

AGRICULTURAL PLASTIC COVERS

SOURCE OF PLASTIC DEBRIS
IN SOIL?

ZACHARIAS STEINMETZ

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ZACHARIAS STEINMETZ

from Frankfurt am Main, Germany

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Thesis examiners:

Prof. Dr. Gabriele E. Schaumann, University of Koblenz–Landau

Prof. Dr. Geert Cornelis, Swedish University of Agricultural Sciences

Prof. Dr. Denise M. Mitrano, ETH Zurich

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Your eyes can deceive you. Don't trust them.

— Obi-Wan Kenobi

DECLARATION

I hereby declare that this dissertation entitled “Agricultural Plastic Covers—Source of Plastic Debris in Soil?” is my own work. All aids and sources have been specified and the contribution of other authors has been documented and referenced. I further confirm that this thesis has never been submitted for the award of any other degree at any university or other tertiary institution.

Landau, May 30, 2022

PARTS OF THIS THESIS AND AUTHOR CONTRIBUTIONS

This cumulative dissertation includes five chapters which have been published in similar form as peer-reviewed research papers. In detail, Chapters 2–6 are based on the respective accepted manuscripts without subsequent formatting by the publishing journal. Upon incorporation of the manuscripts into this dissertation, the wording was aligned across chapters, repetitions were removed or shortened, and spelling mistakes were corrected. Furthermore, all figures were redesigned to fit in size, font, and color schemes.

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My contribution to the scientific work is detailed below.

PUBLICATIONS

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Author contributions: The conceptualization and preliminary literature research for this review started in the framework of an elective master course at University of Koblenz–Landau. Beyond that, Z. Steinmetz took the lead in writing and finalizing the manuscript for publication. Z. Steinmetz prepared Sections 2.1 and 2.2, parts of Section 2.4, as well as Sections 2.5 and 2.7. C. Wollmann contributed Section 2.3 and parts of Section 2.4. M. Schaefer and J. Tröger wrote Section 2.6. C. Buchmann, J. David, K. Muñoz, O. Frör, and G. E. Schaumann supervised the project. All authors gave approval to the final version of the manuscript.

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OTHER RELEVANT CONTRIBUTIONS

In addition to the publications listed above, I contributed to two peer-reviewed publications and one non-peer-reviewed article related to microplastics research which are not part of this thesis.

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Brandes, E., Braun, M., Rillig, M. C., Leifheit, E. F., Steinmetz, Z., Fiener, P., and Thomas, D. (2020). “(Mikro-)Plastik im Boden”. *Bodenschutz* 3, p. 10. ISSN: 1868-7741. DOI: [10.37307/j.1868-7741.2020.03.10](https://doi.org/10.37307/j.1868-7741.2020.03.10).

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SUMMARY

The use of agricultural plastic covers has become common practice for its agronomic benefits such as improving yields and crop quality, managing harvest times better, and increasing pesticide and water use efficiency. However, plastic covers are suspected of partially breaking down into smaller debris and thereby contributing to soil pollution with microplastics. A better understanding of the sources and fate of plastic debris in terrestrial systems has so far been hindered by the lack of adequate analytical techniques for the mass-based and polymer-selective quantification of plastic debris in soil. The aim of this dissertation was thus to assess, develop, and validate thermoanalytical methods for the mass-based quantification of relevant polymers in and around agricultural fields previously covered with fleeces, perforated foils, and plastic mulches. Thermogravimetry/mass spectrometry (TGA/MS) enabled direct plastic analyses of 50 mg of soil without any sample preparation. With polyethylene terephthalate (PET) as a preliminary model, the method limit of detection (LOD) was 0.7 g kg^{-1} . But the missing chromatographic separation complicated the quantification of polymer mixtures. Therefore, a pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) method was developed that additionally exploited the selective solubility of polymers in specific solvents prior to analysis. By dissolving polyethylene (PE), polypropylene (PP), and polystyrene (PS) in a mixture of 1,2,4-trichlorobenzene and *p*-xylene after density separation, up to 50 g soil became amenable to routine plastic analysis. Method LODs were $0.7\text{--}3.3 \text{ mg kg}^{-1}$, and the recovery of 20 mg kg^{-1} PE, PP, and PS from a reference loamy sand was 86–105%. In the reference silty clay, however, poor PS recoveries, potentially induced by the additional separation step, suggested a qualitative evaluation of PS. Yet, the new solvent-based Py-GC/MS method enabled a first exploratory screening of plastic-covered soil. It revealed PE, PP, and PS contents above LOD in six of eight fields (6% of all samples). In three fields, PE levels of $3\text{--}35 \text{ mg kg}^{-1}$ were associated with the use of $40 \mu\text{m}$ thin perforated foils. By contrast, $50 \mu\text{m}$ PE films were not shown to induce plastic levels above LOD. PP and PS contents of $5\text{--}19 \text{ mg kg}^{-1}$ were restricted to single observations in four fields and potentially originated from littering. The results suggest that the short-term use of thicker and more durable plastic covers should be preferred to limit plastic emissions and accumulation in soil. By providing mass-based information on the distribution of the three most common plastics in agricultural soil, this work may facilitate comparisons with modeling and effect data and thus contribute to a better risk assessment and regulation of plastics. However, the fate of plastic debris in the terrestrial environment remains incompletely understood and needs to be scrutinized in future, more systematic research. This should include the study of aging processes, the interaction of plastics with other organic and inorganic compounds, and the environmental impact of biodegradable plastics and nanoplastics.

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1

GENERAL INTRODUCTION AND OBJECTIVES

1.1 PLASTICS IN AGRICULTURE

The use of plastics in agriculture has grown exponentially since the advent of plastics in the 1950s (Mormile et al., 2017; Geyer et al., 2017). Between 2013 and 2019, the German agricultural sector consumed about 1.1 Mt plastics per year. This is equivalent to 4.6% of Germany's total annual plastic consumption (Bertling et al., 2021). The majority (50%) of the agricultural plastics applied to soil is estimated to be films, fleeces, and nets used for greenhouse and low tunnels, complete field coverage, near-ground mulching, or silage storage (Mormile et al., 2017; Bertling et al., 2021). The use and potential implications of plastic mulching in agriculture are detailed in Chapter 2. Further applications are irrigation pipes, seed coatings, and plant pots (Bertling et al., 2021). Conventional, this is petrochemical, polyethylene (PE) and polypropylene (PP) are by far the most used polymers for these products, followed by polystyrene (PS), polyvinyl chloride (PVC), and polyethylene terephthalate (PET) (PlasticsEurope, 2019; Zhang et al., 2021b). Bio-based or biodegradable polymers^[1] like polylactic acid (PLA) or polybutylene adipate terephthalate (PBAT) are still a niche (PlasticsEurope, 2019; Bertling et al., 2021). In addition to those direct and controlled uses of agricultural plastics, agricultural landscapes receive mixed plastic inputs from sewage sludge and compost applications, littering, and erosion (Hurley and Nizzetto, 2018; Bläsing and Amelung, 2018; Stubbins et al., 2021). All this makes agricultural land a particular and highly diverse hotspot for all kinds of plastics (Corradini et al., 2021; Zhang et al., 2021b). However, this multitude of agricultural plastic applications challenges a quantitative discrimination of the various sources of plastic inputs to agricultural soil.

Other than the plastic inputs from littering, sewage sludge, or compost, plastic covers are intentionally applied to agricultural fields for optimizing plant growth (Chapter 2). Although agricultural plastic covers are ideally recovered and recycled after their use, their application is nearly as regulated as other (agro)chemicals (EU REACH Regulation, 2006) or waste (EU Waste Framework Directive, 2008) so that remnants inadvertently left on the field may contribute to soil pollution with plastic debris. A recent modeling study, for instance, suggested that lost agricultural plastic covers account for annual plastic emissions of 4–9 kg ha⁻¹ to agricultural landscapes in Germany (Bertling et al., 2021). Brandes et al. (2021) estimated that

^[1] Biodegradable polymers are specifically designed to dissipate after a certain period of time under predefined conditions, whereas bio-based plastics are conventional polymers stemming from renewable instead of fossil resources (Lambert and Wagner, 2017).

such losses increase the plastic content in agricultural soil by 5–9 mg kg⁻¹ per year. In contrast, sewage sludge and compost applications account for annual plastic emissions of 21 and 7 kg ha⁻¹, respectively (Bertling et al., 2021) leading to a potential plastic accumulation of up to 83 mg kg⁻¹ (Brandes et al., 2021). However, both Bertling et al. (2021) and Brandes et al. (2021) emphasized that plastic emissions from agricultural plastic covers are most likely underestimated, while sewage sludge applications are increasingly restricted in the EU (Collivignarelli et al., 2019). Apart from these estimates, empirical evidence on plastic emissions from agricultural plastic covers is still scarce and comes mostly from non-EU countries (Huang et al., 2020; Zhou et al., 2020). Moreover, it remains incompletely understood under which conditions and at what extent the emitted plastics disintegrate into microplastics, that is debris smaller than 1–5 mm, or even nanoplastics <1 μm (Hartmann et al., 2019). Such small plastic debris may be easily incorporated into the soil environment, which would render soil a potential sink of plastics in the long term. Yet, the fate of plastic debris in the terrestrial environment and particularly in soil remains largely understudied.

These knowledge gaps are probably attributed to the analytical challenges the soil matrix poses for a reliable plastic quantification (Qi et al., 2020). These challenges mostly originate from the diverse and heterogeneous nature of soil as well as structural similarities between the soil matrix and the analyzed plastics (see Section 1.3 and Chapter 5). In this regard, thermoanalytical methods are especially promising since they are well established for the respective characterization of pure polymers and soil (Picó and Barceló, 2020). But they were so far seldom adapted for the quantification of plastics *in* soil. The great advantage of thermoanalytical methods over particle-based Fourier-transform infrared (FTIR) or Raman microspectroscopy is their speed and high sample throughput, which would allow extensive screening and monitoring studies. Moreover, thermoanalytical methods are mass-based and could thus enable direct comparisons with modeling or effect data that are also usually expressed on a mass basis. Contrary to the size limitations of particle-based microspectroscopic methods, thermoanalytical approaches have the potential of quantifying nanoplastics (Chapter 5; Parolini et al., 2021).

1.2 THERMOANALYTICAL METHODS FOR PLASTIC CHARACTERIZATION AND QUANTIFICATION

Thermoanalytical methods such as differential scanning calorimetry (DSC) or evolved gas analysis (EGA) are commonly applied in polymer science to study the material properties of a sample at different temperatures. DSC, for instance, monitors the amount of energy required to change the temperature of a sample. This technique is used to determine the melting, crystallization, and glass transition temperatures of a polymer or any other sample (Menczel et al., 2009). These parameters are informative proxies for characterizing and better understanding the polymer's (supra)molecular structure and morphology, including its molecular weight and degree of crosslinking (Biale et al., 2021). The exposure of plastics to ultraviolet (UV) light, water, or temperature changes, for instance, causes scissions in the polymer backbone, carbonyl formation, and volatilization of oligomers and polymer additives. Such changes are typically summarized as aging and often lead to embrittlement and the eventual disintegration of plastics (Volynskii et al., 2007; White, 2006). DSC can thus help to scrutinize the disintegration potential of a

plastic material into smaller debris.

EGA enables the identification and quantification of gases evolving from a sample at a specific temperature or temperature range using a mass spectrometer (MS) or FTIR detector. Thermogravimetry/mass spectrometry (TGA/MS) couples EGA with a microbalance that simultaneously records the weight loss of the sample (Prime et al., 2009). Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) adds the possibility of chromatographically separating the evolved gases prior to detection (Rial-Otero et al., 2009). Depending on the applied temperature, the main processes leading to gas evolution are thermal desorption and decomposition. Which process prevails at what temperature range depends on the type of sample. The thermal desorption of volatile additives like plasticizers, lubricants, or antioxidants is typically studied between 100 and 300 °C (Reichel et al., 2020; Akoueson et al., 2021). Polymer decomposition sets in above 180 °C and peaks at 300–600 °C (Table 1.1). If the polymer is decomposed in an inert or reductive atmosphere like N₂ or H₂, the process is called pyrolysis and leads to distinct pyrolysis products, also called pyrolysates. Combustion in an O₂ atmosphere would favor the hardly selective formation of CO₂ (Beyler and Hirschler, 2002).

