UNIVERSITÄT KOBLENZ · LANDAU

UMWELT- UND BODENCHEMIE

Agricultural Plastic Covers—Source of Plastic Debris in Soil?

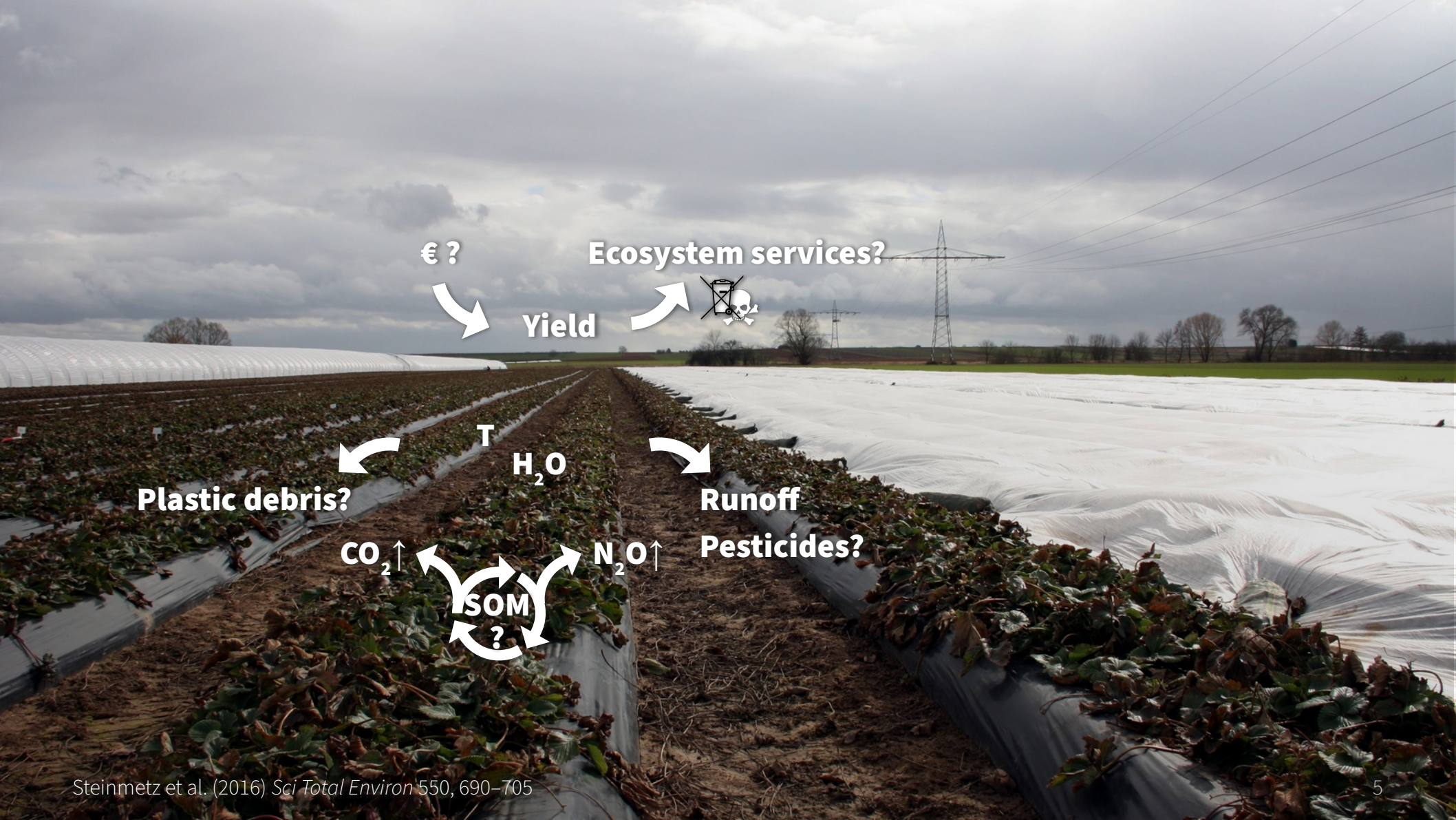
Zacharias Steinmetz

Examiners: Prof. Dr. Gabriele E. Schaumann, Prof. Dr. Geert Cornelis, and Prof. Dr. Denise M. Mitrano

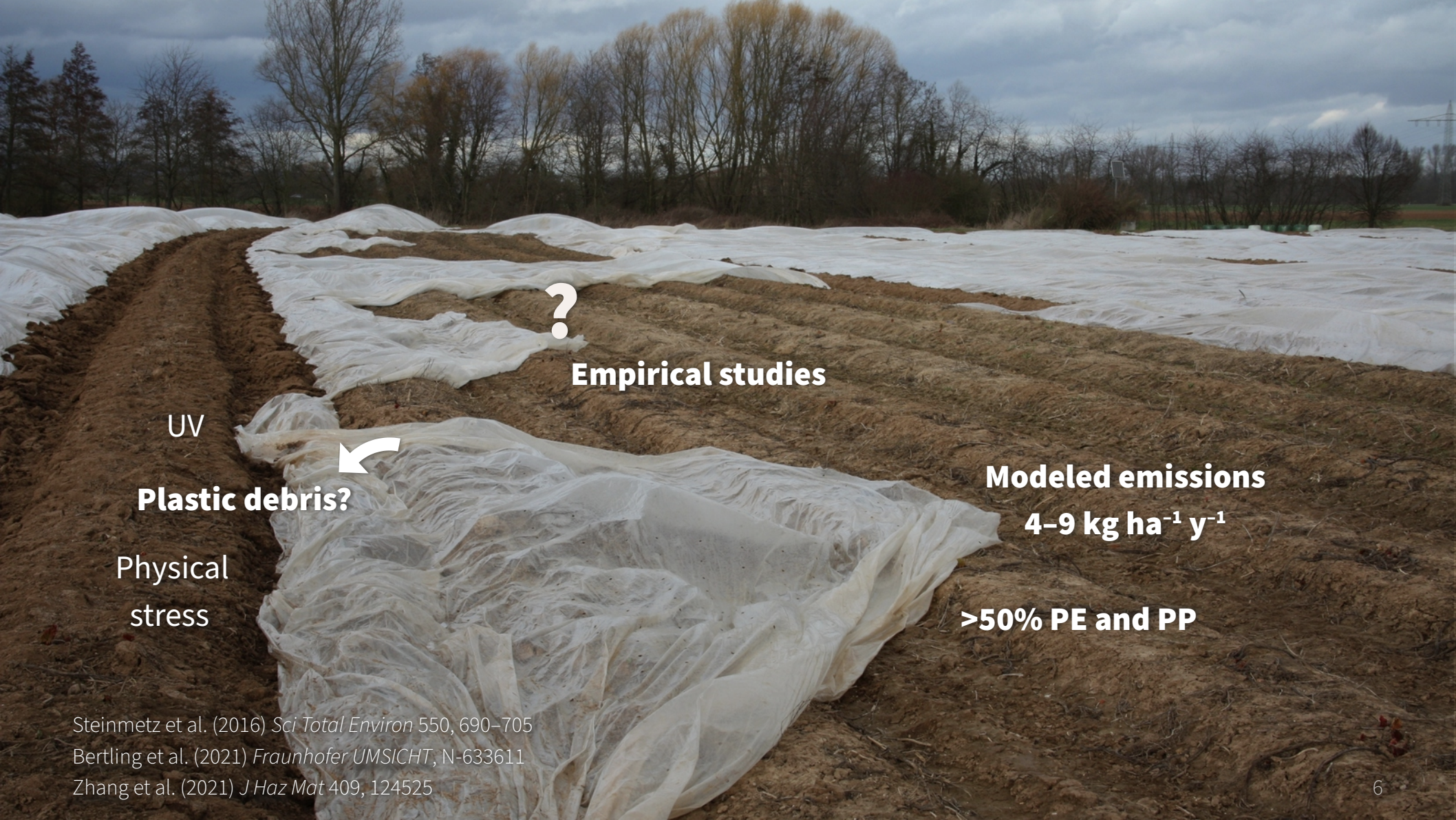
Landau Mörlheim (March 2018)

Bertling et al. (2021) *Fraunhofer UMSICHT*, N-633611
Razza et al. (2019) *Acta Hortic* 1252, 77–84

Steinmetz et al. (2016) *Sci Total Environ* 550, 690–705



Steinmetz et al. (2016) *Sci Total Environ* 550, 690–705



Steinmetz et al. (2016) *Sci Total Environ* 550, 690–705
Bertling et al. (2021) *Fraunhofer UMSICHT*, N-633611
Zhang et al. (2021) *J Haz Mat* 409, 124525

Hypothesis

Agricultural plastic covers pollute the surrounding soil with plastic debris at micrometer scale

Steinmetz et al. (2016) *Sci Total Environ* 550, 690–705

Problem

Available particle-based methods

- **not validated for complex matrices like soil**
- **not comparable to modeling and effect data**

Steinmetz et al. (2016) *Sci Total Environ* 550, 690–705

Photo: M.T. Nguyen

Problem

Mass-based methods for the quantification of plastic debris in soil still at an early stage

