeine** and were present in **low amounts**

Suspect screening: tentatively identified compounds in soils

- In total, **20 organic contaminants** were tentatively identified
- These corresponded to **common pharmaceuticals** used as anti-inflammatory drugs, beta-blockers or stimulants
- Only **one** of these **(caffeine) overlapped** between two experimental sites and treatments.
- Most likely the tentatively identified compounds **were not introduced through BBFs,** but through other previous land management practices.



Das et al., (2023) *Chemosphere*

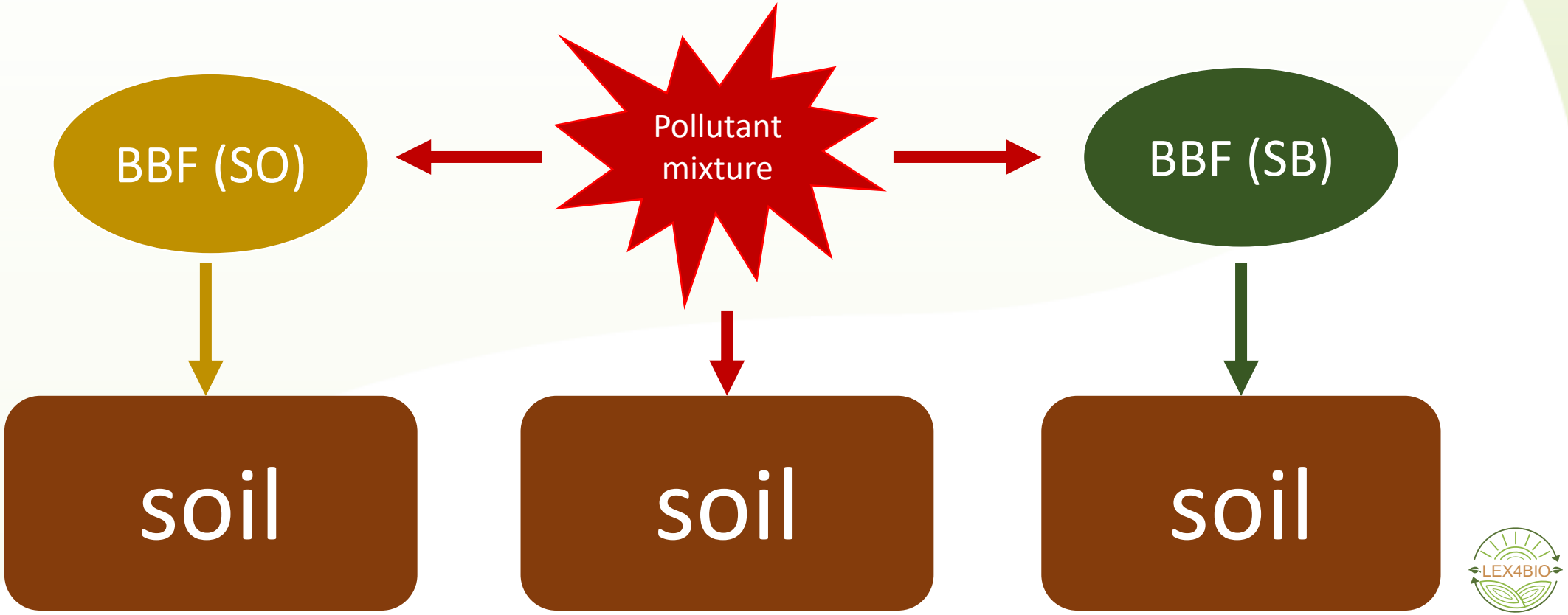
Take-home message screening of BBFs and soil

- The **combination** of **suspect screening** and **target analysis** offers the opportunity to screen **BBFs** and **soils** for a **large number** of potential pollutants **relatively quickly**