Pyrolytic reactions typically involve the random, homolytic cleavage of the polymer backbone into oligomer radicals. A consecutive hydrogen transfer, β-scission, or radical recombination produces stable monomers, oligomers, or derivatives (Bockhorn et al., 1999; Beyler and Hirschler, 2002). The pyrolysis of PE, for instance, results in n-alkanes, n-alkenes, and n-alkadienes of different chain lengths as major pyrolysates (Figure 1.1). PP decomposes into n-pentane and various methylalkenes including 2,4-dimethyl-1-heptene. Pyrolyzing PS mainly yields the styrene monomer, dimer, and trimer, as well as α-methylstyrene. PET thermally decomposes into benzoic acid and 4-(vinylloxycarbonyl) benzoic acid monomers, its respective dimers, and trimers (Figure 1.1; Tsuge et al., 2011).

Quantitative TGA/MS or Py-GC/MS applications aim to identify pyrolysates that can be used as characteristic markers for polymer quantification. At the same time, these marker compounds should not occur in the analyzed soil matrix. To avoid interferences, both instrumental analytics and sample preparation need to be carefully adjusted.

1.3 SOIL—A COMPLEX ANALYTICAL MATRIX

From an analytical perspective, soil is a multiphased, heterogeneous mixture of solids, liquids, and gases. The solid soil matrix consists of various minerals and soil organic matter (SOM) aggregated to a porous system that is filled with soil air and soil solution. The overall soil composition depends on the parent rock and its weathering, past and present climate, vegetation, and land use (Brümmer et al., 2016).

Soil particles are classified by size into sand (63 μm to 2 mm), silt (2–63 μm), and clay (<2 μm) (Sponagel et al., 2005; FAO, 2014)^[2]. Soil mineralogy is dominated by quartz (SiO₂) and feldspars (Na–K–Ca–Al silicates) but also includes Al and Fe oxides like Al(OH)₃ or FeOOH, calcite (CaCO₃), and various clay-sized phyllosilicates. These clay minerals are further grouped into kaolinites, smectites, vermiculites, illites, and chlorites dependent on the number and structure of silicate layers as well as the degree of isomorphous substitution of Si⁴⁺ with Al³⁺. Therefore, clay minerals have a negative surface charge that is typically balanced with K⁺, Na⁺,

Table 1.1: Decomposition temperatures of selected polymers (Beyler and Hirschler, 2002; Ferriol et al., 2003; Shiono et al., 2015).

Polymer	Onset [‡] [°C]	Peak maximum [°C]
LDPE	318	490
HDPE	275	
PP	315	466
PS	330	441
PMMA	282	377
PVC	184	320
PTFE	502	579

[‡] temperature at which 1% of polymer mass loss occurred in an N₂ atmosphere; LDPE = low-density PE; HDPE = high-density PE; PP = polypropylene (isotactic); PS = polystyrene; PMMA = poly(methyl methacrylate); PVC = polyvinyl chloride; PTFE = polytetrafluoroethylene.

^[2] Note that the USDA (1999) classification system defines the upper size limits of sand, silt, and clay at 2 mm, 50 μm, and 2 μm, respectively.

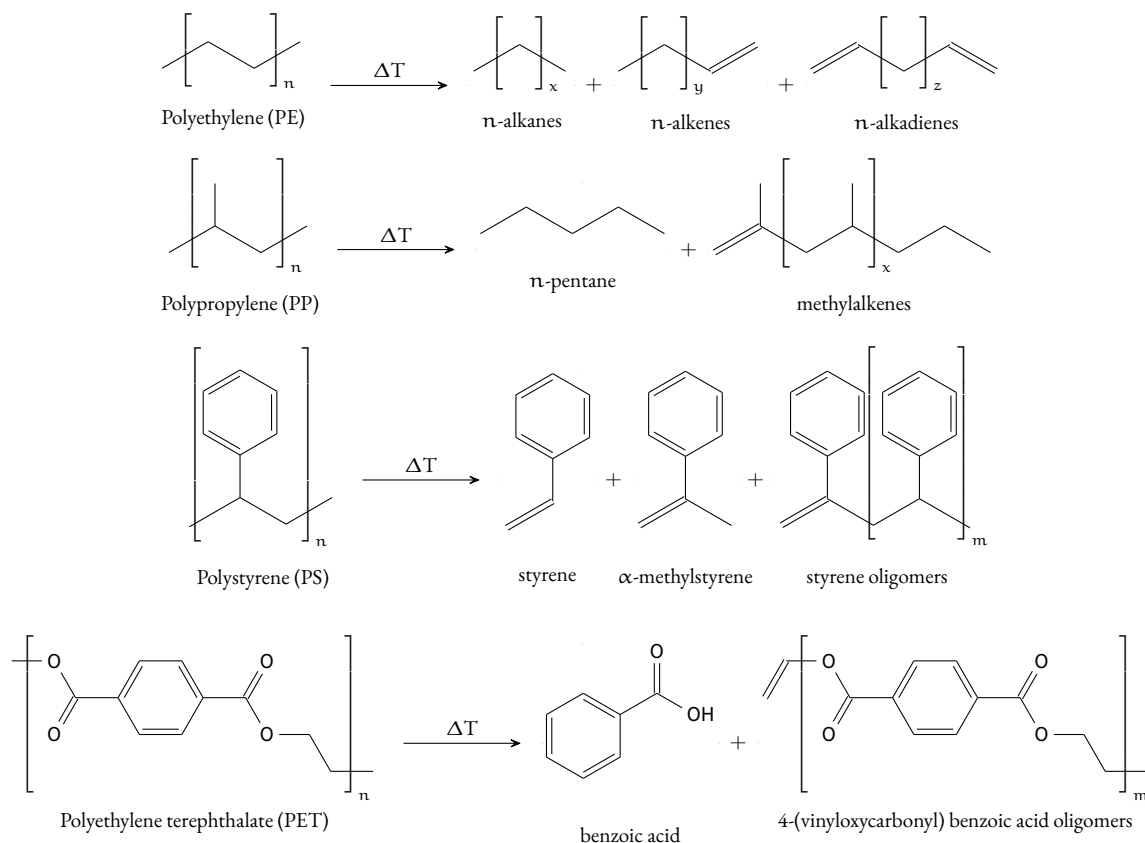


Figure 1.1: Structural formulas of the polymers investigated in this thesis together with their major pyrolysates (Tsuge et al., 2011); the pyrolysates detectable via Py-GC/MS typically have an x , y , and z of 4–36 and m is <3 . See Table 4.2 for a detailed overview of PE, PP, and PS pyrolysates.

or divalent ions. By contrast, the charge of Al and Fe oxides largely depends on the soil pH and may be even positive under acidic or circumneutral conditions (Stahr, 2016).

SOM comprises plant and animal litter at various stages of decomposition. The labile SOM fraction contains easily degradable molecules like peptides, (phospho)lipids, and carbohydrates (Figure 1.2), whereas the stable fraction consists of more complex macromolecules. Such macromolecules may originate from lignin or other natural polymers like chitin or cellulose (Kögel-Knabner, 2016). The amphiphilic domains of the SOM constituents can interact with clay minerals and Al or Fe oxides via electrostatic interactions or van der Waals forces forming organo–mineral complexes (Kleber et al., 2007).

Similar to the thermoanalysis of polymers (Section 1.2), the chemical composition of SOM may be characterized by Py-GC/MS (Ceccanti et al., 2007; Hatcher et al., 2001). SOM pyrolysis typically generates a large variety of different components including alkanes, alkenes, ketones, alkylbenzenes, heterocycles, and their derivatives (Figure 1.2). Whereas alkanes and alkenes are rather unspecific and may originate from any kind of lipid or wax-like structure, ketones such as furfural or levoglucosan can be used as characteristic markers for carbohydrates. Pyrrole and indole are exemplary markers for proteins, and phenolic compounds like cresols or 4-hydroxy-2-methoxycinnamaldehyde are indicative for lignin (Figure 1.2; Hatcher et al., 2001).

The alkanes and alkenes released during the pyrolysis of aliphatic SOM (Figure 1.2) are likely to interfere with the quantification of PE, which relies on alkane and alkene markers (Figure 1.1). Once identical pyrolysates are formed, subsequent chromatography cannot separate them anymore which may result in false positive

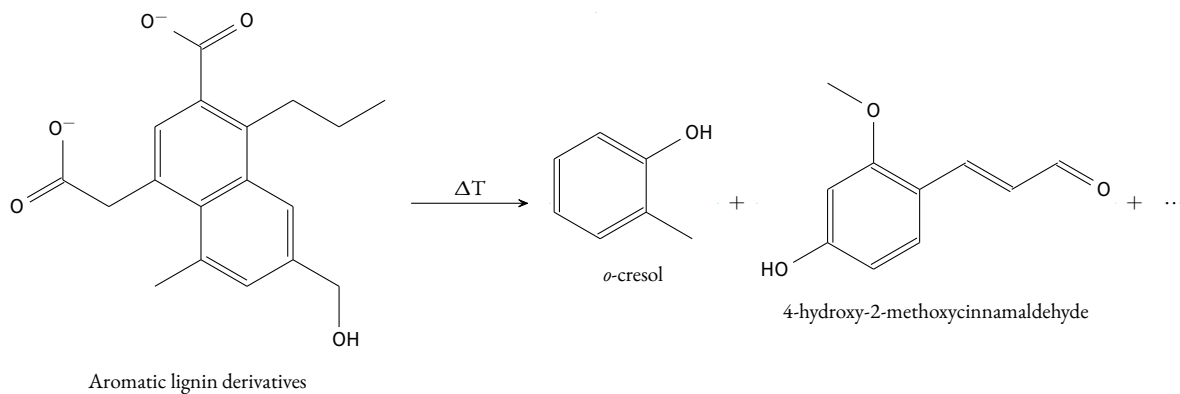
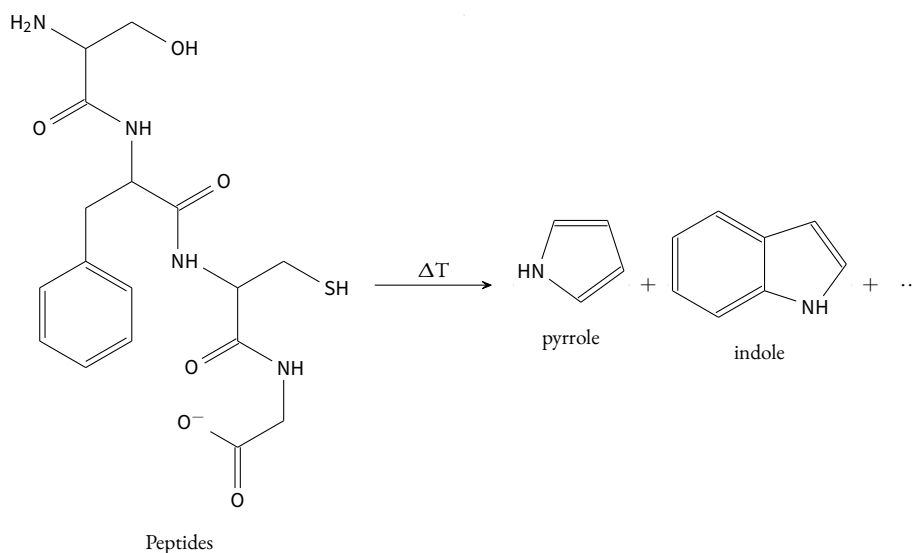
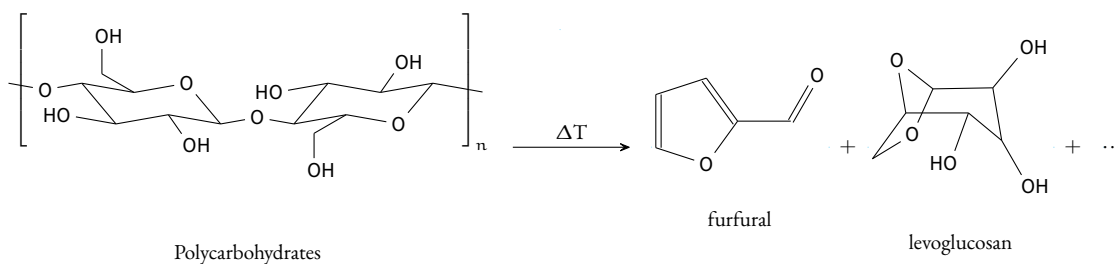
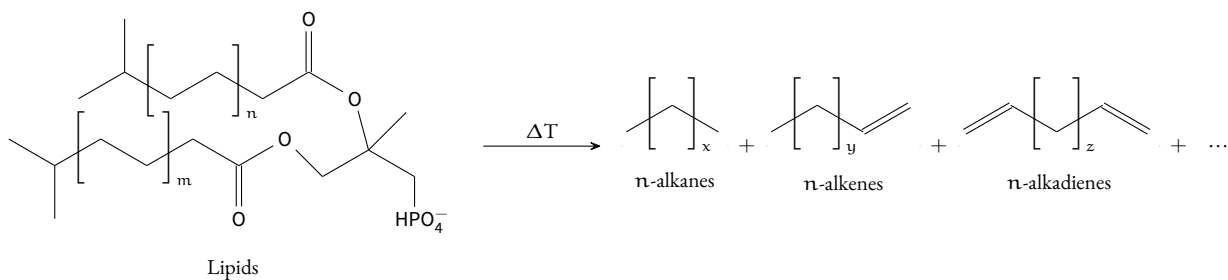