Steinmetz et al. (2016) *Sci Total Environ* 550, 690–705

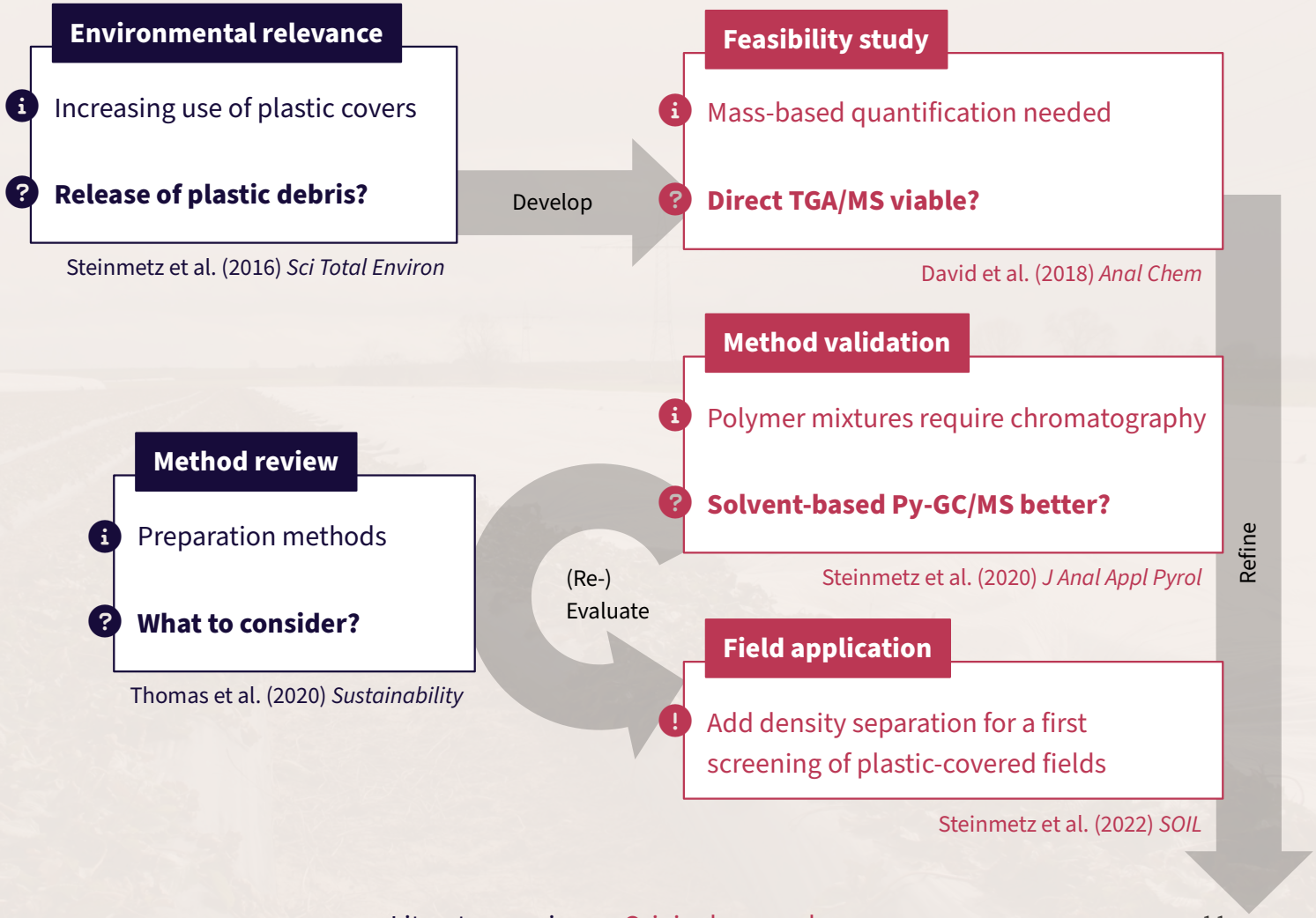
Photo: J. David

Objectives

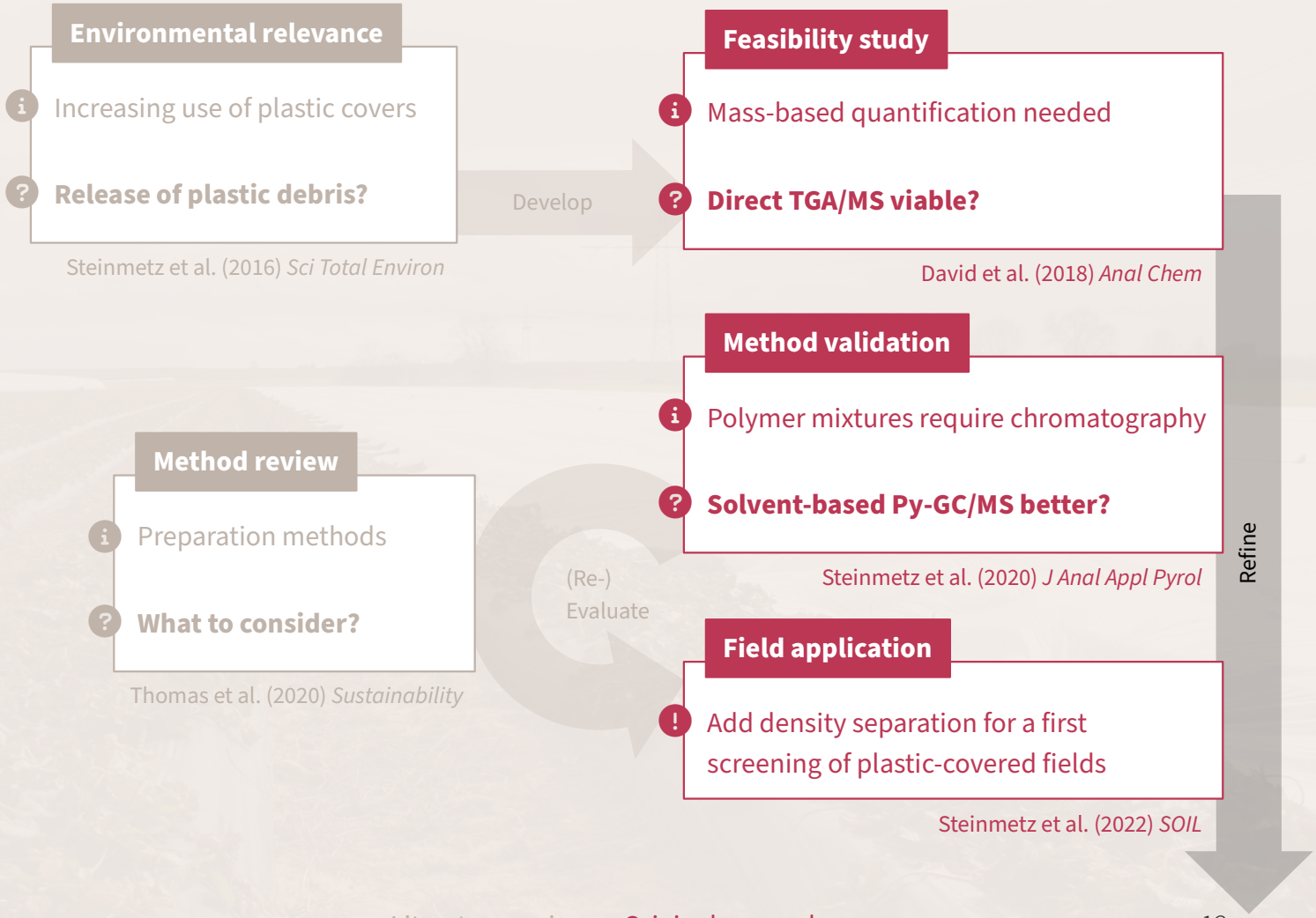
1. Develop and validate a mass-based method for the quantification of plastic debris in soil
2. Scrutinize the extent to which agricultural plastic covers function as a source of plastic debris in soil

Photo: J. David

Overview


Environmental relevance
Increasing use of plastic covers
Release of plastic debris?
Steinmetz et al. (2016) Sci Total Environ
Develop
Feasibility study
Mass-based quantification needed
Direct TGA/MS viable?
David et al. (2018) Anal Chem
Method validation
Polymer mixtures require chromatography
Solvent-based Py-GC/MS better?
Steinmetz et al. (2020) J Anal Appl Pyrol
Refine
Method review
Preparation methods
What to consider?
Thomas et al. (2020) Sustainability
(Re-)
Evaluate
Field application
Add density separation for a first screening of plastic-covered fields
Steinmetz et al. (2022) SOIL

Overview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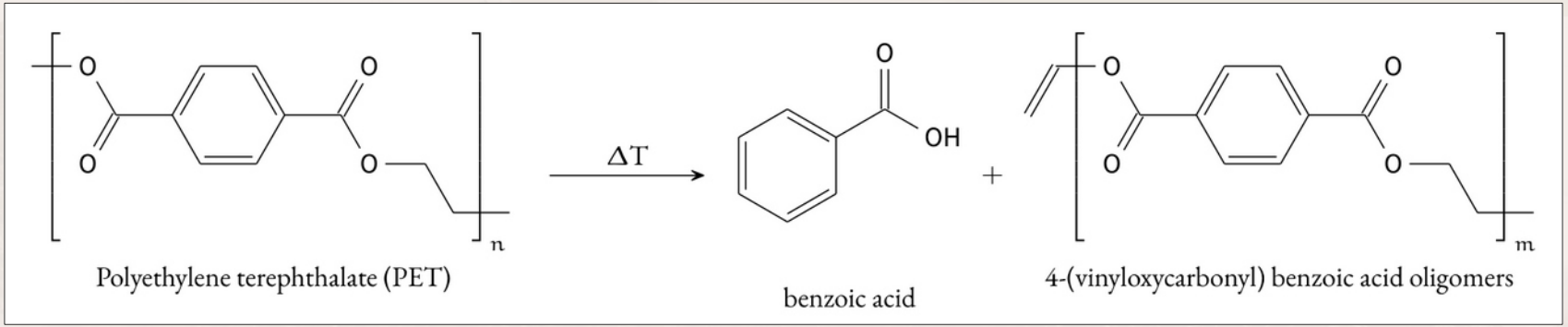
Steinmetz et al. (2022) SOIL

Thermoanalysis for Polymer Quantification



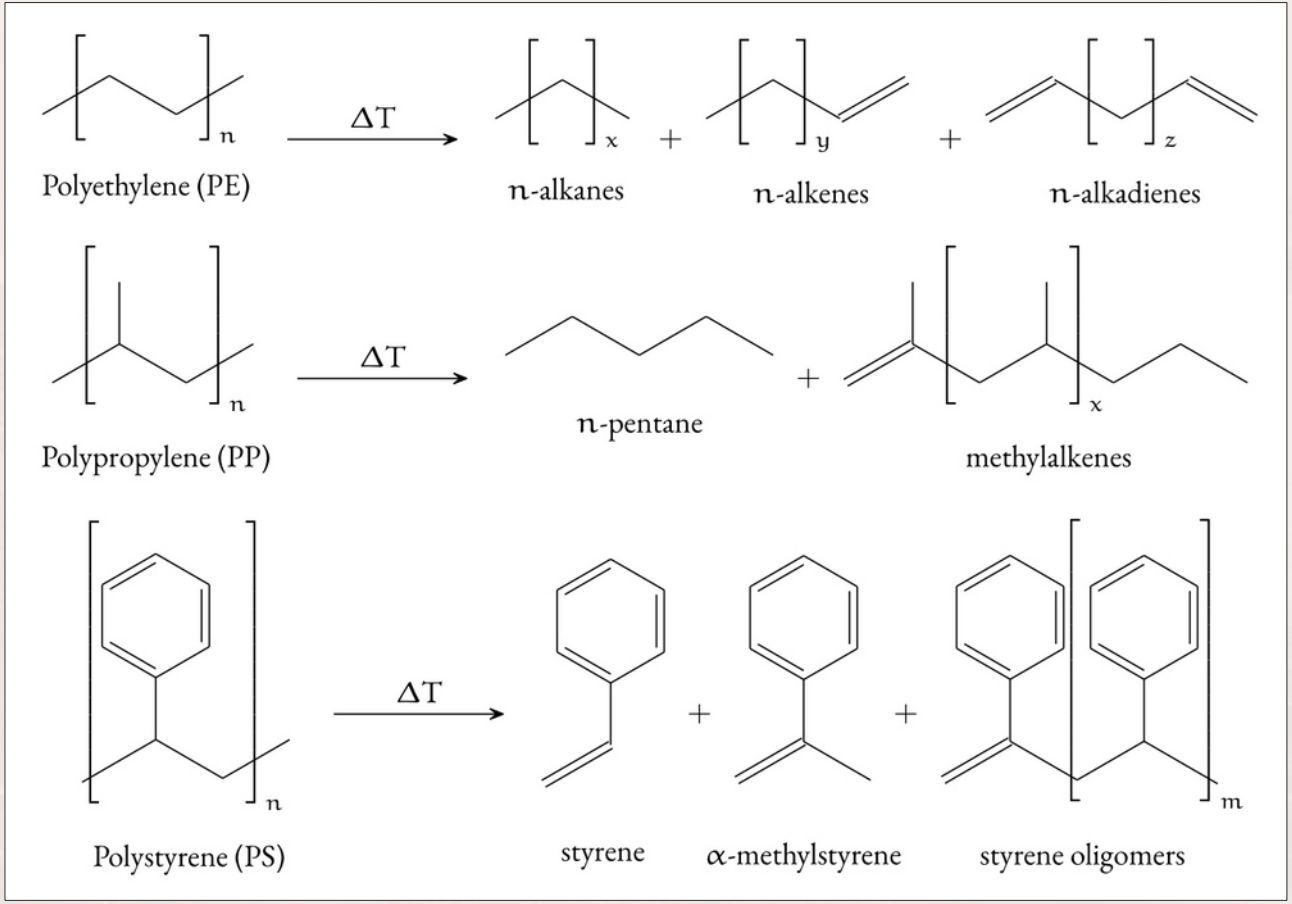
Feasibility study

Method validation

Field application

Tsuge et al. (2011)
Pyrolysis–GC/MS Data Book

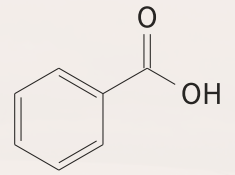
Thermoanalysis for Polymer Quantification

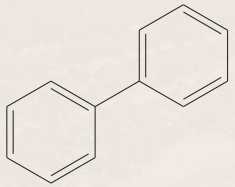


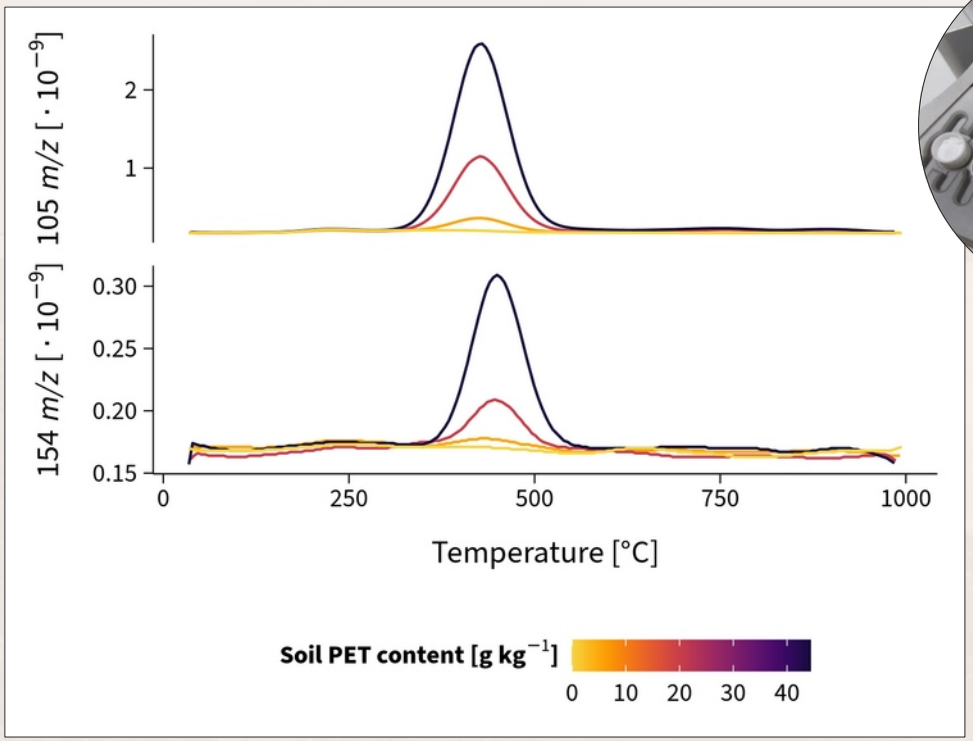
Tsuge et al. (2011)
Pyrolysis–GC/MS Data Book

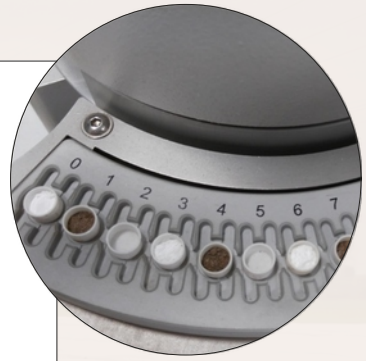
Feasibility study
Method validation
Field application