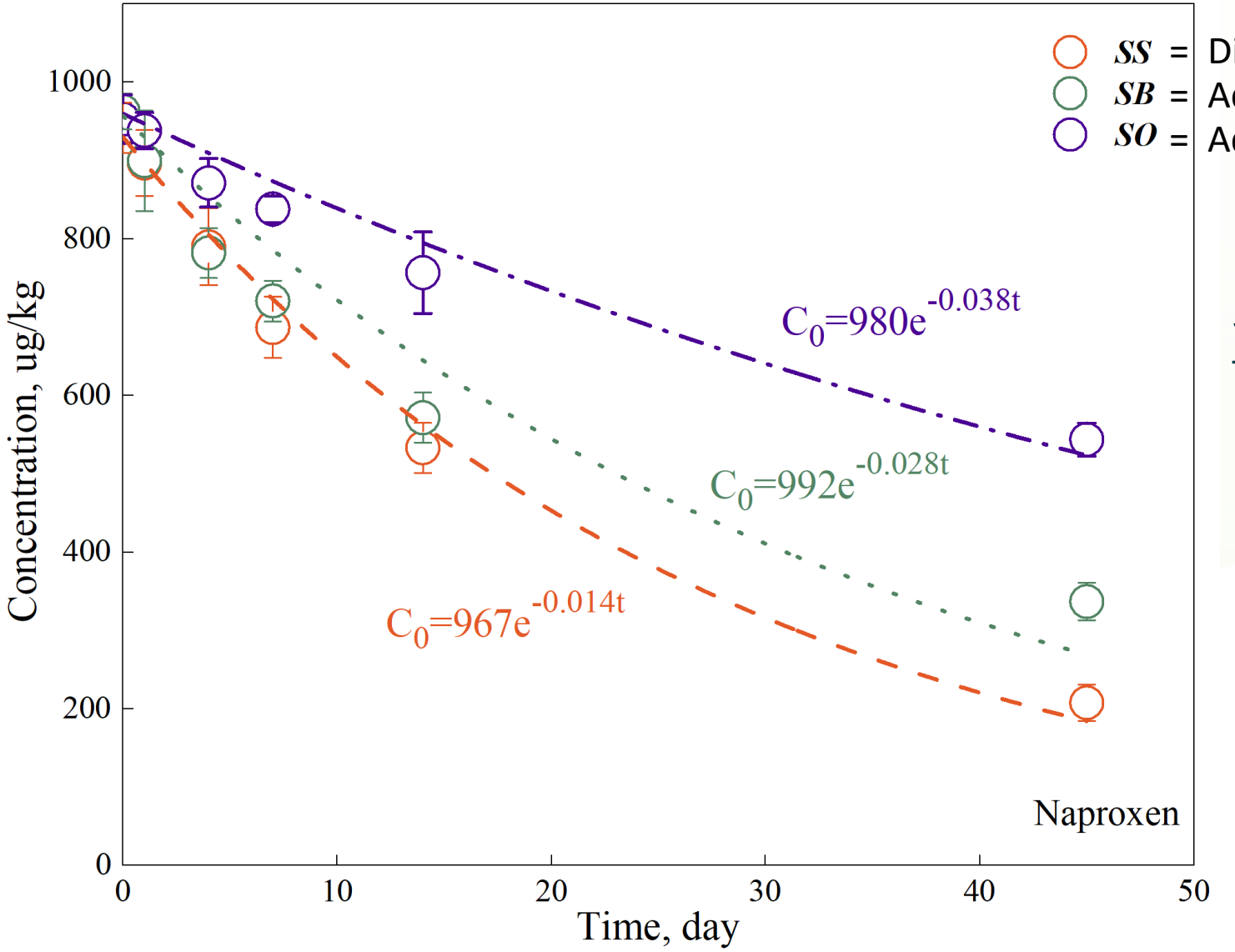
- Target analysis and suspect screening showed **a low threat of soil pollution** with pharmaceuticals and pesticides due to the use of the tested BBFs

Influence of BBFs on persistency in soil

Soil A (Spain: SS) and **a plant base BBF (SB)** and an **animal-based BBF (SO)** spiked with mixture of: Benzafibrate, Carbamazepine, Ketoprofen, Naproxen, Diclofenac, Furosemide, Gemfibrozil, and Ibuprofen



Application via BBF influences persistency



Single 1st order decay function

Dong et al., *Science of the Total Environment* (submitted)

Tentative conclusion persistency study

- All pharmaceuticals tested showed **low to medium persistency** in the soil under study
- Application via BBFs **prolonged the half-lives** of the pharmaceuticals in soil, most likely via adsorption on the BBF matrix.
- The **effect** was the **largest** for the **animal-based BBF**, most likely owing to its molecular composition.

Future outlook

- Finalization of **crop uptake experiments** (currently on-going).

- **Integration of results** within LEX4BIO, and publication of final articles and **EU reports**

- **Final presentation** at
  - **ManuResource** conference (Antwerp 20-21 March 2024) &
  - **NERM** conference (Brussels 16-17 April 2024)

Acknowledgements

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LEX4BIO

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Questions?

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