Figure 1.2: Common soil organic matter (SOM) groups (Newcomb et al., 2017; Kögel-Knabner, 2016) and a selection of their primary pyrolysates (Ceccanti et al., 2007; Hatcher et al., 2001; Tsuge et al., 2011).

PE detections (Dümichen et al., 2015). Interfering SOM pyrolysates will become the most evident when aiming for the analysis of low PE levels in organic-rich soils. It remains worth noticing that such or similar interferences currently affect the majority of microspectroscopic and thermoanalytical methods for the analysis of plastic debris in environmental samples. Different from thermoanalytical methods, microspectroscopic methods are prone to interferences from SOM auto-fluorescence or physical obstruction of plastic particles with soil constituents. This is discussed in detail in Chapter 5. On the contrary, other polymers than PE or PE at levels substantially exceeding the background level of aliphatic SOM may be directly amenable to thermoanalysis. But the quantification of plastic traces will probably require a certain degree of sample preparation prior to their quantification.

Such a sample preparation procedure ideally removes a large part of the interfering matrix while preserving or even enriching the analytes of interest. An effective separation of the sample matrix from the analytes is usually achieved by exploiting differences in their physicochemical properties like their density, their specific interaction with other solid or liquid phases, or their recalcitrance towards acids, bases, or oxidation agents (Chapter 5). The more similar the analyte and the matrix are, the harder becomes their separation. In this respect, soil is a complicated matrix for its heterogeneous, multiphased nature. Separating plastic debris from soil is even more complex as both are particulate phases of polymeric composition which may stabilize each other via organo–mineral or organo–organo interactions (Luo et al., 2020; Schaumann, 2006). Similar to SOM, partly negatively charged polymers like PS may preferably bind to clay minerals or metal oxides. In addition to those structural and functional similarities, plastic particles may be physically protected from separation if they are coated with natural polymers and biofilms or occluded in soil aggregates. All this eventually reduces the recovery of the plastic particles measured after their separation from the soil matrix.

These difficulties may be overcome or at least mitigated with a well designed analytical approach that exploits the selective solubility of certain polymers in a specific organic solvent without co-dissolving interfering matrix constituents like SOM. Dissolving polymers is common practice for the analysis of polymer molecular weights via size exclusion chromatography (SEC) and gel permeation chromatography (GPC) (Table 1.2) but may as well be combined with established sample preparation methods for plastic debris and novel thermoanalytical approaches (Chapters 4 and 5). Besides reducing matrix effects and interferences, polymer dissolution may further increase sample homogeneity as it enables the extraction of plastic debris from sample amounts that are usually too high for direct thermoanalysis. Furthermore, polymer solutions simplify the sample handling and facilitate sample aliquotation, dilution, and preconcentration.

Table 1.2: Solubility characteristics of selected polymers (Bivens, 2016).

Polymer	Solvent	Temperature [°C]
PE	TCB	160
PP	TCB	160
PS	THF	40
PMMA	THF	35
PVC	THF	25

TCB = 1,2,4-trichlorobenzene; THF = tetrahydrofuran.

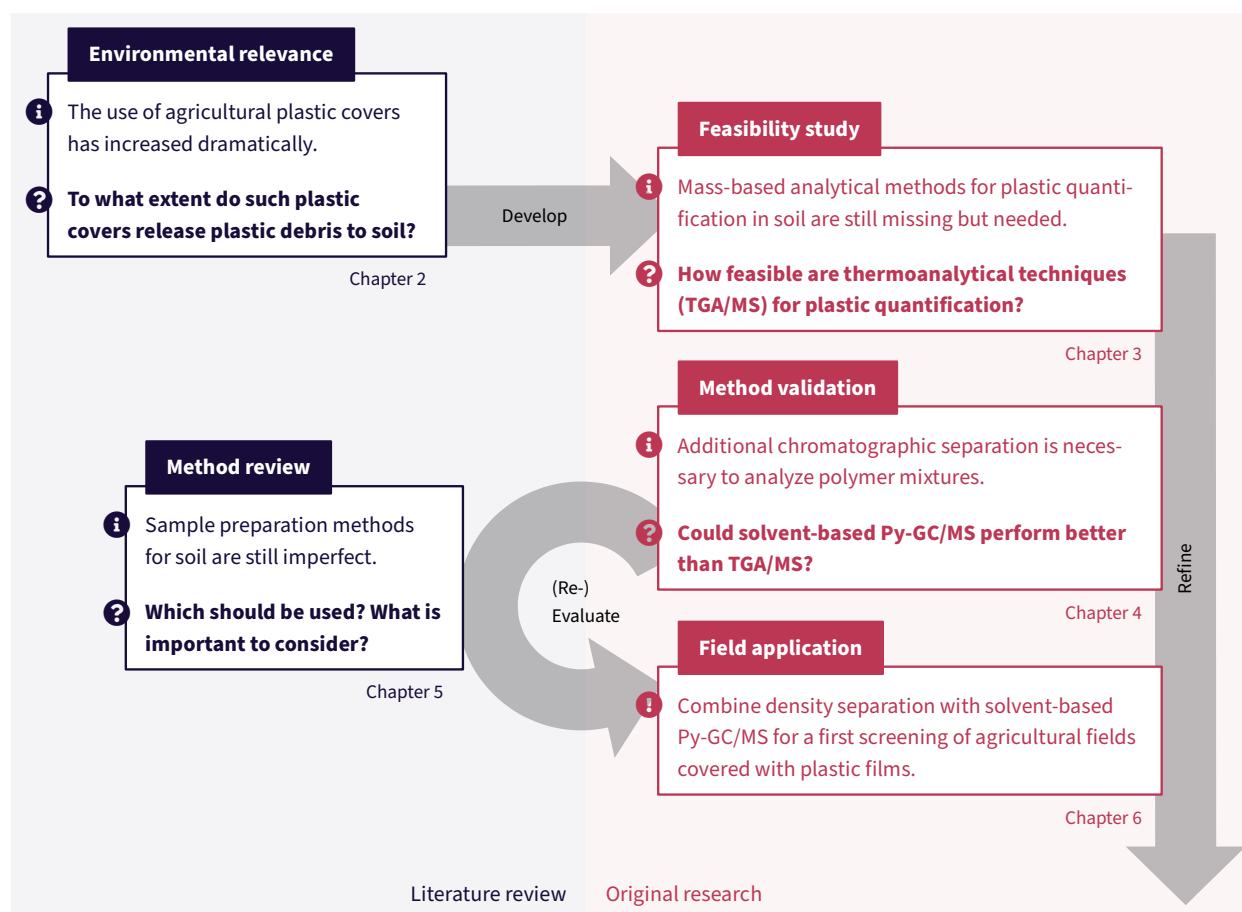
1.4 OBJECTIVES AND OUTLINE OF THIS THESIS

The main objective of this dissertation was to scrutinize the extent to which agricultural plastic covers function as a source of plastic debris in soil. Due to the diverse use cases for agricultural plastic covers, my thesis begins with a comprehensive review of the application of agricultural plastic covers and a critical evaluation of their benefits and potential risks (Chapter 2, Figure 1.3). Driven by the increasing, yet virtually unquestioned application of agricultural plastic covers, I hypothesized

that agricultural plastic covers pollute the surrounding soil with plastic debris at micrometer scale. I expected higher plastic contents in and close to agricultural fields covered with plastic than in the fields' periphery.

However, adequate analytical tools for plastic quantification in soil were still missing at that stage. Prior to addressing my hypothesis, I thus developed and validated new methods for the quantitative analysis of plastic debris in soil. The final method was aimed to be fast, simple, sensitive, and selective to allow for an effective screening of plastic debris in agricultural soil. To facilitate future comparisons with mass-based effect and modeling data, I focused on mass-based thermoanalytical methods. In detail, my method development included the following objectives:

- (1) Assessing the applicability of thermoanalytical methods for the mass-based quantification of plastic debris in soil.
- (2) Making use of additional chromatographic separation to increase the selectivity of the method for polymer mixtures.
- (3) Minimizing matrix interferences and increasing sample homogeneity by dissolving the polymer analytes in an organic solvent prior to quantification.
- (4) Applying the final method in a first, exploratory screening of agricultural soil covered with plastic films.



Objectives (1) to (4) were addressed consecutively as each objective relied on the outcome of the previous objective. Objective (1) is covered in Chapter 3. This first

Figure 1.3: Conceptual overview and research questions addressed in this thesis.

proof-of-principle study used PET as a model compound and one reference soil to investigate the potential of TGA/MS for plastic quantification. The method was designed to enable the rapid analysis of 50 mg soil without any sample preparation. To facilitate the analysis of polymer mixtures and increase instrumental sensitivity, I continued method development using Py-GC/MS (objective (2)). However, Py-GC/MS is typically restricted to sample amounts <1 mg which poses high requirements on sample homogeneity. To overcome this and to reduce the risk of potential matrix interferences, I used 1,2,4-trichlorobenzene (TCB) to selectively dissolve PE, PP, and PS in three different reference soils (objective (3)). This new solvent-based Py-GC/MS approach made up to 4 g of soil amenable to the quantification of plastic debris (Chapter 4). Chapter 5 critically (re-)evaluates this and other analytical techniques. With this knowledge at hand, I further refined my method for its subsequent application (objective (4), Chapter 6). This involved adjustments in the extraction mixture to increase polymer solubility and the addition of a suitable yet simple sample preparation technique to the existing Py-GC/MS approach. Thereby, plastic debris could be quantified from 50 g soil. This sample amount was considered sufficiently large for a representative screening study of eight agricultural fields covered with plastic films (Chapter 6). Therein and in the following discussion (Chapter 7), I conclusively address the key hypothesis of this thesis and reflect on the implications of my findings.