Direct TGA/MS









cysteine as internal standard

Feasibility study

Method validation

Field application

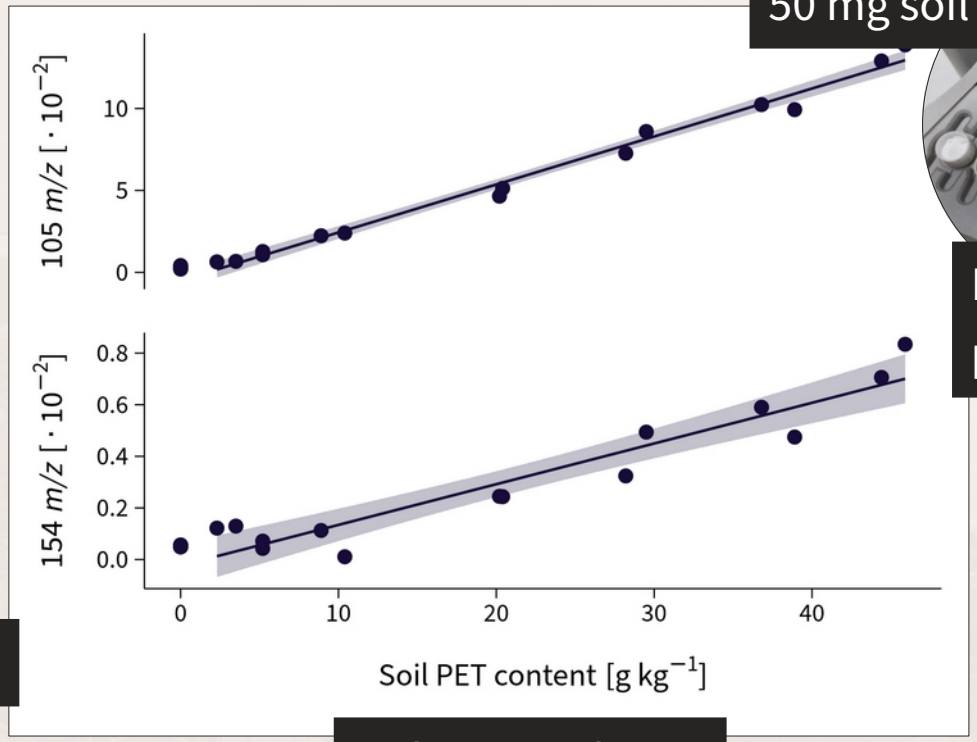
David et al. (2018) *Anal Chem* 90, 8793–8799

Photo: J. David

Direct TGA/MS

50 mg soil

No sample preparation



LOD = 0.7 g kg^{-1}

Only one polymer

Feasibility study

Method validation

Field application

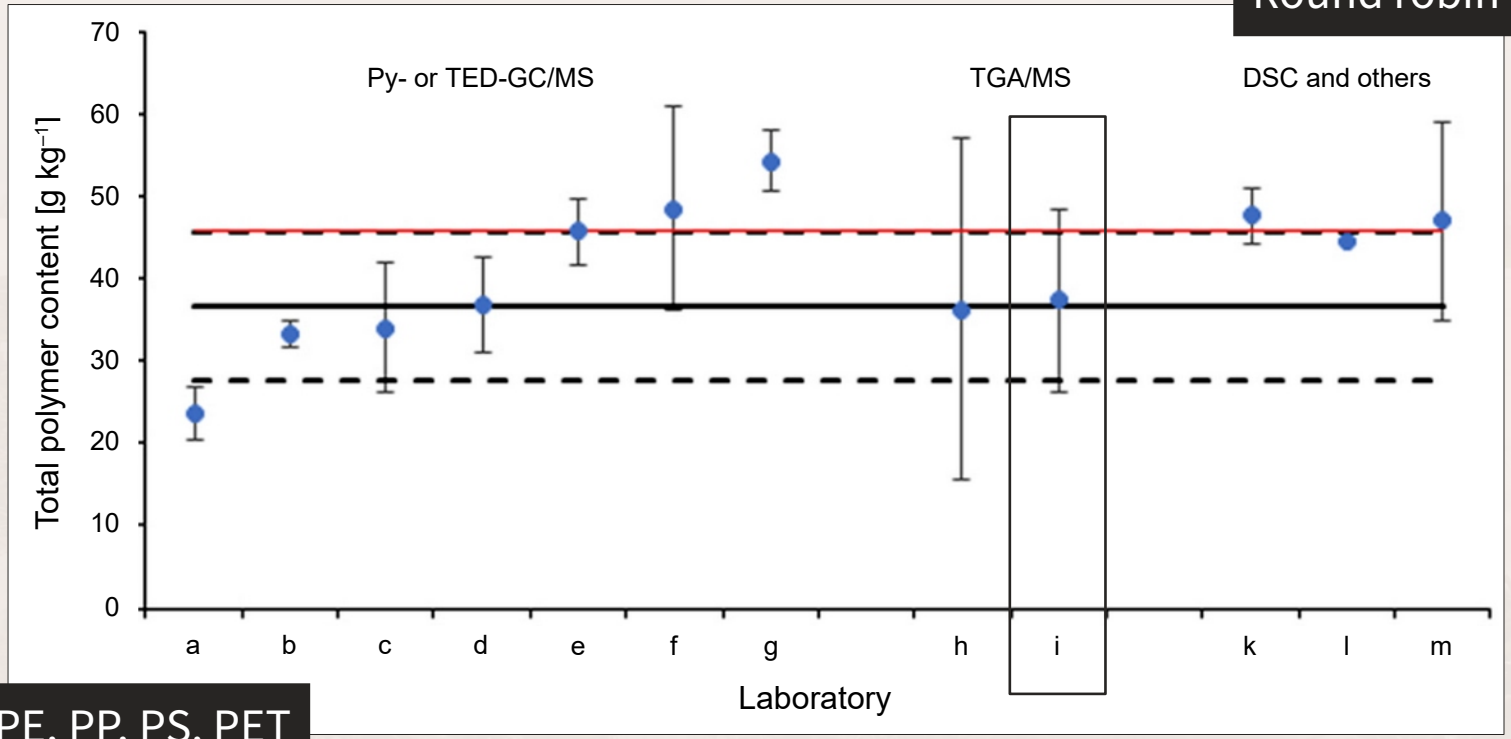
Steinmetz (2018) *envalysis* 0.3.3

David et al. (2018) *Anal Chem* 90, 8793–8799

Photo: J. David

Direct TGA/MS

Round robin test



PE, PP, PS, PET

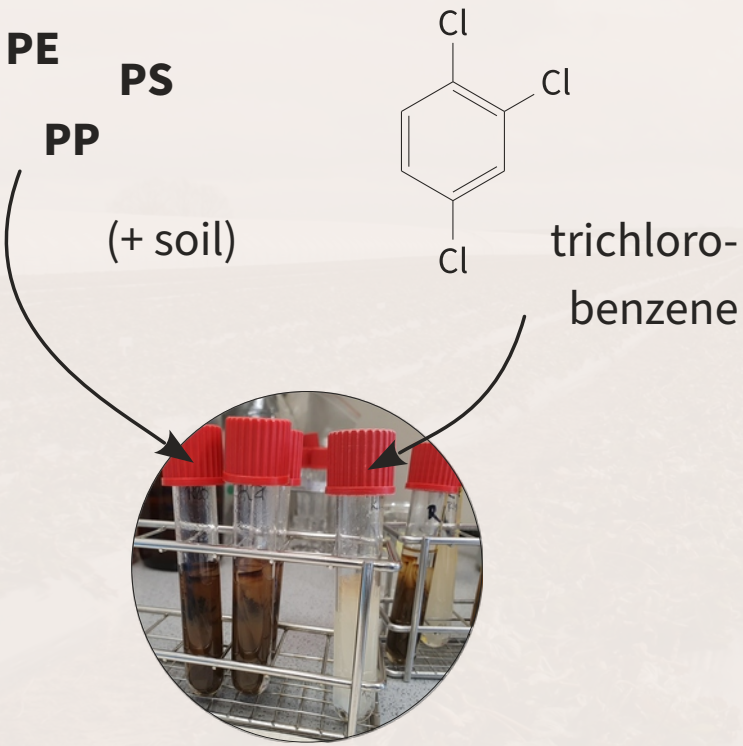
Feasibility study

Method validation

Field application

Becker et al. (2020) *J Anal Appl Pyrol* 148, 104829

Solvent-based Py-GC/MS



Feasibility study

Method validation

Field application

Steinmetz et al. (2020) *J Anal Appl Pyrol* 147, 104803

Photos: W.M. Heinze

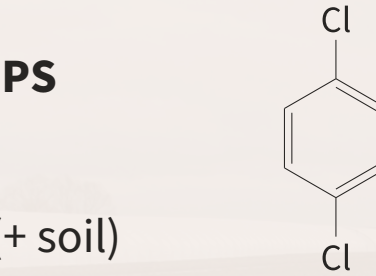
Solvent-based Py-GC/MS

PE

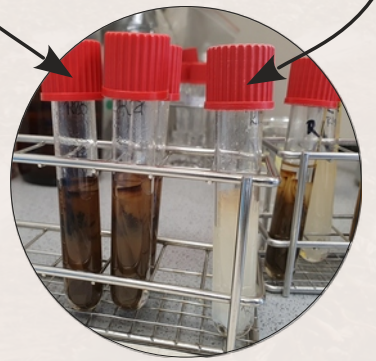
PS

PP

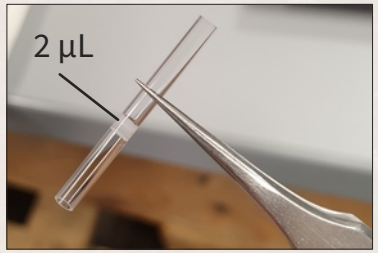
(+ soil)



trichloro-
benzene



120 °C, 1 h



Aliquotation

Feasibility study

Method validation

Field application

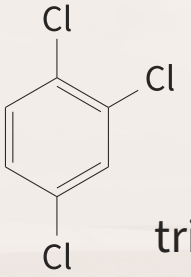
Steinmetz et al. (2020) *J Anal Appl Pyrol* 147, 104803

Photos: W.M. Heinze

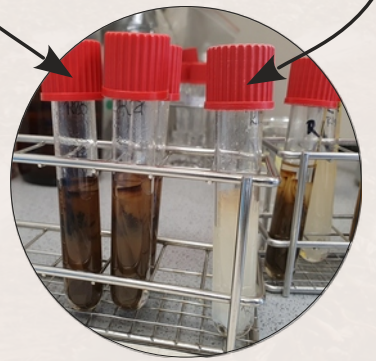
Solvent-based Py-GC/MS

PE **PS** **PP**

(+ soil)



trichloro-benzene



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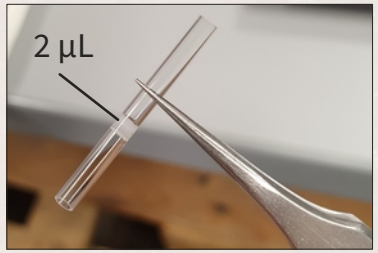
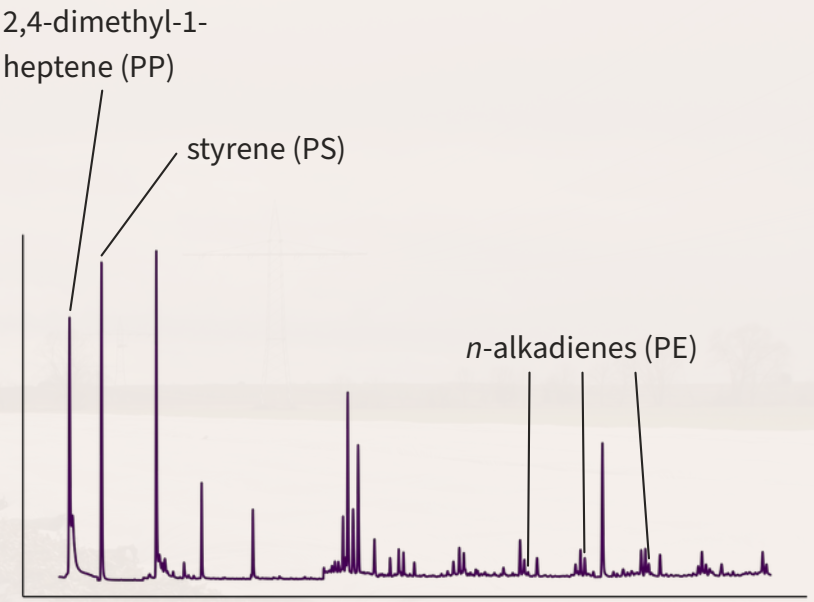