2

PLASTIC MULCHING IN AGRICULTURE

Abstract Plastic mulching has become a globally applied agricultural practice for its instant economic benefits such as higher yields, earlier harvests, improved fruit quality, and increased water use efficiency. However, knowledge of the sustainability of plastic mulching remains vague in terms of both an environmental and agronomic perspective. This chapter critically discusses the current understanding of the environmental impact of plastic mulch use by linking knowledge of agricultural benefits and research on the life cycle of plastic mulches with direct and indirect implications for long-term soil quality and ecosystem services. Adverse effects may arise from plastic additives, enhanced pesticide runoff, and plastic residues likely to fragment into micro- or nanoplastics but remaining chemically intact and accumulating in soil where they can successively sorb agrochemicals. The quantification of plastic debris in soil remains challenging due to the lack of appropriate analytical techniques. The cost and effort of recovering and recycling used mulching films may offset the aforementioned benefits in the long term. However, comparative and long-term agronomic assessments have not yet been conducted. Furthermore, plastic mulches have the potential to alter the soil quality by shifting the edaphic biocoenosis, accelerate C/N metabolism eventually depleting SOM stocks, increase soil water repellency, and favor the release of greenhouse gases. A substantial process understanding of the interactions between the soil microclimate, water supply, and biological activity under plastic mulches is still lacking but required to estimate potential risks for long-term soil quality. Currently, farmers mostly base their decision to apply plastic mulches rather on expected short-term benefits than on the consideration of long-term consequences. Future interdisciplinary research should therefore gain a deeper understanding of the incentives for farmers and public perception from both a psychological and economic perspective to develop new support strategies for the transition into a more environment-friendly food production.

2.1 INTRODUCTION

Rapid population growth poses a major challenge for both efficient and sustainable agricultural practices given the limited availability of arable land. In order to meet the increasing food demand (Godfray et al., 2010), plastic mulching has become a widely used technique for its instant economic benefits such as higher yields and

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See Parts of this Thesis and Author Contributions, page ix, for details.

^[1] See Kasirajan and Ngouajio (2012) for an extensive historical review.

improved crop quality (Lamont, 1993). However, after six decades of research^[1], the knowledge of the sustainability of plastic mulches remains vague in terms of both an environmental and agronomic perspective.

Plastic mulches are primarily used to protect seedlings and shoots through insulation and evaporation prevention, thus maintaining or slightly increasing soil temperature and humidity (Tarara, 2000). Furthermore, the application of plastic covers is known to reduce weed and pest pressure (McKenzie et al., 2001). Often reported benefits are minimization of the development time for seed and fruit, yield increase, the prevention of soil erosion and weed growth, and consequently reduction of herbicide and fertilizer use (Chalker-Scott, 2007; Espí et al., 2006; Lamont, 1993; Scarascia-Mugnozza et al., 2011). These prospects have made plastic films an upcoming technology, nowadays making up by far the largest proportion of covered agricultural surface in Europe (4270 km²), an area four times larger than that covered by greenhouses and six times that of low tunnels (Scarascia-Mugnozza et al., 2011). While the agricultural surface covered with mulching films remains constant or shows only slightly growing trends throughout the world (5.7% annual growth until 2019) (Transparency Market Research, 2013), the covering rate in China increased dramatically between 1991 and 2004 with a growth rate of 30% per year (Espí et al., 2006). The National Bureau of Statistics of China (2012) reported a four-fold increase of plastic mulch use from 319 to 1245 Mt between 1991 and 2011.

However, modifying the microclimatic conditions under plastic mulches not only enhances plant productivity but also increases biological degradation of litter and SOM, which has recently been discussed as a trigger to rapid depletion of soil nutrients in general and carbon stocks in particular (Domagała-Świątkiewicz and Siwek, 2013; Zhang et al., 2015a). This may eventually reduce soil quality in terms of impeding the soil's capability to serve its intended purpose (Doran and Parkin, 1994). Furthermore, the excessive use of hardly degradable PE has been apprehended to lead to substantial amounts of plastic waste residues accumulating each year (Albertsson et al., 1987). This, in turn, may potentially release toxic additives into the soil (Ramos et al., 2015).

The majority of reviews published on agricultural plastic mulching strongly focuses on the feasibility or efficacy assessments of biodegradable films (Brodhagen et al., 2015; Kasirajan and Ngouajio, 2012) which have so far been hardly accepted as a functional alternative to PE. More general contributions compared various synthetic and natural mulching materials with each other (Chalker-Scott, 2007; Greer and Dole, 2003) or with respect to certain agricultural practices, such as ridge-furrow systems (Gan et al., 2013) and integrated weed control (Bond and Grundy, 2001; Case et al., 2005). The first and most general reviews published on plastic mulching (Lamont, 1993; Tarara, 2000) were animated with the beneficial prospects of plastic mulch use, however, merely discussing potential drawbacks. This trend still applies to the majority of current research articles emphasizing individual effects of plastic mulching with particular focus on short-term agronomic benefits (for instance, He et al., 2013; López-López et al., 2015; Wang et al., 2010). In contrast, the long-term impact of plastic mulching as a standard agricultural practice is still virtually unknown in terms of potentially deteriorating soil quality or their post-crop fate, and therefore presents a challenge to bear a holistic sustainability evaluation. For this, it is important to combine the various results from individual studies to derive a system-based and interdisciplinary understanding of

the processes governing the impact of plastic mulches on agroecosystems.

This review aims at evaluating the sustainability of plastic mulch use in agriculture from the perspective of soil biogeochemistry, environmental chemistry, agronomy, and society. We link current knowledge of agricultural benefits and research on the fate and life cycle of plastic mulches with direct and indirect implications of plastic mulching for short- and long-term soil quality. In this respect, we first outline the fate of PE mulches while in use and after their life cycle has come to an end by explaining possible degradation pathways of buried mulch fragments. In addition to the fate of the plastic itself, we evaluate the long-term impact of plastic mulches on soil quality with respect to microbial diversity and SOM composition and degradation, both important but often neglected factors influencing ecosystem functions (Power, 2010). On this basis, we assess the value of plastic mulches in an agronomic context in order to provide first insights into its sustainability. We finally identify the need of research for a better comprehension of the processes and factors influencing wanted and unwanted effects of agricultural plastic mulches.

2.2 METHODS

We searched both Web of Science and Google Scholar literature databases for search terms including plastic or PE mulch, cover, film, or tarp used in agriculture^[2]. Based on these findings and supplemented with cross references, we selected 572 original research articles, 53 reviews, 23 books or book chapters, 21 reports and doctoral theses, and 7 patents and industrial standards for further evaluation. The literature covered the following major subtopics: use, properties, fate, impact on soil quality, and economic effects. For a more comprehensive perspective on the economics of plastic mulches we selected and followed the concept of ecosystem services (Millennium Ecosystem Assessment, 2005) to identify economic elements linked to plastic mulching and to provide an integral overview of the current state of agronomic knowledge of the impacts of plastic mulch.

^[2] Exact search string: (plastic* OR polyethylene) AND (mulch* OR cover* OR film OR tarp) AND (soil OR agricultur*).

2.3 USE AND PROPERTIES OF PLASTIC MULCHES

The largest benefits plastic mulches are used for on immense scales worldwide stem from their distinct optical and material properties that allow transmission or reflectance of specific wavelengths of incoming solar radiation (Brown and Channell-Butcher, 2001; Chalker-Scott, 2007; Csizinszky et al., 1995; Gordon et al., 2008; Haynes, 1987). In order to produce highly customizable materials with high flexibility, durability, easy processing, and freedom from odor and toxicity (Wright and Mudway, 2019), PE has become by far the most frequently used base material in agricultural mulch production (Díaz-Pérez, 2010; Kara and Atar, 2013; Locascio et al., 2005; Sivan, 2011). Its properties are usually modified by additives such as plasticizers, colored pigments, UV stabilizers, or other polymers. The main types of PE used in agriculture are low- and high-density PE and linear low-density PE. High-density PE is used to reduce weight and cost, contributes to the tear strength of the material, and provides a reliable moisture barrier (Lamont, 2005). Linear low-density PE is used for its elasticity and high puncture resistance (Anthony and Kurtz, 1983). Numerous other PE mulching variations have already been patented, for instance composite mulches such as paper covered in styrene butadiene latex (Dalebroux et al., 1997). Sabbagh (2010) patented a non-degradable

and mechanically stable mulch barrier consisting of low-density PE, linear low-density PE, and polyamide (PA)/nylon impermeable to soil fumigants. However, the degradability of such materials, the tendency to create microplastic debris, and their practical application are unknown. Mulches containing PVC were prohibited for mulching in the US for their toxicity and carcinogenic potential (US EPA, 2012) and have been restricted to greenhouse covering and irrigation pipes (Scarascia-Mugnozza et al., 2011). In order to achieve longer life cycles of three years or more (Brückner et al., 2008) as specifically needed for strawberries and asparagus growth, ethylene vinyl acetate and ethylene butyl acrylate are added to PE mulches as copolymers (Espí et al., 2006).

Although this depends on regional climatic conditions and land use practices, maximum yields are mainly achieved by optimizing the amount of solar radiation absorbed by the crop. Further microclimatic parameters to be modified include the root zone and leaf temperature, humidity, and therewith soil moisture and plant transpiration rates, for example to manage soil temperatures at night or in colder regions by preventing evaporative cooling and emission of long-wave radiation from the soil (Ham et al., 1993). This is achieved by controlling the gas and heat exchange between the soil and the environment (Lamont, 1993; Tarara, 2000). For such purposes, black, transparent, and white mulches are the colors used most commonly. However, the color selection strongly depends on the crop type and the crop's environment, as well as the temperature that can be tolerated by plants and seedlings (Lamont, 1993; Tarara, 2000).

Black is the predominant mulch color since it can both absorb and re-emit radiation as thermal energy or long-wavelength infrared (IR) (Lamont, 1993; Lamont, 2005). Black mulches are favored in moderate climate zones in order to increase soil warming by up to 6 °C and double soil moisture, resulting in extended growing seasons. In very hot regions or for special use cases such as asparagus growing, white or white-on-black mulches are used to maintain or slightly lower soil temperatures by up to 2 °C compared to bare soil (Ham et al., 1993; Heißner et al., 2005). The effects of plastic mulches on soil temperature and moisture typically decrease with soil depth, becoming mostly insignificant below 40 cm (Díaz-Hernández and Salmerón, 2012; Heißner et al., 2005). By contrast, transparent plastic films are poor absorbers of solar radiation but able to transmit 85–95% of radiation (Ham et al., 1993). The condensed water below the film surface absorbs the IR radiation reflected by the soil so that the heat is retained. This greenhouse effect makes transparent films profitable in colder regions (for instance, Haynes, 1987; Streck et al., 1995). However, the disadvantage of the high transmittance properties of transparent mulches is the lack of weed control, which continue to grow when exposed to sun light (Lamont, 1993). In arid regions, transparent films are primarily used for soil solarization due to the extraordinarily high temperatures occurring under transparent mulches. Soil solarization is a soil sterilization method applied before planting to eradicate soilborne pathogens and devitalize weed growth (Horowitz et al., 1983; Tamietti and Valentino, 2006). In addition, photoselective films are capable of reflecting photosynthetically active radiation to above-film leaves and transmitting IR light, representing a compromise between transparent and black mulches (Paul et al., 2005). For pest and pathogen control, pesticide (Subrahmaniyan et al., 2011) or aluminum (Csizinszky et al., 1995) coatings may additionally be applied^[3]. Other colors such as red, blue, yellow, or orange have also been tested for special requirements in vegetable production such

^[3] See Greer and Dole (2003) for a detailed overview.

as repelling certain pests or attracting beneficial insects (Csizinszky et al., 1995; Lamont et al., 1990; Orzolek, 1993).

Apart from the evaluation of specifically intended effects of the variety of different plastic materials, none of the aforementioned studies focused on implications for other soil processes. In order to assess the impact of plastic mulching on soil quality, the current focus on the evaluation and optimization of the benefits of plastic mulching must be extended by the evaluation of potential unwanted side effects in soil and surrounding ecosystems. A comprehensive understanding of these effects will require an integrated assessment of application-specific impacts as well as process-orientated research on soil quality and the fate of mulch residues in soil that both the mulch and the soil are subjected to with respect to different environmental and agricultural conditions in particular regions of the world. In the following sections, we will thus discuss the current knowledge of these aspects.

2.4 FATE OF PLASTIC MULCHES AND THEIR ADDITIVES

2.4.1 LIFE CYCLE AND DEGRADABILITY OF PE

A polymer is typically defined as “environmentally degradable” or “biologically degradable” if it has the ability to undergo disintegration, this is deterioration in mechanical properties, possible fragmentation, followed by microbial attack (Krzan et al., 2006). European standards further define that after six months more than 90% of the initial compound must be broken down to biomass, water, and CO₂ (DIN EN 13432, 2000). In this sense, chemically inert PE can be treated as virtually non-biodegradable (Albertsson et al., 1987). Studies on the degradability of PE have been recently reviewed in two articles (Krueger et al., 2015; Restrepo-Flórez et al., 2014). They reported that PE degradation takes place to a certain extent. However, the authors agreed that this process is very slow under environmental conditions. Although the stability of PE is beneficial for the lifetime extension of the mulch in use, this inertness is likewise the most problematic property concerning the disposal of used mulch films.

The typical application time of plastic mulches in agriculture lasts only a few months and can be reduced even further when exposed to extreme weather events such as hail and storms due to physical fragmentation and chemical aging processes (Scarascia-Mugnozza et al., 2011). More resilient mulches are required for perennial crops like strawberry or asparagus (Hablott et al., 2014). The thinner the film the more difficult and time consuming it becomes to remove the complete film from the field at the end of a crop cycle without leaving residues in the soil. For this reason, plastic films or parts thereof are often intentionally or unintentionally left on the field to be further broken down mechanically (Moreno et al., 2014). Despite its high relevance, there is no information up to now on the amount of plastic residues in soil. However, 10-year laboratory experiments showed that low-density PE buried in soil reduced its weight by only 0.2% per year (Albertsson et al., 1987). Long-term (32–37 years) studies by Ohtake et al. (1998) estimated a period of approximately 300 years required for complete degradation of a 60 µm thin low-density PE layer. In pure PE without any degradation-promoting additives, polymer chain scission is, if at all, a very slow process. PE mulches are resistant to hydrolysis and are not readily attacked by microorganisms (Stevens, 2002). The

most efficient way of chemical degradation involves a photo-oxidation step when exposed to sunlight. During this process, carbonyl groups are formed which can be attacked by microorganisms so that the polymeric chains are broken down further. These processes are summarized as oxodegradation, this is the fragmentation of plastic under the influence of UV radiation and temperature (Sivan, 2011). According to the definition of the American Society for Testing and Materials (ASTM D5488-94, 1994), such processes cannot be referred to as biodegradation since carbonyl formation during photo-oxidation is not an enzymatic activity. Moreover, mulching films that are buried in the soil are not subject to photo-oxidation and therefore unlikely to be attacked by microorganisms due to the lack of carbonyl formation (Moreno et al., 2014).

If not removed from the field, plastic waste accumulates in the environment where it may pose a considerable threat to terrestrial and aquatic wildlife when taken up in the food chain (Barnes et al., 2009; Duis and Coors, 2016; Rillig, 2012; Sivan, 2011; Teuten et al., 2009). Eventually, the plastic loses its integrity and breaks down into smaller and smaller particles for which the term “microplastics” was coined by Thompson et al. (2004). Although numerous articles have already reported the formation of plastic residues of various sizes (700 μm^2 to 2850 cm^2) originating from mulching (for example, Briassoulis et al., 2015a; Feuilloley et al., 2005; Kyrikou and Briassoulis, 2007; Ramos et al., 2015), the assessment of their fate in soil is still challenged for the development of adequate analytical methods to detect and quantify plastic residues in complex, heterogeneous environmental matrices (Rillig, 2012). Recently, Dümichen et al. (2015) suggested a first approach for the determination of PE plastic debris in solid media using thermal extraction and desorption-gas chromatography/mass spectrometry (TED-GC/MS). However, the authors stressed the need for further research in terms of improving TED-GC/MS measurements as well as developing alternative techniques for the quantification of other polymer types in different environmental media.

The compiled findings suggest a successive enrichment of the plastic residues in the soil—whether or not they are left in the soil intentionally or unintentionally. For a more detailed assessment of the environmental fate of plastic residues, a more comprehensive understanding of the fate of plastic debris in soil is essential. This assessment, however, urgently requires further advances in analytical techniques to detect, identify, and quantify plastic debris in heterogeneous samples like soil.

2.4.2 PHTHALATES

Among typical PE mulch additives, plasticizing agents from the group of phthalic acid esters (PAEs) with its model compound bis(2-ethylhexyl) phthalate (DEHP) belong to the most discussed soil contaminants (Fu and Du, 2011; Magdouli et al., 2013; Wang et al., 2013). Similar to other PAEs, DEHP is suspected of being carcinogenic and endocrine-disrupting (Erkekoglu and Kocer-Gumusel, 2014). The fate of such compounds is highly relevant when assessing the risks potentially originating from plastic mulches. However, demonstrating a connection between plastic mulch application and elevated PAE concentrations in soil or plants is not trivial since agrochemicals, wastewater irrigation, and atmospheric background concentrations represent further potential PAE sources (Hongjun et al., 2013; Wang et al., 2013; He et al., 2014). In PE mulches, PAE are only loosely incorporated in the polymer structure without covalent bonding and can

therefore be leached out easily. Even PAE derivatives with low water solubility, low vapor pressure, and high octanol–water partitioning coefficients (K_{ow} s) such as DEHP (Magdouli et al., 2013), have been found ubiquitously in the environment (Fernández et al., 2012). While typical background concentrations of PAEs in soil vary between 0.2 and 33.6 mg kg⁻¹ (Zeng et al., 2008), PAE levels in plastic mulches were detected in ranges from 50 to 120 mg kg⁻¹ (Wang et al., 2013). Plastic-mulched crop land revealed concentrations of six major PAEs between 74 and 208% higher than in non-mulched farmlands in China (Kong et al., 2012). Most concentrations of DEHP and dibutyl phthalate found in Chinese-grown vegetables and soil exceeded US and EU food security standards and environmental risk limits of 0.7 and 1.0 mg kg⁻¹, respectively (van Wezel et al., 2000; Wang et al., 2015).

Once released from the mulching film, PAE may be distributed in environmental compartments by plant uptake, evaporation into the atmosphere, and runoff into groundwater and surface waters (He et al., 2014). In soil, PAE are degraded by microorganisms to different extent in dependence of the ester chain length. While short-chain esters, such as diethyl phthalate, are to a certain extent susceptible to biodegradation, longer chains as in DEHP render the PAE persistent. When subjected to UV radiation, PAEs can degrade to phthalate monoesters and phthalic acid (Hankett et al., 2013). In natural environments, the governing microbial degradation processes are hydrolysis, both aerobic and anaerobic, followed by aromatic ring cleavage (Magdouli et al., 2013; Staples et al., 1997). Furthermore, microbial degradation of PAEs is dependent on its metabolic yield: Whereas diethyl phthalate is rapidly degraded and assimilated, DEHP and bis(2-ethylhexyl) adipate are more recalcitrant and only cometabolically degraded in the presence of an additional carbon source (Cartwright et al., 2000; Nalli et al., 2002). This typically results in the formation of ethylhexanoic acid and ethylhexanol, both toxic to aquatic organisms and particularly resistant to further degradation (Horn et al., 2004). Although laboratory-derived half lives of PAEs in soil range from days to months, current research rather suggests that at least some of them persist for significantly longer periods in soil (Rüdel et al., 1993). Thus, the use of plasticizer-containing mulches involves a clear potential for accumulation of these xenobiotics in soil and a successively increasing risk of bioaccumulation and biomagnification in the food web.

Besides affecting the abundance and diversity of soil organism communities, crop quality can be impaired significantly when PAEs are taken up by plants (Kaplanen et al., 2008; Wang et al., 2015). Through this pathway, phthalates may eventually enter the food supply chain representing an additional and probably significant source of exposure to humans.

2.4.3 POLYMER DEGRADATION-PROMOTING AGENTS

Due to the generally known high persistence of plastic residues and their additives in soil, the development of biodegradable plastics or the promotion of biodegradation of plastic materials is a promising option to avoid the accumulation of plastic in soil. First attempts were made to use different bacterial strains, for example from the gut of the Indian meal moth (*Plodia interpunctella*), which were able to degrade 6–10% PE during a 60 d incubation period (Hadad et al., 2005; Krueger et al., 2015; Yang et al., 2015). However, such selective treatments have been restricted to

laboratory conditions. They seem both too difficult and expensive to be applied on large agricultural scales and bear the risk of potentially introducing invasive or detrimental species into productive systems. Certain agrochemicals, such as paraquat and mancozeb were found to accelerate the oxidation rate and embrittlement of the PE foil during laboratory experiments, while sulfur and chlorpyrifos did not show significant effects (Yeh et al., 2015). By contrast, various types of other PE additives have already been successfully tested and applied for their ability to promote the breakdown of mulches. Kyrikou and Briassoulis (2007) provided a comprehensive collection of data on various types of mulches and investigated under which conditions and to which extent they are (bio)degradable. In order to promote oxodegradation, additives can be used to facilitate chain cleavage and microbial attack. Polymer breakdown is induced by radicals produced by pro-oxidants and the subsequent production of oxidized carbon chains (Briassoulis et al., 2015b). Such pro-oxidants mainly contain carbonyl groups and compounds containing transition metals like Fe, Co, and Mn (Kyrikou and Briassoulis, 2007). However, added organic compounds or metals of environmental concern may lead to increasing soil contamination (Koutny et al., 2006; Scarascia-Mugnozza et al., 2011). It has not yet been satisfactorily shown to what extent the oxidation products are truly biodegradable under realistic environmental conditions. In several standardized laboratory biodegradability tests, less than 2% of a pro-oxidant-containing PE mulch was degraded over a two-year period (Feuilloley et al., 2005). Comparable results were shown in a 7-year field experiment after exposing pro-oxidant-containing linear low-density PE films to enhanced UV radiation and heat in the laboratory. The results suggested a predominance of mechanical rather than chemical breakdown in soil and a successive formation of microplastics invisible to the naked eye (Briassoulis et al., 2015b). In another field study (8.5 years), linear low-density PE mulch films containing pro-oxidants exhibited a degradation in mechanical properties due to the formation of carbonyl groups during the cultivation period, but they did not disintegrate chemically. After the cultivation period, the almost intactly recovered films successively decreased in carbonyl groups, possibly due to leaching of carboxylic acids by soil water, which reduces available sites for microbial attack even further (Briassoulis et al., 2015a). This leads to the hypothesis that pro-oxidant-containing mulches undergo fragmentation but are not subject to subsequent microbial degradation, so that they accumulate in the soil as polymers of reduced chain length. Therefore, such films can be classified neither as biodegradable nor as environmentally degradable according to the definition given above. Although referred to ubiquitously, the definition of “biodegradable” does not necessarily state an approximate period of time for biodegradation by which plastic can be accepted as such. A reasonable time frame for complete degradation would be until the beginning of the new crop cycle in order to avoid plastic fragments and additives being incorporated into the soil.

The compromise between the need to sustain the mulch’s property during use and the requirement to be rapidly biodegraded after use remains a major challenge for material science. This is further aggravated by the requirement that biodegradation must take place in the field, under less well-defined and less optimal conditions than performed in standard degradation tests. Thus, up to now, it seems open whether in the future truly biodegradable mulching films will be available for application in agriculture.