Flash pyrolysis at 750 °C



Feasibility study

Method validation

Field application

Steinmetz et al. (2020) *J Anal Appl Pyrol* 147, 104803

Photos: W.M. Heinze

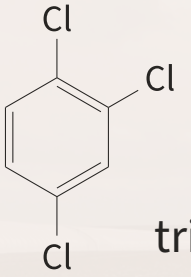
Solvent-based Py-GC/MS

PE

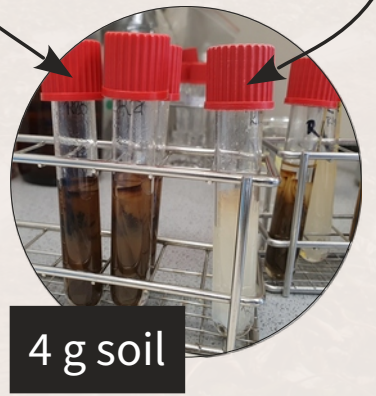
PS

PP

(+ soil)

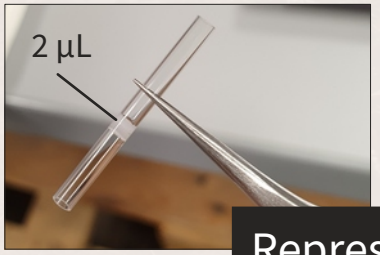


trichloro-
benzene

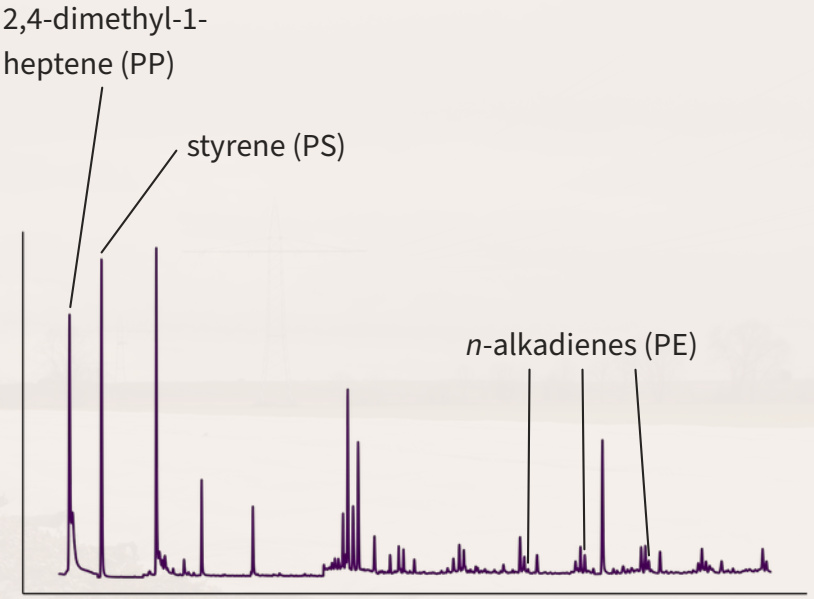


4 g soil

120 °C, 1 h



Representative subsample



Feasibility study

Method validation

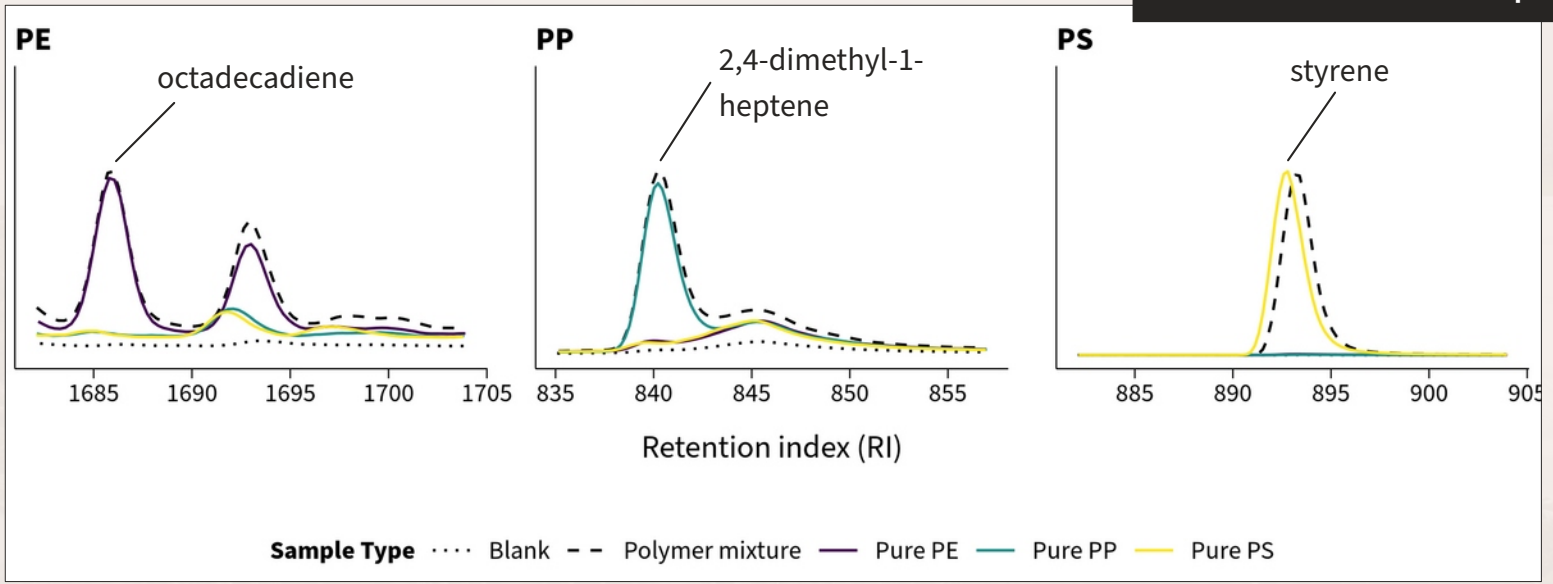
Field application

Steinmetz et al. (2020) *J Anal Appl Pyrol* 147, 104803

Photos: W.M. Heinze

Solvent-based Py-GC/MS

Selective for each polymer



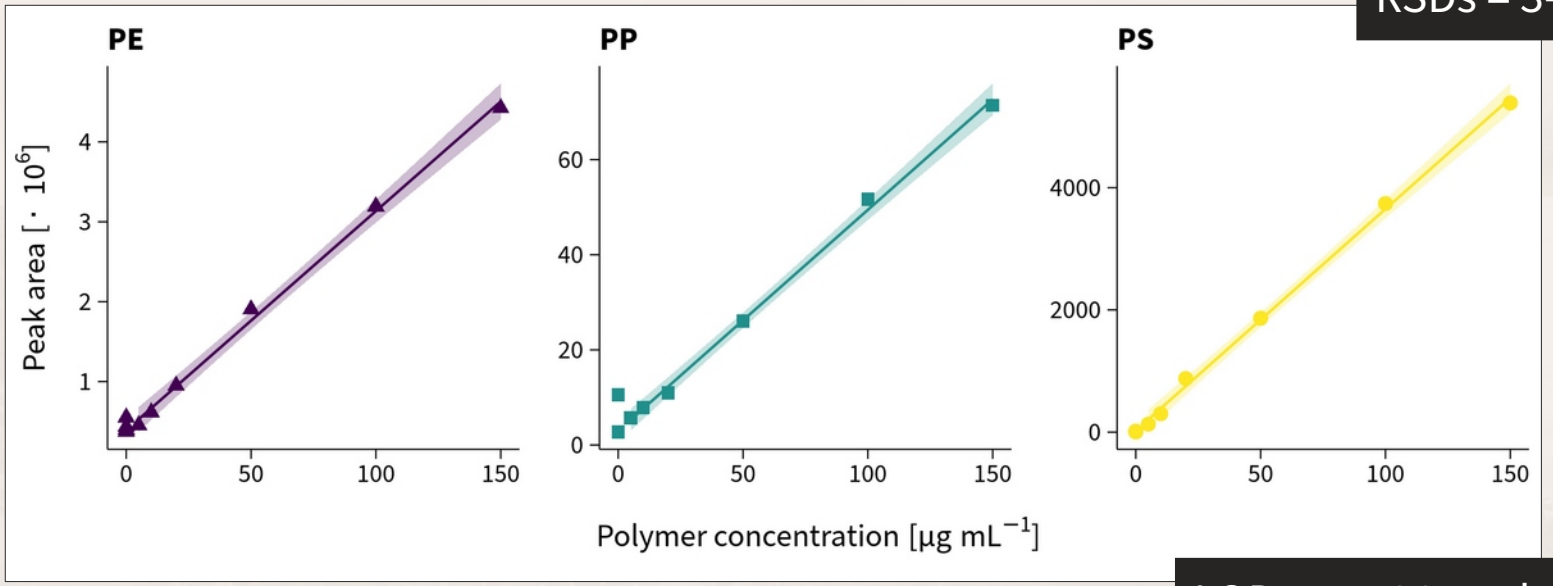
Feasibility study

Method validation

Field application

Steinmetz et al. (2020) *J Anal Appl Pyrol* 147, 104803

Solvent-based Py-GC/MS



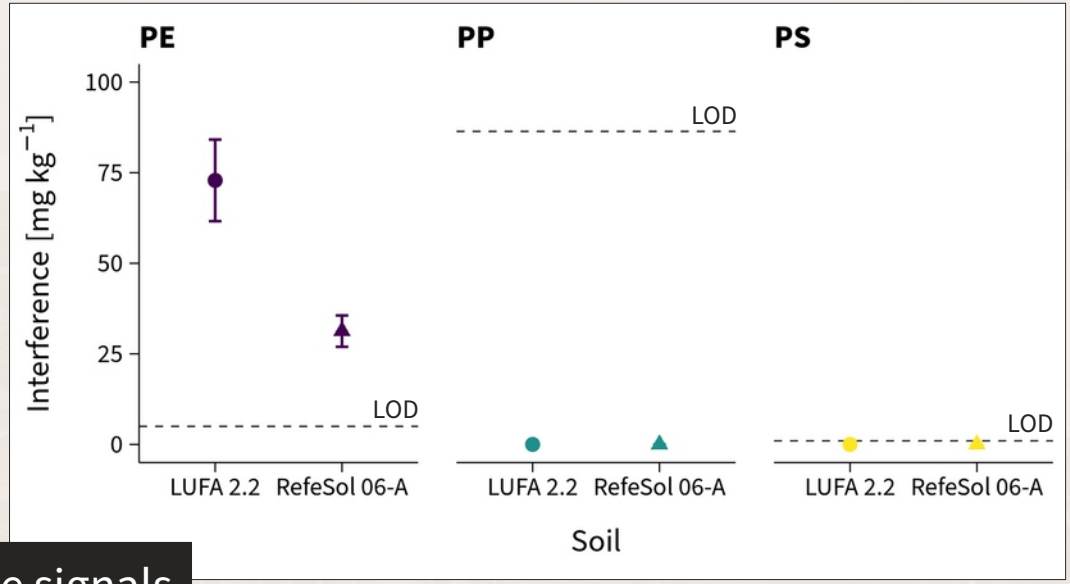
Feasibility study

Method validation

Field application

Steinmetz (2020) *envalysis* 0.4.0
Steinmetz et al. (2020) *J Anal Appl Pyrol* 147, 104803

Solvent-based Py-GC/MS



False positive signals from blank soil

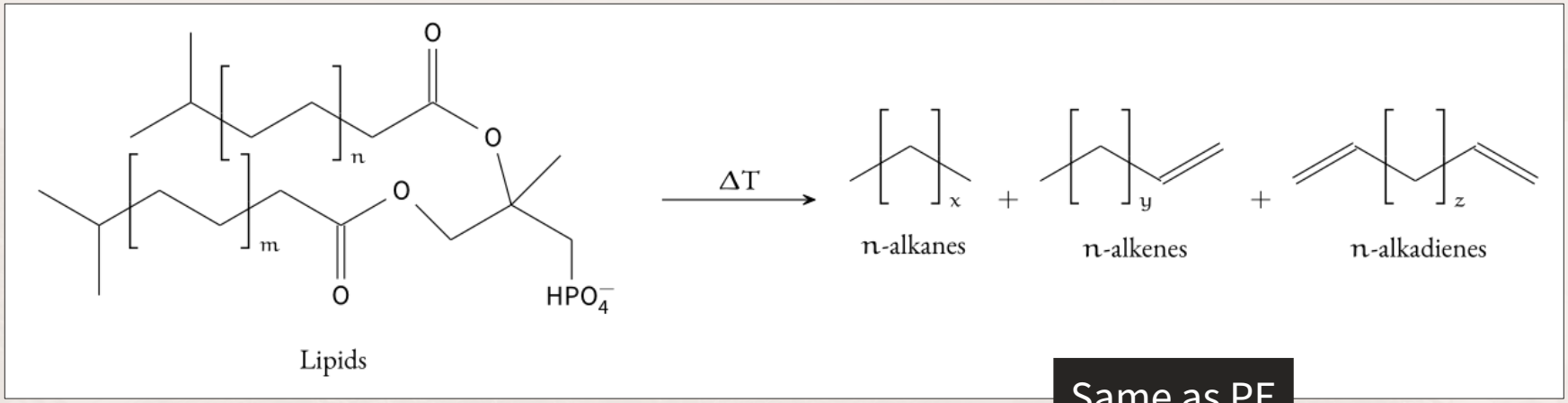
Feasibility study

Method validation

Field application

Steinmetz et al. (2020) *J Anal Appl Pyrol* 147, 104803

SOM Pyrolysis



Same as PE

Feasibility study

Method validation

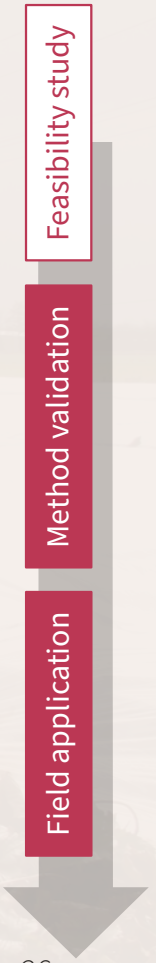
Field application

Ceccanti et al. (2007) *Soil Tillage Res* 97(1), 71–78
Hatcher et al. (2001) *Soil Sci* 166(11), 770–794