2.4.4 DISPOSAL AND RECYCLING OF USED PLASTIC MULCHES

The fate of plastic mulches not only deals with fragments buried in the soil, but also with plastic waste collected from the field. Its disposal represents a task both laborious and costly. When removed from the field, one of the major problems in plastic disposal and recycling is its contamination with soil and agrochemicals (González-Sánchez et al., 2014; Scarascia-Mugnozza et al., 2011). In Europe, regulations concerning landfilling vary considerably between countries. While in Central Europe and Scandinavia (excepting Finland) less than 10% of both agricultural and non-agricultural plastic waste is disposed of in landfills or landfill bans are implemented, in Spain and most eastern and southeastern countries more than 50% of plastic waste are estimated to be landfilled (PlasticsEurope, 2015). However, contaminated mulches are mostly unsuitable for landfilling due to the risk of pesticide leaching (Garthe, 2004; Wang et al., 2013). PE sheets may even function as a vector and facilitate transfer of pesticides into the soil by absorbing the pesticide in the non-crystalline areas of the film (Huckins et al., 1993; Nerín et al., 1996) and further migration of the pesticide to the soil matrix (Ramos et al., 2015). The decreasing space available for landfills and concerns over the disposal of contaminated plastic render incineration of plastics a viable alternative, especially for power production (Garthe, 2004). High-temperature combustion ($>1000\text{ }^{\circ}\text{C}$) of PE and PVC produces as emission products mainly the ozone-damaging greenhouse gas CO_2 , CO, and polycyclic aromatic hydrocarbons (Wang et al., 2003). Illegal on-site burning of halide-containing plastics may even release carcinogenic dioxins at levels 20 times that of controlled high temperature incineration and 40 times that of atmospheric particulate matter (Levitan and Barros, 2003).

A desired alternative to landfill disposal and incineration is the recycling of used mulching films. In 1991, a patent application was filed that proposed the use of a recycling machine designed for cleaning and shredding agricultural plastic waste (Vacchelli, 1992). However, no information is available whether such machinery was or is being used at some point. This may imply that the cost and effort exceed the benefits of small-scale recycling machines. Recycling used mulch is only possible if contaminants make up less than 5% of the total weight of the mulch (Clarke, 1996). Studies have shown that this 5% threshold is exceeded dramatically with the actual contaminant weight being up to 40–50% (Hussain and Hamid, 2003; Levitan and Barros, 2003; Nerín and Batlle, 1999). This leaves large amounts of mulching films not being recycled at all—a problem scarcely stressed in the scientific literature but in a US newspaper for agricultural operators (Kotrba, 2008). Also, the EU Waste Framework Directive (2008) does not specify disposal or recycling procedures concerning agricultural plastic waste. Since plastic disposal in an environmentally safe manner is more recommendatory than effectively implemented in terms of regulations both in the US and the EU, the fate of used plastic mulches is largely unknown. For want of alternatives, farmers may dispose of the waste through illegal on-site burning or unsuitable pits (Hemphill, 1993; Scarascia-Mugnozza et al., 2011). In the UK, for example, only two plants are known to reprocess agricultural plastic waste, which makes the collection of the mulch and transport to the plant excessively costly for remote and small-scale operators (Scottish Executive Environment Group, 2006). In Germany, the environmental agencies of the federal states list the temporary storage and disposal of used mulch in the statement of costs for vegetable farmers (Bayerische Landesanstalt für Landwirtschaft, 2005).

Although no precise instructions have been established for mulch disposal in Germany, transport to reprocessing plants appears to be common practice (Straeter, 2011).

The lack of recycling options has led to the development of mulch materials which are completely free from plastic, like paper mulch mats made of recycled waste paper (EcoCover) which has, however, not produced any company-external research. Even the development and use of fully biodegradable plastic would not be without negative effects: Gerngross (1999) argued that the life cycle of fermentation-derived polymers, for example from paper or corn starch, could be considered non-sustainable and environmentally more harmful than that of conventional plastic films due to side effects such as air acidification, eutrophication, and increased carbon emissions. Vegetable mulches from straw, coconut, or other barks further pose an increased hazard of pests which would be more detrimental than beneficial to crop production (Howard and Oropeza, 1998). Moreover, organic mulches cannot provide resistance to extreme weather conditions as plastic mulches can, and inconsistent weather conditions may lead to degradation or disintegration of the mulch before the end of the crop cycle and, thereby, to a high variability in plant growth and yield. Moreover, exotic mulches like coconut bark are only available in small amounts and certain areas of the world which makes their purchase a highly costly and laborious matter (Briassoulis et al., 2015b).

In summary, the overarching problem of agricultural plastic waste remains the requirement to dispose of large quantities of used mulching films that are difficult to collect, recycle, and reuse. Besides the accumulation of chemically resistant PE itself, the leaching of mulch additives and sorbed agrochemicals is of particular concern regarding soil contamination and impaired soil quality. According to our knowledge, only one life cycle assessment on PE mulching has been published so far, and particularly focused on different soil and pest management techniques in an olive plantation (Russo et al., 2015). In comparison with mulching with de-oiled olive pomace^[4], nonwoven PP fleece, PE foil, chemical and mechanical weeding, PP and PE mulches produced the lowest environmental burdens in total including plastic production, installation, collection, transport, and disposal. However, they scored worse in primary energy demand and the potential of volatilizing organic compounds to create photochemical ozone. Russo et al. (2015) further stated that not all environmental impacts of agricultural practices are actually assessable by the current methodology of life cycle assessments and called for a longer-term soil monitoring when mulching techniques are applied. Long-term life cycle assessments should further include the most frequently used plastic mulch materials in order to better and more quantitatively judge the potential risks of plastic mulch applications. In addition to the risks originating from the plastic materials and its additives, knowledge of the impact of plastic mulching on soil quality is crucial. This aspect will be discussed in the following paragraphs.

^[4] This is the solid waste product from olive oil mills.

2.5 IMPACT OF PLASTIC MULCHES ON SOIL QUALITY

2.5.1 SOIL POROSITY AND WATER TRANSPORT

Surface covering prevents mechanical perturbations in the topsoil, such as from tillage, rainfall, or crust forming (Khan et al., 2000; Subrahmaniyan et al., 2006).

Due to the isolation from direct natural water recharge, covered soil is particularly dependent on lateral water transport (Li et al., 2003) and often requires irrigation. However, once irrigation is applied, plastic mulching typically increases the water use efficiency by 20–60% due to reduced evaporation (Qin et al., 2015; Zribi et al., 2015). Plastic mulches impede the gas exchange between the soil and the atmosphere (Khan et al., 2000). Both gas and water transport can be managed using perforated plastic sheets. However, the desired effects of increased temperature and moisture conditions on the soil surface are typically less pronounced than under closed synthetic covers (Li et al., 2003). The same applies to so called “biodegradable” mulches which have a higher permeability due to gradual disintegration on site (Moreno and Moreno, 2008).

The mechanical protection of surface soil, together with an enhanced root development, mucilage production, and soil fauna activity, promotes the stabilization of soil aggregates (Six et al., 2004). This is apparent in a shift in aggregate size distribution towards large (2.5–4.0 mm) and water stable aggregates following mulching (Domagała-Świątkiewicz and Siwek, 2013; Zhang et al., 2013). The increase in aggregate size is accompanied by a slight decrease in soil bulk density, consequently reducing soil compaction (Mbah et al., 2010; Tindall et al., 1991). Both effects are associated with increased pore sizes and soil aeration (Khan et al., 2000), feeding back positively to root development and soil biota activity (Schonbeck and Evanylo, 1998). The resulting loose and friable soil structure further allows an increased water holding capacity (Domagała-Świątkiewicz and Siwek, 2013; Mbah et al., 2010) and reduces vertical water transport (Peeyush et al., 2008). A higher water use efficiency decreases irrigation requirements and thereby the risk of soil salinization (Dong et al., 2008) and leaching of nutrients (Kim et al., 2014), fertilizers (Haraguchi et al., 2004), and pesticides (Leib et al., 2000). Arid and sandy topsoil, however, may generally become dry or even hydrophobic under artificial or deficit water supply in a long-term perspective (Jaramillo et al., 2000; Robinson, 1999). Drying of soil hydrogels like mucilage can lead to a further increase in soil water repellency (Ahmed et al., 2016; Carminati, 2013). In such cases, sealing the soil off from rainfall makes it more likely to lose potential benefits of an increased water holding capacity. However, it is still unclear under which conditions processes inducing soil water repellency or processes reducing water holding capacity are favored. For this, a comprehensive mechanistic understanding of the processes affecting soil wettability is required in order to judge the relevance of this risk. Up to now, the mechanisms and factors leading to soil water repellency are still under discussion (Diehl, 2013).

Contrary to the water retention underneath the films, the surface of mulched ridges enhances water runoff into furrows which are particularly susceptible to soil erosion and loss of soil structural stability (Rice et al., 2001; Wan and El-Swaify, 1999; Zhang et al., 2013). The study by Roose and Barthès (2001) showed that the positive aspects of plastic mulching on soil structure do not necessarily express in all types of soil: Applying plastic mulch to an already heavily degraded nutrient-deficient and previously uncovered arid soil only temporarily reduced erosion. In contrast, the measure created even more fragile soil structures in the long term. In this case, natural attenuation processes may have already been lastingly deteriorated a priori so that negative effects of plastic mulching, such as inducing water repellency or an increased erosion potential, could no longer be compensated.

2.5.2 IMPACT OF PLASTIC MULCHING ON THE FATE OF AGRO-CHEMICALS AND METALS

As discussed before, plastic mulching may significantly increase the mean runoff and soil loss from the field, especially to furrows (Wan and El-Swaify, 1999; Zhang et al., 2014; Zhang et al., 2015b). Accordingly, total pesticide loads are often found elevated around plastic-mulched fields compared to bare soil or organic mulches. This poses the risk of pesticide runoff into the environment where they may adversely affect both aquatic and soil organisms (Arnold et al., 2004; Dietrich and Gallagher, 2014). For instance, runoff from PE films increased chlorothalonil and α - and β -endosulfan by 19, 6, and 9 times, respectively, with respect to the hairy vetch-mulched control (Rice et al., 2001). The same research group observed up to 8 times higher runoff volumes containing the pesticides chlorothalonil, thiodan, endosulfan, and esfenvalerate from PE mulch than from bare furrows (Rice et al., 2007). Similar results were observed in a pineapple cultivation with the nematicide bromacil (Alavi et al., 2007). Higher levels of dissolved copper and metolachlor were measured in the runoff water coming directly from covered tomato crops (Arnold et al., 2004; Rice et al., 2002). Fenoll et al. (2010) reported that soil solarization promoted fungicide dissipation from soil. Furthermore, some studies showed an increased uptake of toxic metals by plants covered with plastic mulch: Moreno et al. (2002) observed increased toxic metal accumulation in the aboveground plant biomass of Chinese cabbage; with total contents of Zn, Cd, Cu, and Pb elevated by up to 90% compared with uncovered plants. Potato plants mulched with PE extracted up to three times more metals than uncovered treatments which, in turn, decreased soil metal contents (Baghour et al., 2001; Baghour et al., 2002). These and other soil processes will be discussed in the following paragraph.

2.5.3 SOIL BIOLOGICAL METABOLISM AND DIVERSITY

Given a sufficient nutrient supply and the absence of toxicants, elevated temperatures and soil moisture increase soil biological activity (Subrahmanian et al., 2006) and metabolism (Li et al., 2004b). CO₂ originating from soil respiration can be retained by PE covers and acts as fertilizer for daytime photosynthesis when slowly diffusing through the plastic films itself or through holes punched for stems. This may lead to an enhanced carbon sequestration by 12–15% (An et al., 2015) and reduced CO₂ emissions into the atmosphere by approximately 100 g m⁻² C despite up to three-fold higher CO₂ concentrations in mulched soils (Li et al., 2011). Promoted plant growth through CO₂ fertilization may further stimulate root development and increase the exudation of mucilage. Nutrient uptake and availability for soil microorganisms will also be enhanced thereby (Liu et al., 2015; Subrahmanian et al., 2006), particularly in the rhizosphere (Lin et al., 2008; Maul et al., 2014). As a consequence of an increased nutrient uptake and plant metabolism, phenolic compounds, flavenols, and vitamins were found to be increased, for instance in North American carrot and grapevine cultivations (Antonious and Kasperbauer, 2002; Coventry et al., 2005). As discussed before, increased mineral uptake may also include the uptake of potentially co-present contaminants which has to be accounted for in terms of concerns over food safety (Moreno et al., 2003).