Additional Steps

- Additional sample purification required

- Higher sample amounts for more representative measurements



Thomas et al. (2020) *Sustainability* 12(21), 9074

Final Method Validation and Field Application

8 sites covered for 1–2 seasons

LUFA 2.2 Loamy sand, 1.7% C_{org}

+

RefeSol 06-A Silty clay, 2.5% C_{org}

Mostly clayey silts, 0.9–1.5% C_{org}

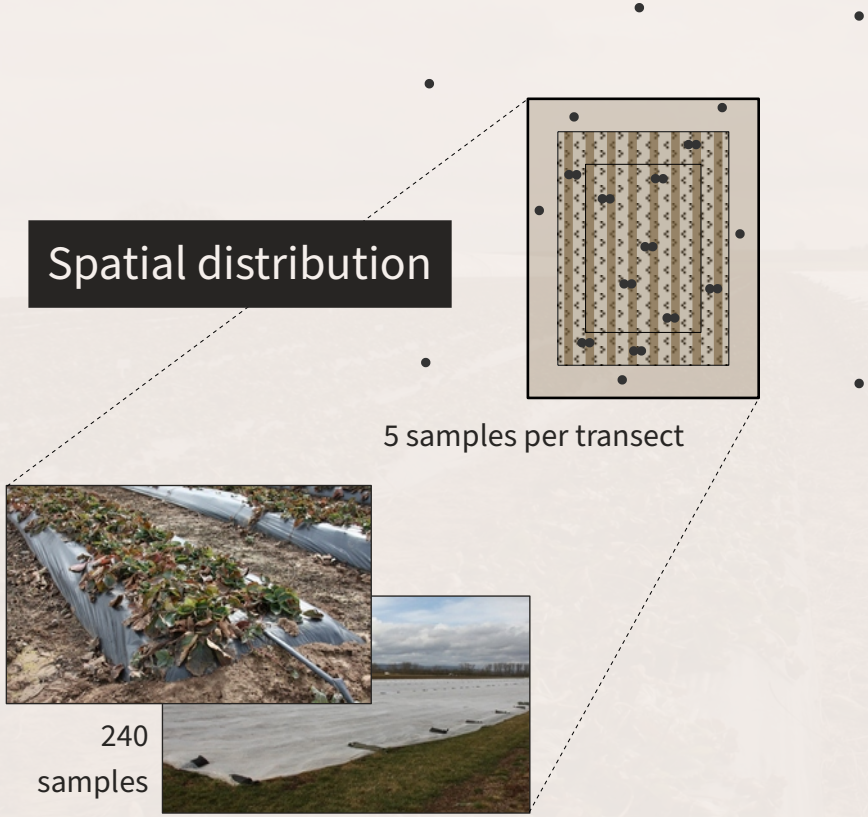
Located in Landau and Schifferstadt, Germany

Feasibility study

Method validation

Field application

Field Sampling



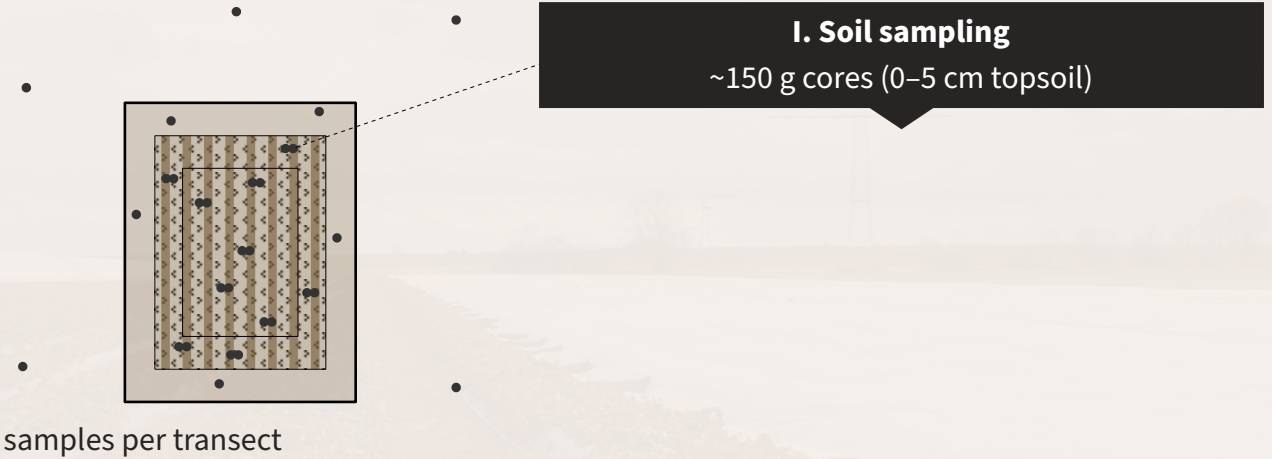
Feasibility study

Method validation

Field application

Steinmetz et al. (2022) *SOIL* 8(1), 31–47

Field Sampling



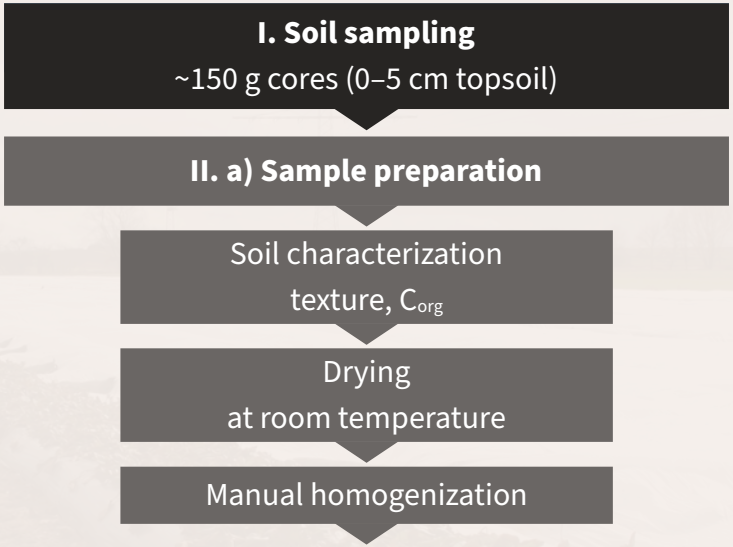
Feasibility study

Method validation

Field application

Thomas et al. (2020) *Sustainability* 12(21), 9074
Steinmetz et al. (2022) *SOIL* 8(1), 31–47

Sample Preparation



Feasibility study

Method validation

Field application

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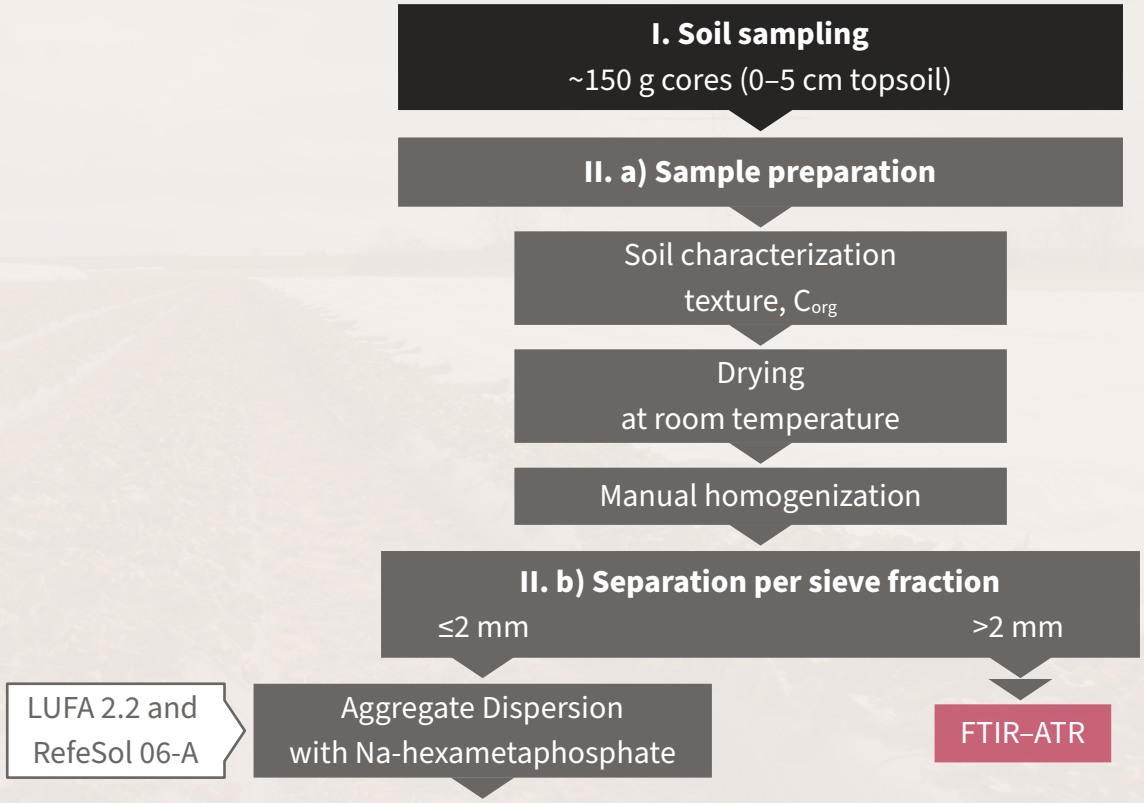


Thomas et al. (2020) *Sustainability* 12(21), 9074
Steinmetz et al. (2022) *SOIL* 8(1), 31–47

Extraction

II. b) Separation per sieve fraction

≤2 mm

Dominant soil constituent?

Inorganic

Density separation
$\rho = 1.2\ g\ cm^{-3}$

50 g soil

+ 250 mL NaCl solution

1 L separation funnels
Filtration at 4–12 µm

Feasibility study

Method validation

Field application

Thomas et al. (2020) *Sustainability* 12(21), 9074
Steinmetz et al. (2022) *SOIL* 8(1), 31–47

Photos: W.M. Heinze

Solvent-based Py-GC/MS

II. b) Separation per sieve fraction

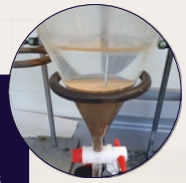
≤2 mm

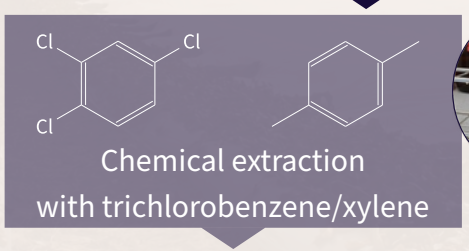
Dominant soil constituent?

Inorganic

Density separation

$\rho = 1.2\ g\ cm^{-3}$





Chemical extraction with trichlorobenzene/xylene

Batch extraction

150 °C / 1 h

Feasibility study

Method validation

Field application

Thomas et al. (2020) *Sustainability* 12(21), 9074

Steinmetz et al. (2022) *SOIL* 8(1), 31–47

Photos: W.M. Heinze

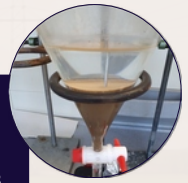
Solvent-based Py-GC/MS

II. b) Separation per sieve fraction

≤2 mm

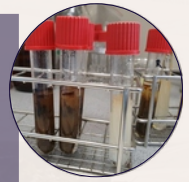
Dominant soil constituent?