While 25 to 60% of soil carbon may be retained in microbial biomass (An et al.,

2015), the remaining accessible fraction can undergo metabolism (Zhou et al., 2012). The impeded gas exchange through PE mulches can furthermore induce suboxic soil conditions, resulting in redox potentials below -200 mV (Blok et al., 2000). Anoxic redox conditions of -500 mV have been reached in non-flooded, water-saving ground cover rice production systems (Kreye et al., 2007). Such low redox potentials first lead to impaired nitrification or increased denitrification and further promote methanogenesis, ultimately increasing N_2O and CH_4 emissions (Akiyama and Tsuruta, 2003; Kim et al., 2014; Li et al., 2014). Under oxidizing conditions, increased N_2O fluxes resulting in an increased global warming potential by up to 80% were observed predominantly during and after solarization and disinfection measures, or when the soil was fertilized substantially with inorganic nitrogen of 300 – 1600 $kg\ ha^{-1}$ N (Arriaga et al., 2011; Cuello et al., 2015; Nishimura et al., 2012). Plastic mulching for its yield-increasing purpose together with moderate fertilization (<180 $kg\ ha^{-1}$ N), in contrast, mostly led to N_2O emissions comparable to those of non-mulched soil, for instance planted with radish and cotton in South Korea and China, respectively (Berger et al., 2013; Li et al., 2014). For a reliable risk estimation of the contribution of mulched soils to the emission of climate relevant gases, a comprehensive understanding of the interactions between oxygen availability, soil temperature, crop and soil moisture is required. Such knowledge is, however, still incomplete (see for example Butterbach-Bahl et al., 2013; Signor and Cerri, 2013).

Along with alterations in physical properties, soil nutrient availability, and microbial activity, plastic mulching can induce shifts in the soil microbial community (Hasegawa et al., 2004; Maul et al., 2014), for instance towards mycotoxigenic fungi (Muñoz et al., 2015). Soil solarization practices were reported to generally decrease bacterial and fungal richness by favoring thermophilic, facultatively anaerobic and detritivorous species (Bonanomi et al., 2008; Simmons et al., 2014). This means that soil solarization is to a certain extent non-selective, particularly when applied in combination with soil fumigation (for instance, Chellemi et al., 2013). Contrarily, ordinary plastic mulching for its yield-increasing purpose led to no significant decreases (Kapanen et al., 2008) or even slight increases in total microbial diversity compared to non-mulched soil (Chen et al., 2014; Liu et al., 2011). In this respect, organic or vegetative mulches alone or in combination with plastic mulches were shown to perform considerably better than plastic mulches (Carrera et al., 2007; Maul et al., 2014). Additional nutrient input and a more diverse habitat structure as provided by organic material was likely to increase soil microbial abundances and diversity (Doğan et al., 2013; Muñoz et al., 2015; Schonbeck and Evanylo, 1998). However, first studies on the use of plastic mulch in asparagus crops suggested a risk of increased mycotoxin production in soil, this is deoxynivalenol (Muñoz et al., 2015). If this observation holds further verification, the implications of plastic mulching for mycotoxin production and food contamination by mycotoxins need to be considered in future research as well.

The effects of plastic covers on soil microbes can propagate in different ways to higher trophic levels of the food web, for example by positively affecting overall arthropod diversity and doubling omnivorous insect abundance but decreasing springtail (Addison et al., 2013), predatory nematode (Forge et al., 2003), ground beetle (Miñarro and Dapena, 2003), or earthworm abundances (Schonbeck and Evanylo, 1998) by factors of 2 to 3. The latter are of particular importance for maintaining a loose soil structure. Besides the partial information on specific sce-

narios, the overall impact of plastic mulching on the microbial biocoenosis, their functional diversity as well as their influence on nitrogen and carbon degradation and on the food web has been widely neglected, and remains only partially understood. With respect to the resilience of agroecosystems, it may be helpful to understand the impact of plastic mulching over time on the most relevant ecosystem functions related to soil biology and microbial diversity. Furthermore, it will be important to assess which conditions favor or suppress the development of potentially pathogenic microorganisms and mycotoxin producing fungi.

2.5.4 SOM COMPOSITION AND STABILITY

Regardless of differing regional conditions or cropping scenarios, the enhanced productivity under plastic mulches has often been reported to result in lower contents of Mg, K, P, and N when compared to bare soil (Domagała-Świątkiewicz and Siwek, 2013; Li et al., 2007; Schonbeck and Evanylo, 1998). Furthermore, Moreno and Moreno (2008), Li et al. (2004a), Li et al. (2007), and Zhang et al. (2015a) found significant SOM losses within one to three years of mulching due to temperature-induced, accelerated biodegradation, which were closely linked and intertwined with decreasing C/N ratios (Jia et al., 2006; Zhou et al., 2012). Higher temperatures, as required for soil solarization, may even deplete up to 85% of soil carbon in less than one month (Simmons et al., 2013). By contrast, SOM contents remained stable during one to two years of plastic mulching when the soil carbon pool was maintained by organic matter input from crop residues or additional vegetative mulching (Schonbeck and Evanylo, 1998; Tindall et al., 1991). These effects are most probably due to the generally high temperature sensitivity of SOM decomposition processes (Larionova et al., 2014; von Lützwow and Kögel-Knabner, 2009). Gan et al. (2013) hypothesized that such a decrease in SOM is only temporary and would be compensated by the carbon input from root residues after some crop rotations. This is supported by recent findings by Luo et al. (2015), who showed that the carbon stocks decreased only in the top soil (<20 cm depth), but increased in the rooting zone (20–40 cm depth) after four years of plastic mulching. However, it is still unknown under which conditions and to what extent changes in SOM contents are governed, rather by an increased net primary production or by accelerated microbial decomposition. This knowledge is particularly relevant for carbon storage estimates in intensive land use scenarios and agricultural practices in which the majority of plant material is removed at harvest (Chapman et al., 2012; Pardo et al., 2012; Tian et al., 2012). For soils with limited natural carbon input, Zhang et al. (2015a) recommended a strict SOM budgeting to avoid soil degradation.

Besides alterations in SOM quantity, it remains largely unresolved how the potentially accelerated turnover of soil organic carbon (C_{org}) may affect SOM structure (Diacono and Montemurro, 2010). This extends to the temporal development of SOM quality under plastic films in terms of maintaining its benefits for agricultural soil use in a long-term perspective (Doran and Parkin, 1994) and, possibly even more important, its ecosystem functions. In general, the rapid soil respiration and mineralization, soil erosion, and leaching (Bolan et al., 2011) are known to impede SOM humification and to reduce SOM stability (Sollins et al., 1996) and are thus suspected to reduce overall soil quality (Lal, 2009). Contrary to that, the formation of larger soil aggregates mediated by plant residues and

soil biota can stabilize SOM by increasing the amount of organic matter spatially inaccessible to microbial attack (Sollins et al., 1996; von Lützow et al., 2006). This humified SOM acts as an important binding agent on the microscale through the formation of organo–clay and mineral complexes which may favor soil structural stabilization on the macroscale (Bronick and Lal, 2005; Zhang et al., 2015a).

Under mulched soils, information on SOM formation and degradation processes is often estimated from microbial respiration rates (Li et al., 2004a; Moreno and Moreno, 2008). However, such proxies do not provide any information on the change in SOM composition and SOM structure. To our knowledge, there is only one study so far which assessed in detail changes in SOM structure and quality following plastic mulching: Ceccanti et al. (2007) analyzed mineralization indices (furfural/pyrrole/phenol ratios), humification indices (benzene/toluene), and aliphatic/aromatic ratios before and after four months of PE mulching by means of pyrolysis-gas chromatography. The obtained indices indicated no difference between PE-mulched compared to bare or fertilized soil. In contrast to this detailed but short-term experiment, long-term effects of multiannual plastic mulching on SOM composition have often been reported in less detail. Those studies mostly used density fractionation techniques to address differences between the light or labile SOM fraction containing low-density, easily degradable, but temporarily not yet completely decomposed organic material such as roots and leaf litter and the heavy or stable SOM fraction (Sollins et al., 1984). Although this classification is merely operational, the light fraction is known to have residence times of a few years to several decades (von Lützow et al., 2006) and is therefore adduced as a sensitive indicator for changes in SOM induced by land use (Janzen et al., 1992). Liu et al. (2013), Luo et al. (2015), and Zhou et al. (2012) reported up to two-fold increases of readily available labile carbon after two to four years of plastic mulching; all using the same fractionation scheme. This trend was similarly reflected by a 10-year study in which a mulched soil cultivated with non-flooded rice and wheat revealed 50–60% more labile dissolved organic matter compared to uncovered soil (Tian et al., 2013). Slight increases in both light and heavy SOM fractions under mulch were only reported for an alfalfa grassland in China (Jia et al., 2006). Although not been studied in further detail with respect to plastic mulching, information on the implications of alterations in the SOM development can be deduced from studies on other soils: If not removed at harvest, the light fraction may be incorporated into SOM and promote the accumulation of more stable and humified SOM structures (Zhou et al., 2012) with narrower C/N ratios (Sollins et al., 1984), or it may be incorporated into soil aggregates, where it is protected physically from microbial attack (Sollins et al., 1996; von Lützow et al., 2006), as discussed above. Under natural conditions, this intermediate to stable SOM fraction has an estimated residence time of hundreds to several thousands of years (von Lützow et al., 2006), however, its stability and resistance towards mineralization are particularly more sensitive to temperature changes ($Q_{10} = 4.3$) than the corresponding fraction of labile SOM ($Q_{10} = 2.4$) (Larionova et al., 2014; von Lützow and Kögel-Knabner, 2009). At a mean temperature of 22 °C, this may result in a mean lifetime^[5] of stable SOM reduced to 35 years (Larionova et al., 2014). Moreover, elevated contents in labile carbon have been hypothesized to potentiate stable SOM breakdown (Guenet et al., 2012). Both aspects can lead to an increased degradation of the intermediate to stable SOM fraction. Thus, the current general knowledge of stabilization and destabilization mechanisms

^[5] This is the reciprocal of the decay constant.

of SOM suggests that the processes under plastic mulch favor degradation and destabilization of SOM. With regard to the long residence times of stable SOM, a mulching-induced decrease in this SOM fraction is likely to persist even when the measure has stopped. However, these hypotheses still need to be verified with respect to plastic mulching. Here, it will be important to study the interaction between the enhanced stabilization of organic matter by aggregates on the one hand, and the enhanced potential to be degraded due to higher temperatures and modified soil moisture on the other hand. This requires a process-orientated mechanistic knowledge of the SOM degradation processes under the conditions of plastic mulching.

Although comprehensive evidence on the further long-term development and recovery potential of SOM structures and quality under plastic mulch is still missing, all current findings point into the same direction: Multiannual plastic mulching favors the formation of labile organic matter or degradation of intermediate to stable organic matter. This can be regarded as an alarming indicator for decreasing soil quality and may constitute a potential risk of the soil becoming a CO₂ emittent. The accelerated soil processes under plastic mulch can thus be deemed a major driver altering SOM composition and quality (Schmidt et al., 2011; von Lützow and Kögel-Knabner, 2009). This involves (1) increased soil metabolism and mineralization, particularly of stable SOM structures, (2) rapid nutrient turnover and (3) soil aging, this is degradation in soil quality. Since photosynthesis has a lower temperature sensitivity than degradation kinetics (Kirschbaum, 2000), it seems unlikely that a mulching-induced accelerated net primary production may compensate or overbalance net SOM degradation. However, this relation is currently largely unknown.