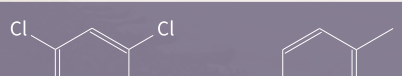
Inorganic



Density separation

$\rho = 1.2\ g\ cm^{-3}$





Chemical extraction with trichlorobenzene/xylene

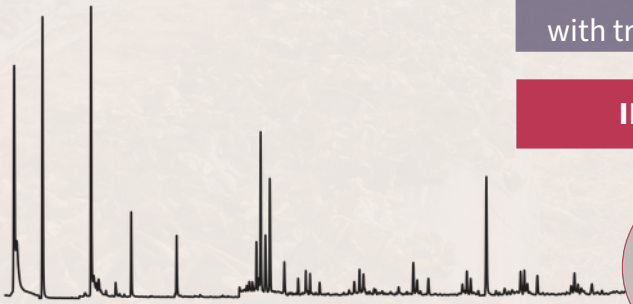
2 µL aliquot

III. Quantification

Mass

Py-GC/MS

700 °C



PS-d5 as internal standard

Feasibility study

Method validation

Field application

Final Method Validation

Polymer	LOD [mg kg^{-1}]	LOQ [mg kg^{-1}]	Interference [mg kg^{-1}]	Recovery at 20 mg kg^{-1} [%]
LUFA 2.2				
PE	1.9	9.5	0.9±0.3	105±3
PP	2.9	2.9	0±0	93±5
PS	3.3	6.2	0±0	86±4
RefeSol 06-A				
PE	1.2	9.5		50±10
PP	0.8	2.5		62±1
PS	0.7	6.2		12±5

Feasibility study

Method validation

Field application

Final Method Validation

Polymer	LOD [mg kg^{-1}]	LOQ [mg kg^{-1}]	Interference [mg kg^{-1}]	
LUFA 2.2				
PE	1.9	9.5	0.9±0.3	105±3
PP	2.9	2.9	0±0	93±5
PS	3.3	6.2	0±0	86±4
RefeSol 06-A			< LOD	
PE	1.2	9.5		50±10
PP	0.8	2.5		62±1
PS	0.7	6.2		12±5

Blank soil + 40 mg kg^{-1} non-target polymers

PET, PVC, PMMA, TWD

Feasibility study

Method validation

Field application

Steinmetz et al. (2022) *SOIL* 8(1), 31–47

Final Method Validation

Polymer	LOD [mg kg^{-1}]	LOQ [mg kg^{-1}]	Interference [mg kg^{-1}]	Recovery at 20 mg kg^{-1} [%]
LUFA 2.2				
PE	1.9	9.5	9% clay	105±3
PP	2.9	2.9	0±0	93±5
PS	3.3	6.2	0±0	86±4
RefeSol 06-A				
PE	1.2	9.5	47% clay	50±10
PP	0.8	2.5		62±1
PS				12±5

Clay–polymer interactions

Feasibility study

Method validation

Field application

Final Method Validation

Polymer	LOD [mg kg^{-1}]	LOQ [mg kg^{-1}]	Interference [mg kg^{-1}]	Recovery at 20 mg kg^{-1} [%]
LUFA 2.2				
PE	1.9	9.5	0.9±0.3	105±3
PP	2.9	2.9	0±0	93±5
PS	3.3			86±4
RefeSol 06-A				
PE	1.2	9.5		50±10
PP	0.8	2.5		62±1
PS	0.7	6.2		12±5

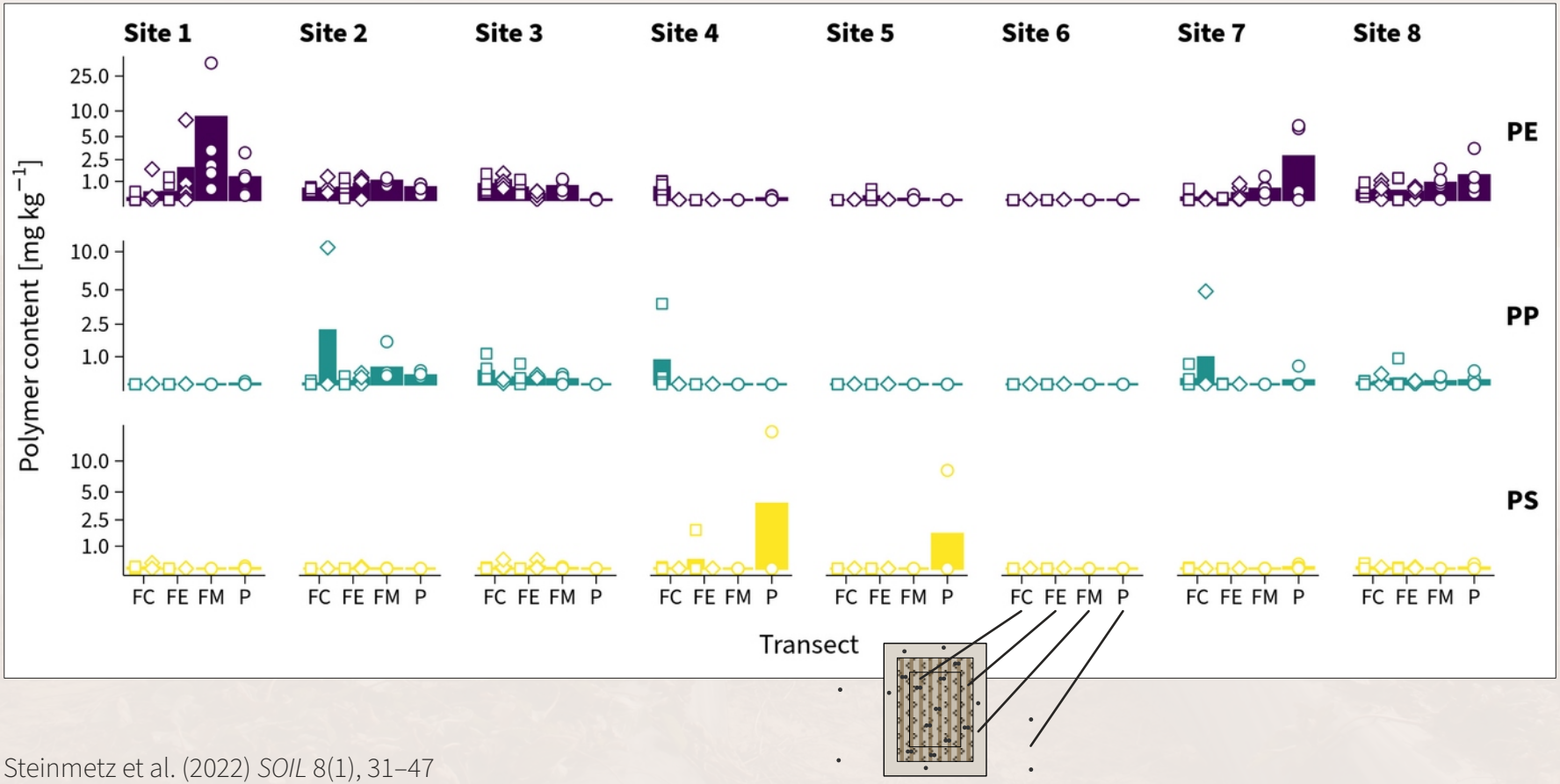
Clay content in the field: 10–36%

Feasibility study

Method validation

Field application

Soil-associated Plastic Debris ≤2 mm

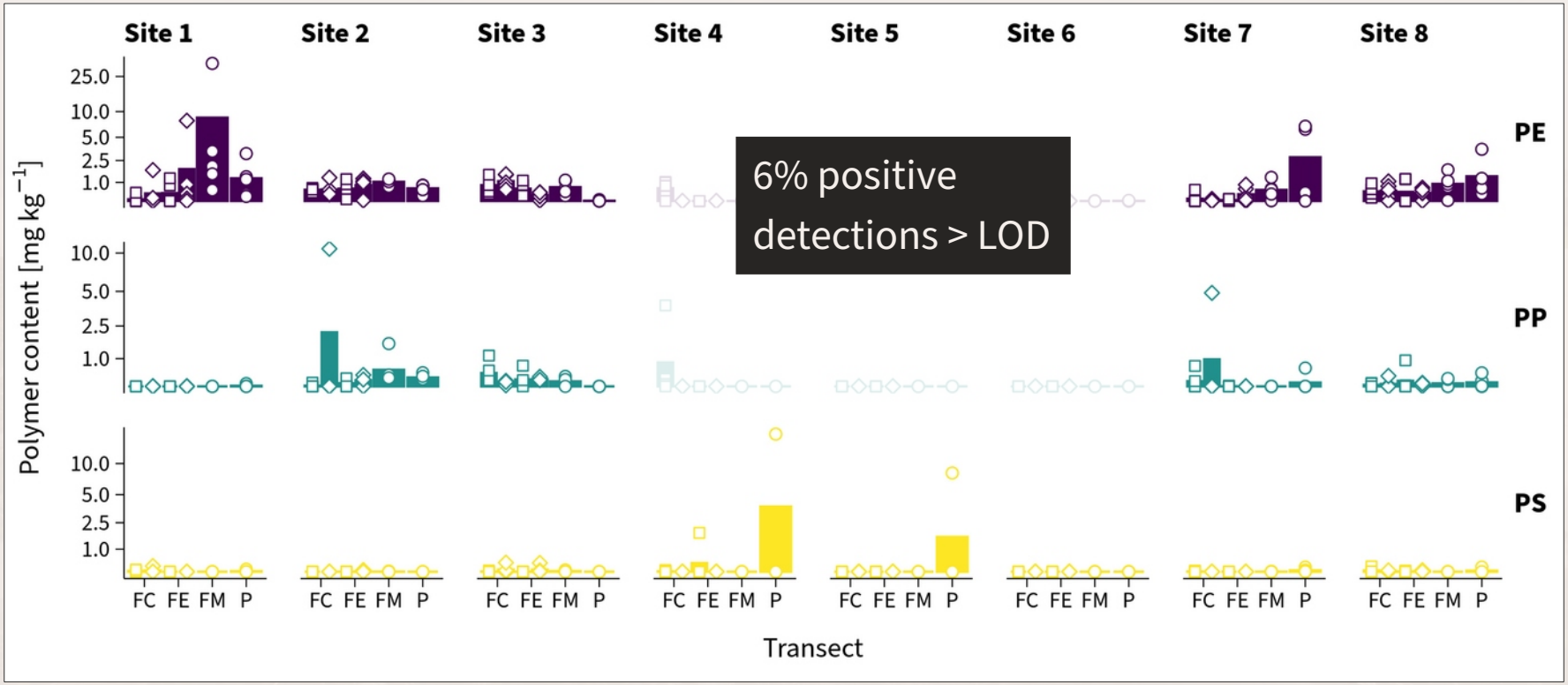


Feasibility study

Method validation

Field application

Soil-associated Plastic Debris ≤2 mm



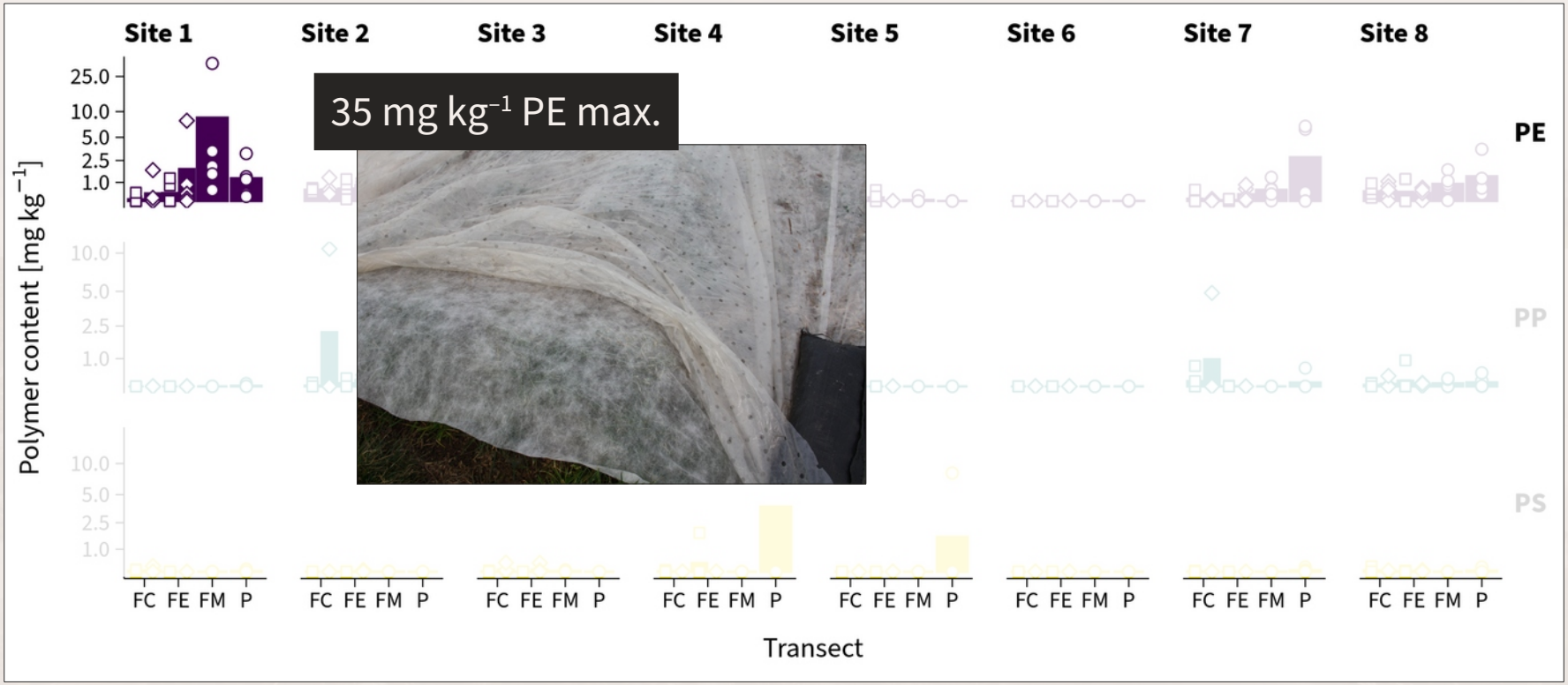
Feasibility study

Method validation

Field application

Steinmetz et al. (2022) *SOIL* 8(1), 31–47

Soil-associated Plastic Debris ≤2 mm

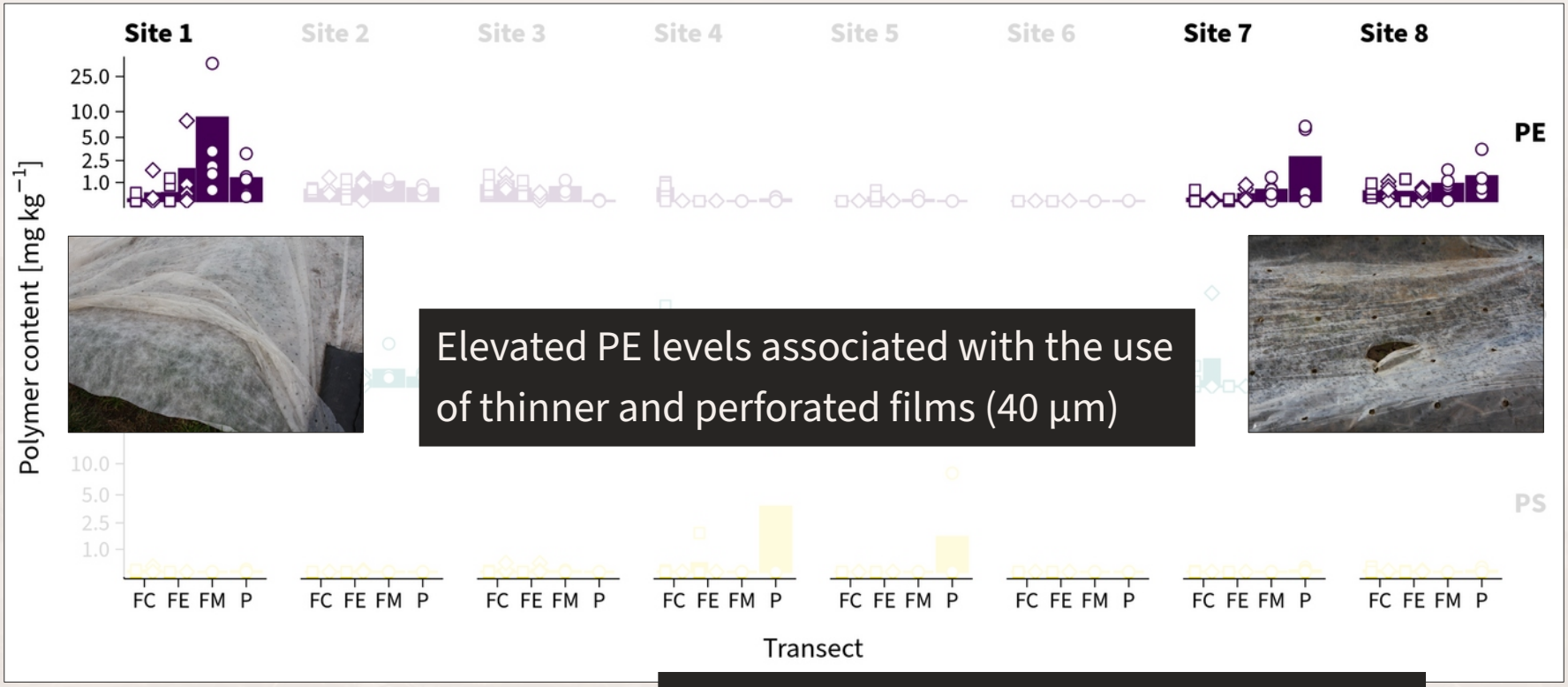


Feasibility study

Method validation

Field application

Soil-associated Plastic Debris ≤2 mm



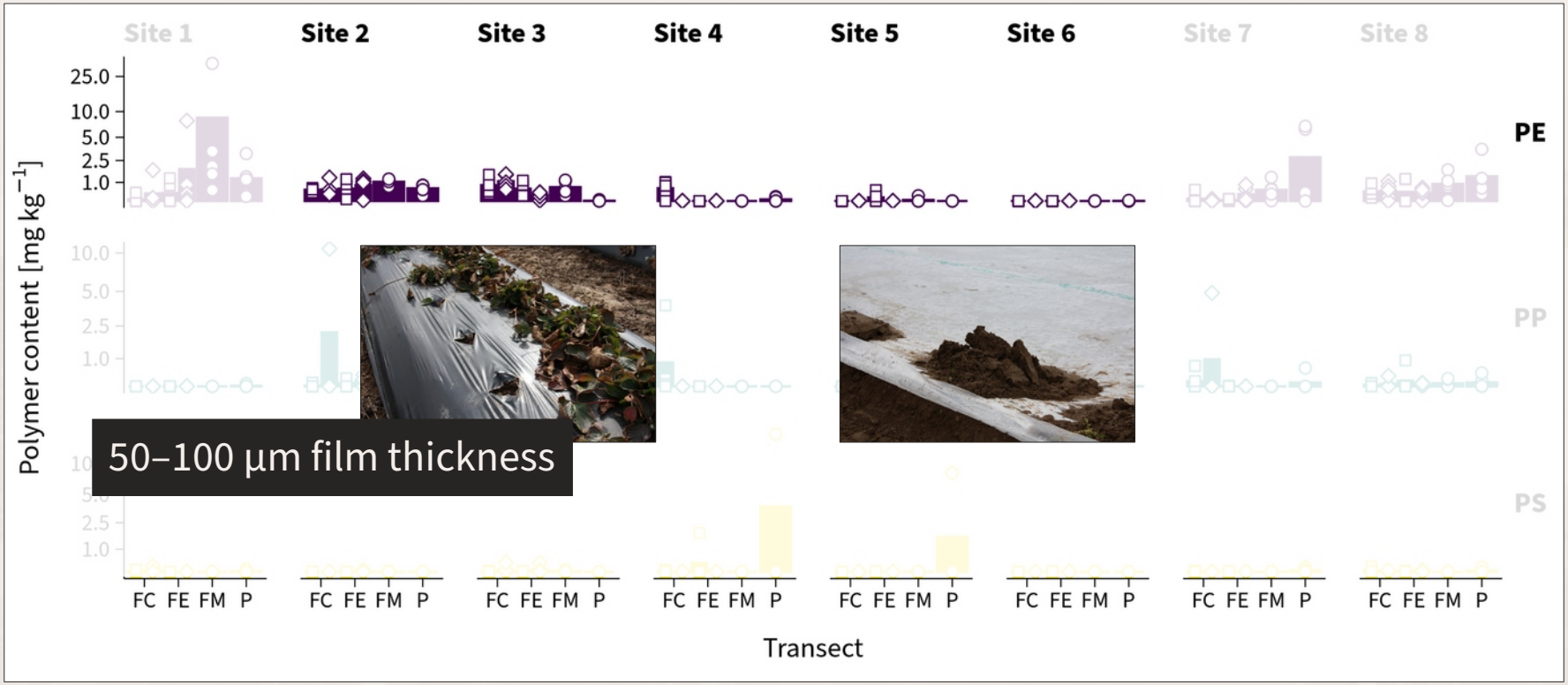
Feasibility study

Method validation

Field application

Steinmetz et al. (2022) *SOIL* 8(1), 31–47

Soil-associated Plastic Debris ≤2 mm

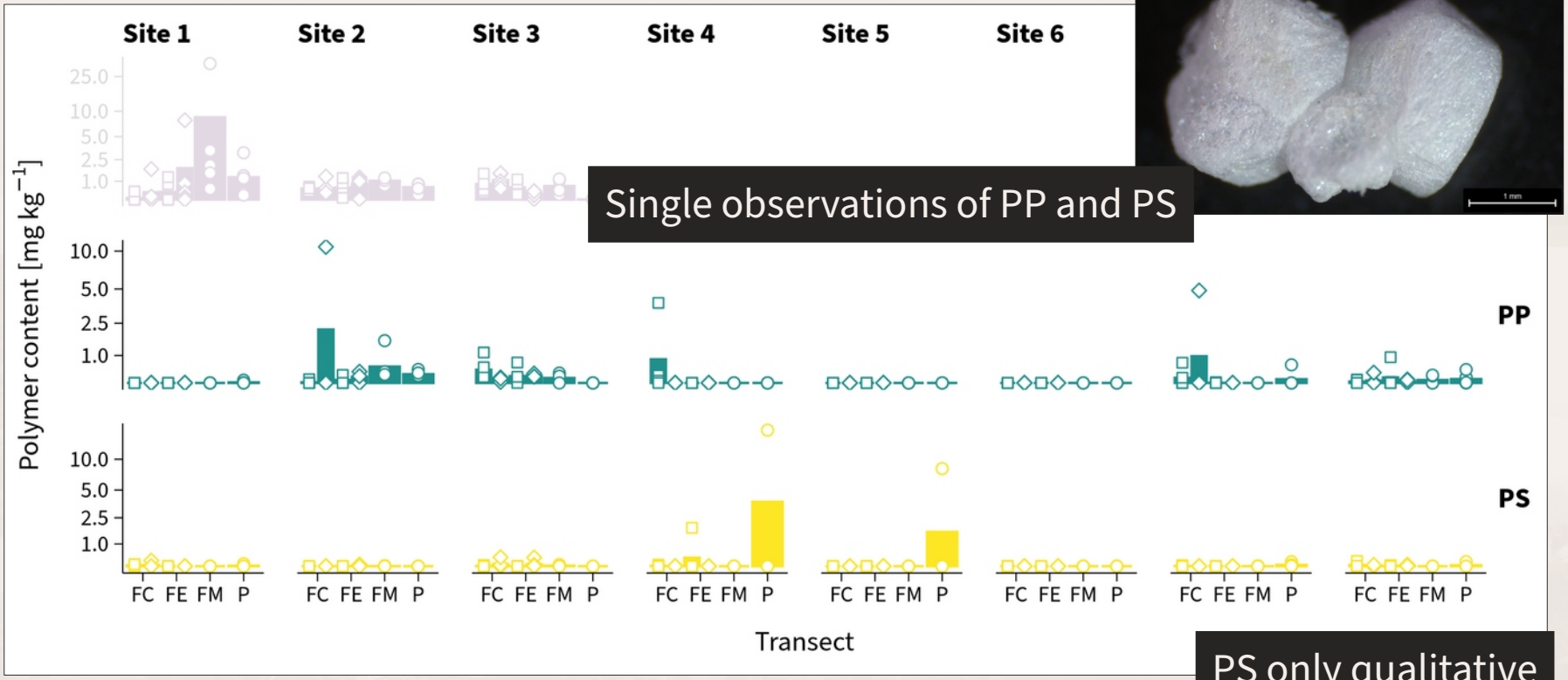


Feasibility study

Method validation

Field application

Soil-associated Plastic Debris ≤2 mm



Single observations of PP and PS

PS only qualitative

Feasibility study

Method validation

Field application

Steinmetz et al. (2022) *SOIL* 8(1), 31–47

Synthesis

Feasibility study

Mass-based quantification needed

Direct TGA/MS viable?

David et al. (2018) *Anal Chem*

Method validation

Polymer mixtures require chromatography

Solvent-based Py-GC/MS better?

Steinmetz et al. (2020) *J Anal Appl Pyrol*

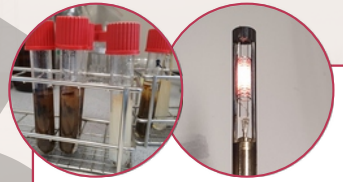
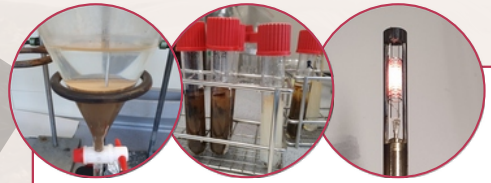
Field application

Add density separation for a first screening of plastic-covered fields

Steinmetz et al. (2022) *SOIL*

Refine

Synthesis

LODs	Sample amounts	
0.7 g kg^{-1}	50 mg	 **Direct TGA/MS**
1–86 mg kg^{-1}	4 g	 **Solvent-based GC/MS**
1–3 mg kg^{-1}	50 g	 **Density separation + solvent-based Py-GC/MS**

Refine

Photos: J. David & W.M. Heinze

Synthesis

C_{org}?

Clay content?

Easy sample handling

High sample throughput

Density separation
+ solvent-based Py-GC/MS

Refine

Photos: J. David & W.M. Heinze

Synthesis

- Solvent-based Py-GC/MS viable for simple & fast mass-based plastic analyses in soil
- Further development required for
  - polymers other than PE, PP (and PS)
  - more “complicated” matrices

C_{org}?

Clay content?

Easy sample handling

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Density separation
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Refine

Photos: J. David & W.M. Heinze

Synthesis

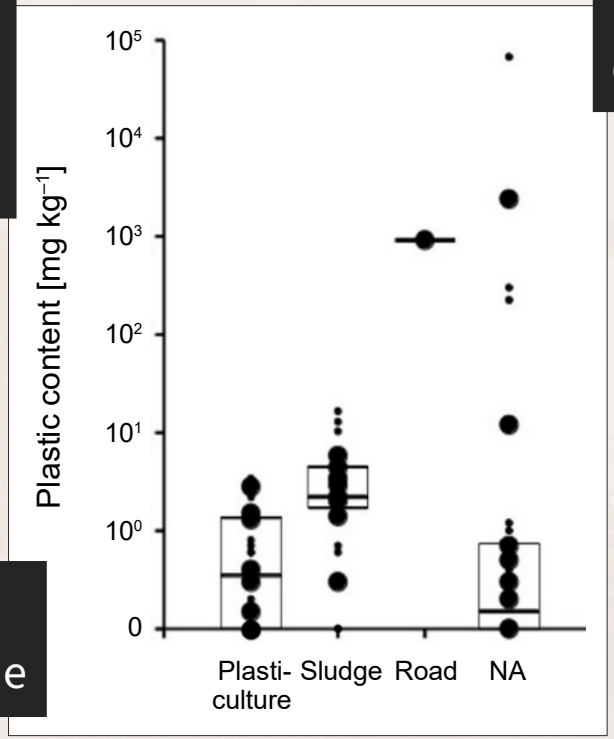
- Solvent-based Py-GC/MS viable for simple & fast mass-based plastic analyses in soil
- Further development required for
  - polymers other than PE, PP (and PS)
  - more “complicated” matrices

- More systematic field studies to discriminate sources better

Estimated Plastic Contents in Soil

Continuous plastic mulching (<10 µm thick) in China

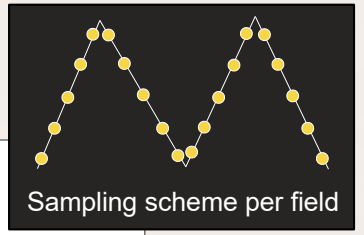
Difficult to exclude other sources

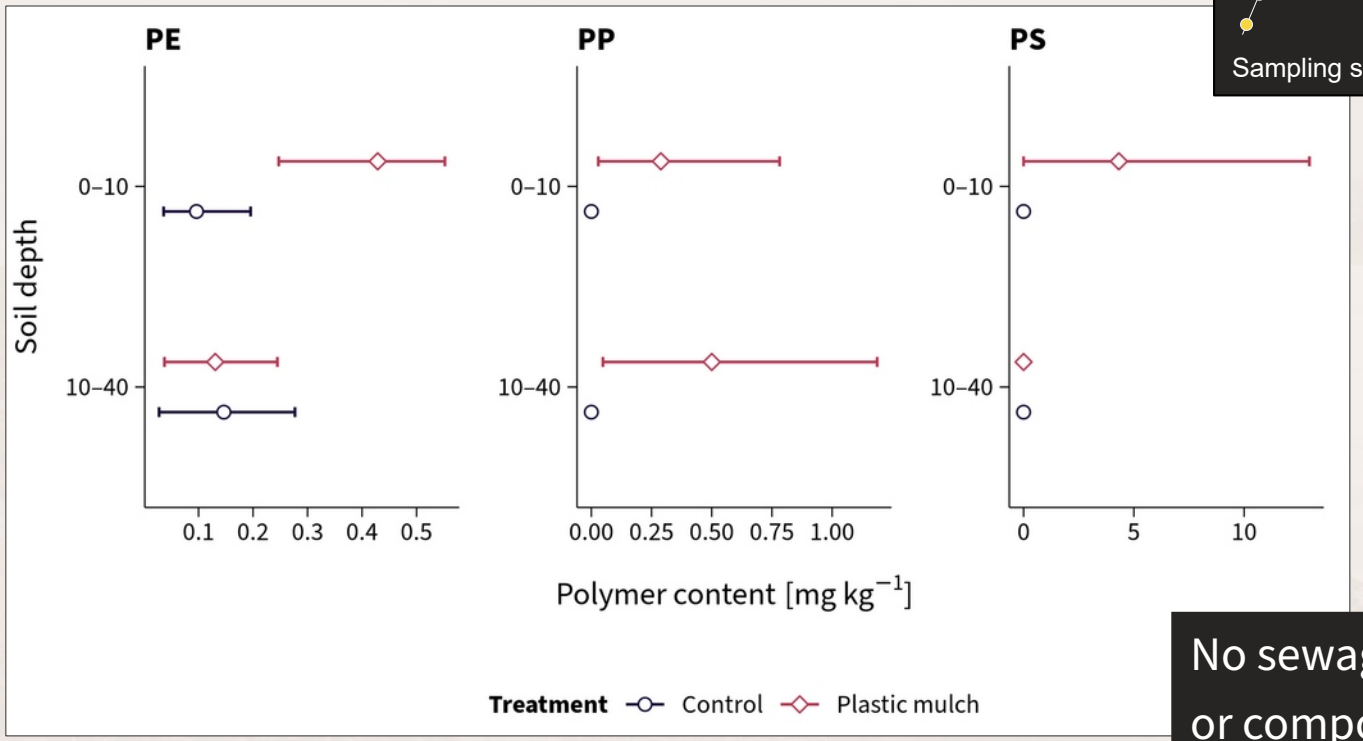


Particle-to-mass conversions error-prone

Büks & Kaupenjohann (2020) *SOIL* 6(2), 649–662

More Mass-based Field Studies



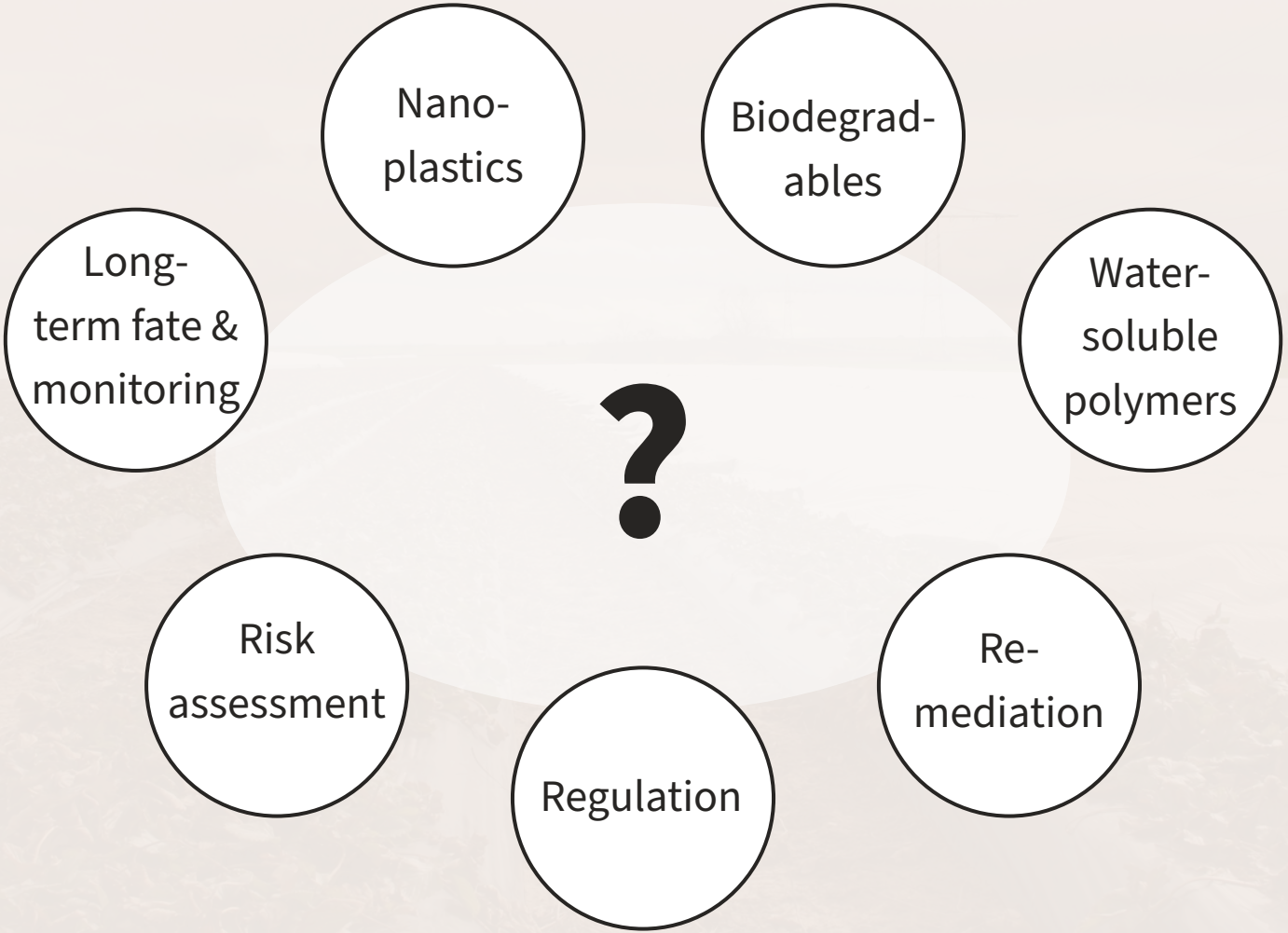


No sewage sludge or compost applied

Agricultural Plastic Covers—Source of Plastic Debris in Soil?

- Yes but limited
- Particularly for films <40 µm
- Explains drastic findings from China (<10 µm films)

Outlook


Nano-plastics
Biodegrad-ables
Long-term fate & monitoring
Water-soluble polymers
?
Risk assessment
Re-mediation
Regulation

Outlook

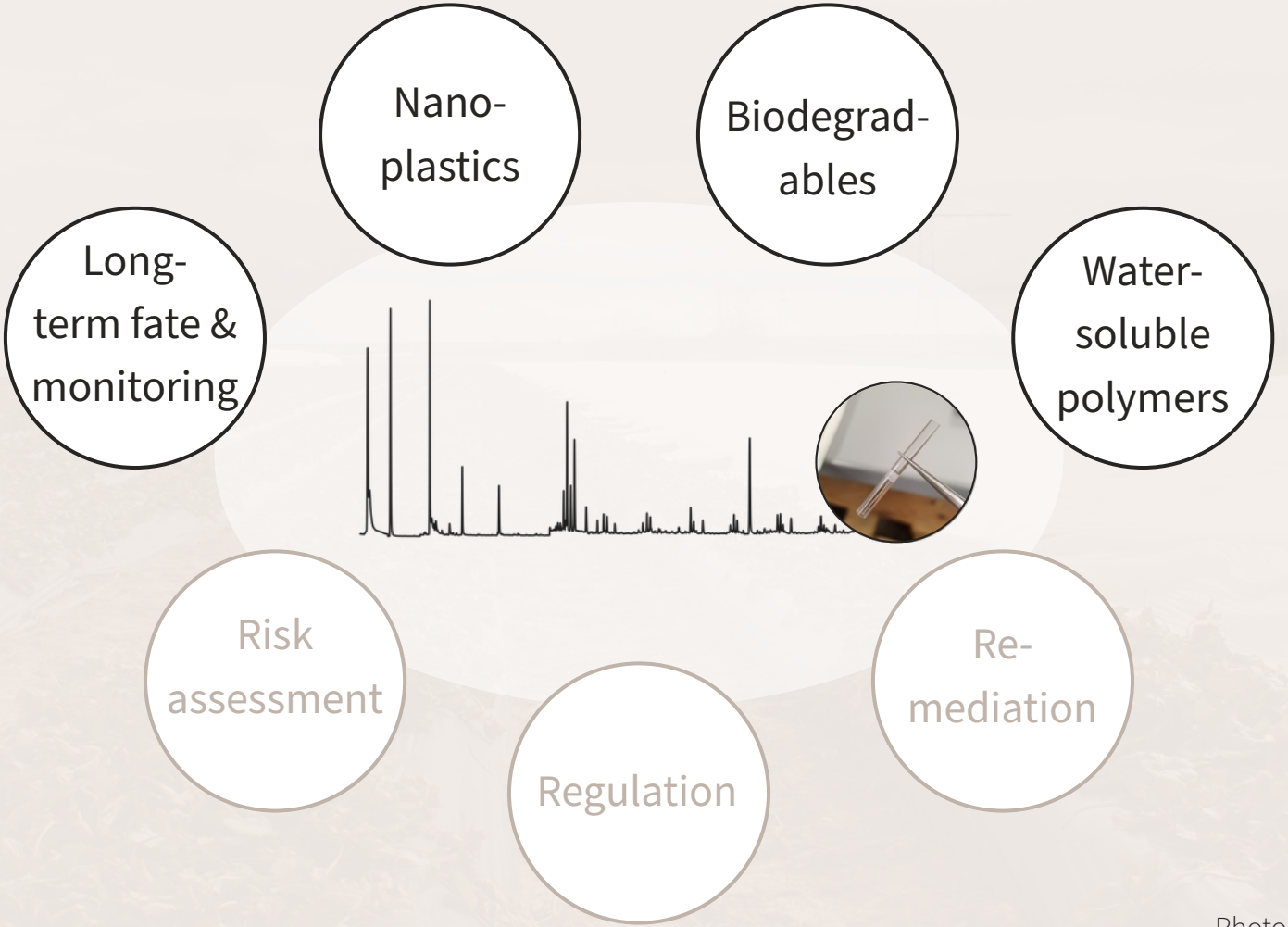


Photo: W.M. Heinze

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MINISTERIUM FÜR WISSENSCHAFT, WEITERBILDUNG UND KULTUR

BILDUNG MENSCH UMWELT

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