Even though most PE-mulched soils are still comparatively young and fertile, low carbon stocks and degraded SOM are well known characteristics of weathered soils located in regions with high mean annual temperatures, as is, for example reported for soils in the tropics or those expected to be subjected to global warming (Davidson and Janssens, 2006). Many of such soils are characterized by a labile, highly dynamic equilibrium between rapid organic matter supply and rapid degradation with a lower relevance of organic matter stabilized by minerals (Zech et al., 1997). Once this fragile equilibrium has been disturbed due to removal of native vegetation and agricultural activity, mineralization increases (Richards et al., 2007), soil nutrients are rapidly exhausted and overall soil quality decreases (van Straaten et al., 2015). This is accompanied by preferential degradation of aliphatic SOM, subsequently followed by a decrease in “mature” constituents (Pardo et al., 2012). Furthermore, the cleavage of organo–mineral complexes decreases SOM stability (Shang and Tiessen, 1997). Since SOM of temperate soils is even more sensitive to increasing temperatures (Grisi et al., 1998), these processes may become increasingly relevant in soils subjected to plastic mulching, eventually resulting in a gradual but severe degradation of arable soils. These consequences may even render potential benefits of plastic mulches void, such as erosion and leaching reduction or improved plant–soil interactions. Considering the scarce knowledge of SOM composition of soils subjected to plastic mulching, a transfer of the process knowledge in tropical soils may be a first step in extrapolating potential risks of plastic mulching. However, it is worth noticing that the current assumptions are only based on inferences from scarcely available literature information. They must in any case be corroborated by further long-term research on the development of

the SOM composition and its function in the soil system in order to promote the sustainable use and functioning of soil as a resource, although potentially reducing short-term gross productivity. Considering that the risk of plastic mulching for sustaining SOM quality is significant and cannot be neglected, the question arises why plastic mulching is nevertheless a measure used increasingly in agriculture. One reason may be their significant short-term economic benefits as reviewed and discussed in the following section.

2.6 AGRONOMIC IMPLICATIONS

2.6.1 COSTS AND BENEFITS

So far, the main interests and criteria of an agronomic evaluation of plastic mulching have largely been determined by measuring short-term benefits, first of all higher annual marketable yields. Furthermore, farmers may decide to use plastic mulches in expectation of a competitive advantage and a higher revenue originating from earlier marketing opportunities, an increased quality of the product, and anticipated water savings (Ingman et al., 2015; Johnson and Fennimore, 2005; Kwabiah, 2003).

While numerous studies have demonstrated beyond doubt that the use of plastic mulch increases product quantity and quality (for instance, Laugale et al., 2015; Overbeck et al., 2013; Ruíz-Machuca et al., 2015), particularly in combination with drip irrigation (Biswas et al., 2015; López-López et al., 2015), it remains unresolved under which specific conditions the revenues offset the costs of plastic mulch purchase, management, and disposal (Fisher, 1995; Mugalla et al., 1996). In this regard, scientific literature is still particularly incomplete and contradictory: In Venezuela, plastic mulch use for a melon cultivation increased annual costs by approximately 6% while doubling the revenue leading to a more than five-fold profit increase (Nava, 2011). However, in two other studies conducted in India (Tiwari et al., 1998; Tiwari et al., 2003), benefit–cost ratios of a drip-irrigated okra and cabbage cultivation were worse when plastic mulching was added to the treatment despite higher yields. Decreasing profits were most likely caused by higher costs for the mulch purchase. Furthermore, Xie et al. (2005) found that plastic mulching in wheat fields was only cost effective under highly deficit irrigation (40% of the field capacity), whereas non-mulched treatments succeeded when the field capacity reached 60 to 85%. Comparable results were obtained by Biswas et al. (2015) cultivating tomatoes. In forestry, Leclerc (1997) stated that plastic mulches were not shown to have any economically beneficial effect at all. On the contrary, Böhlenius and Övergaard (2015) presented that plastic mulching increased the growth of a hybrid poplar during the first two years after planting by 200% compared to plants with no vegetation control. In Europe, however, plastic mulching is mostly applied for premium and highly seasonal commodities such as asparagus and strawberries (Heißner et al., 2005; Stevens et al., 2011), in order to shorten the fruit development time and market the product as early as possible. This, in turn, enables farmers and sellers to charge higher prices (Johnson and Fennimore, 2005; Poling et al., 1991) which sustains their profits.

Generally, the most pronounced economic effects reported in the scientific literature have been achieved by water savings (up to 25%) and reduced labor costs for weed and pest control (Ingman et al., 2015; Jabran et al., 2015), however,

only taking into account basic assets, such as material acquisition and marketable resource consumption, without calculating the effort to apply and remove plastic covers. Although mulch application has been facilitated with the introduction of mulch laying machinery (Singh et al., 2014), Schonbeck (1999) warned that plastic mulch removal and disposal remained labor- and cost-intensive so that the costs of total labor requirements for mulching may cancel out savings in the long term, for instance in weed or pest management. Except for the aforementioned study, we were not able to find any up-to-date information on estimated costs for plastic removal and disposal. Therefore, it is unknown how including such costs would affect benefit–cost ratios of modern plastic mulching techniques. Present findings indicate that the cost efficiency of plastic mulches is highly dependent on the cultivated crop as well as on local or regional preconditions such as marketing opportunities, average wages, or water availability. Particularly in arid regions and for the sale and distribution of seasonal fruits, plastic mulching has been shown to be economically beneficial. The farmers may therefore decide to apply plastic mulching on a case-by-case evaluation. However, comprehensive knowledge of the overall costs and benefits of plastic mulches in the scientific literature is still scarce and incomplete. More detailed and comparative analyses on the life cycle of plastic mulches are needed under particular consideration of their long-term agronomic viability and environmental impact over multiple decades of application (Ayala and Rao, 2002). For such an assessment, the concept of ecosystem services could be useful.

2.6.2 ECOSYSTEM SERVICES

Whenever human activity interferes with extra-urban landscapes, as is often the case in agriculture, it potentially affects ecosystems and their services to humans (Foley et al., 2005). Ecosystem services are defined as all the benefits society attains from ecosystems, including provisioning, supporting, regulating, and cultural services; the supporting services being the basis for the others (Millennium Ecosystem Assessment, 2005). One key aspect of all ecosystem services is biodiversity, as the stability of an ecosystem depends on the interaction between its non-living components and living organisms (Haines-Young and Potschin, 2010). Agroecosystems are ecological systems, though modified by man in order to produce food, fiber, or fuel. Traditionally, agroecosystems have been valued mainly as sources of the aforementioned provisioning services, which are crucial for the sustenance and enhancement of human life (Power, 2010). At the same time, “dis-services” such as unsustainable nutrient depletion, soil erosion, or the contamination of natural habitats should be avoided (Zhang et al., 2007). Furthermore, ecosystem services like cultural, recreational, or aesthetic values have an impact on society (Ulrich, 1986). Essential to all ecosystem services are the supporting services, which in the context of agroecosystems include soil formation and fertility, nutrient and water cycling, primary production, and conservation of genetic variability (Millennium Ecosystem Assessment, 2005). However, agroecosystem services have always been valued differently depending on their perceived importance as well as their profitability. While market ecosystem services can easily be quantified by the direct profit they generate, non-market or only indirectly marketable services are difficult to measure since they have no visible price attached. Thus, they are usually considered less important by the producer although they play an important role

for the supply of provisioning services, especially in the long run (Swinton et al., 2007).

2.6.3 EFFECTS OF PLASTIC MULCH ON REGULATING AND SUPPORTING SERVICES

As reviewed in the previous sections, the modified soil conditions under plastic mulches are expected to accelerate soil degradation and may lead to undesirable shifts in soil organism communities and affect ecosystem engineers such as earthworms or nematodes. The chemical and biological quality and functioning of the soil plays an essential role for the regulation of organic matter decomposition, carbon sequestration, and nutrient mineralization. Therefore, it is crucial for the preservation of soil health (Stork and Eggleton, 1992). PE mulches further generate significant amounts of non-degradable, hardly recyclable waste (see discussion further above and Delgado and Stenmark, 2006), which is likely to pollute the environment either through incineration emissions, landfill leaching, or microplastic residues. Plastic mulching may therefore pose a significant risk to sustaining the aforementioned ecosystem services in agricultural landscapes.

2.6.4 CULTURAL ECOSYSTEM SERVICES

Plastic mulches modify rural landscapes since they are highly visible and cover large areas of agriculturally used land. This raises the questions of how visually pleasing or environmentally harmful plastic-covered landscapes are perceived by the public and other stakeholders, and if and to what extent recreational qualities of natural landscapes are changed when fields are covered with plastic mulches. The recreational potential of rural landscapes can be perceived as a cultural ecosystem service (Ulrich, 1986).

To our knowledge, experimental research on the specific visual and affective impacts of plastic mulches from a psychological and sociocultural perspective has not yet been conducted. However, potential effects can be derived from studies on the public opinion on agriculture (Special Eurobarometer 410, 2014) or from psychological studies on landscape preferences and recreational environments (Steg et al., 2012).

The Special Eurobarometer 410 (2014), a representative survey commissioned by the EU, showed that citizens' awareness of agriculture and agricultural policy is not very pronounced. 53% of the European citizens agreed that agriculture in rural areas is a very important subject in the future. Developing rural areas was judged very important by 46% of the European citizens, while the economic support of farmers and food supply ranked higher. The responsibility of farmers was perceived more strongly with regards to economic factors. The protection of the environment as important responsibility of the farmers was only supported by 32% of the Europeans.

Psychological studies found evidence that people prefer diversified and protective landscapes that are rich in natural elements (for example, Kaplan, 1995; Lohr and Pearson-Mims, 2006). Covering large areas with plastic would contradict that preference. However, it is worth noticing that individual experiences and personal relationships strongly influence people's affective preferences of certain landscapes and their relationship to nature (for example, Hunziker et al., 2007; Strumse, 1996). When comprehensively understood, this interplay could be used

to encourage farmers to consider impacts of their agricultural practice on the conservation of diversified and protective landscapes and ways how to communicate these aspects to their customers.

Although dependent on personal preferences and sociocultural influences, Arriaza et al. (2004) argued that the perceived visual landscape quality often increases with the degree of wilderness and the presence of vegetation whilst decreasing with the presence of negatively evaluated manmade elements and monoculture. Yao et al. (2011) found that green landscapes of both manmade and natural origin were perceived more attractive than industrial sites featuring gray and black colors. In this respect, the application of plastic materials in the environment interferes with a certain visual attractiveness. More recent studies applied remote sensing techniques to estimate the degree of “aesthetic pollution” mulches may generate (Levin et al., 2007; Picuno et al., 2011). Thereby, Picuno et al. (2011) identified substantial pollution caused by plastic mulches and suggested a 10% maximum threshold “above which the impacts on the agricultural landscape should be considered unacceptable”. The authors further recommended using more aesthetically pleasing colors to mitigate impacts on cultural ecosystem services. However, the selection of an appropriate mulch color is limited when specific optical properties of the material are required (see also Section 2.3). Skroch et al. (1992) rated the aesthetic value of various mulch materials based on the authors’ subjective perception. Although their results may be strongly biased, the authors reported that landscape attractiveness increased with the amount of organic material such as longleaf pine needles applied to the plots. Consequently, reintroducing organic mulches would offer a solution to benefit from mulch technology. Currently, however, organic mulches are denied greater acceptance by farmers (Goldberger et al., 2015) since their use may promote the dispersal of pests (Howard and Oropeza, 1998).

Due to the lack of substantial knowledge about influences of plastic mulching from a psychological and sociocultural point of view, future empirical studies should particularly focus on the perceived visual quality, subjective preference ratings as well as affective, cognitive, and psychophysiological influences caused by the presence of plastic covers in rural areas. It needs to be addressed how fields with and without plastic mulches are perceived by the observers and which preexistent attitudes shape the people’s perceptions and judgments about plastic covers. Potential mediators, such as knowledge of chances and risks attributed to plastic mulching, would be of further interest to precisely understand why this agricultural technique is applied on a large scale.

In summary, Figure 2.1 depicts our understanding of the direct effects of plastic mulching and their implications for soil quality, environmental pollution, farm profitability, and ecosystem services. While in the short-term plastic mulches may improve soil conditions (temperature and moisture control) in terms of leading to higher product yield and quality and consequently to higher revenues for farmers, the described negative impacts of mulching regarding their fate and changes in soil processes are expected to reduce soil quality, namely the soils’ capacity to generate provisioning and supporting ecosystem services, in the long term. In addition, a potential decrease in biodiversity and unwanted effects on the visual appearance of agricultural landscapes may reduce the value of the public goods. Without comprehensive knowledge of the interactions of the described processes and their impact on ecosystem services, farmers will not be able to make sound and sustainable economic decisions regarding the use of mulching technologies. In

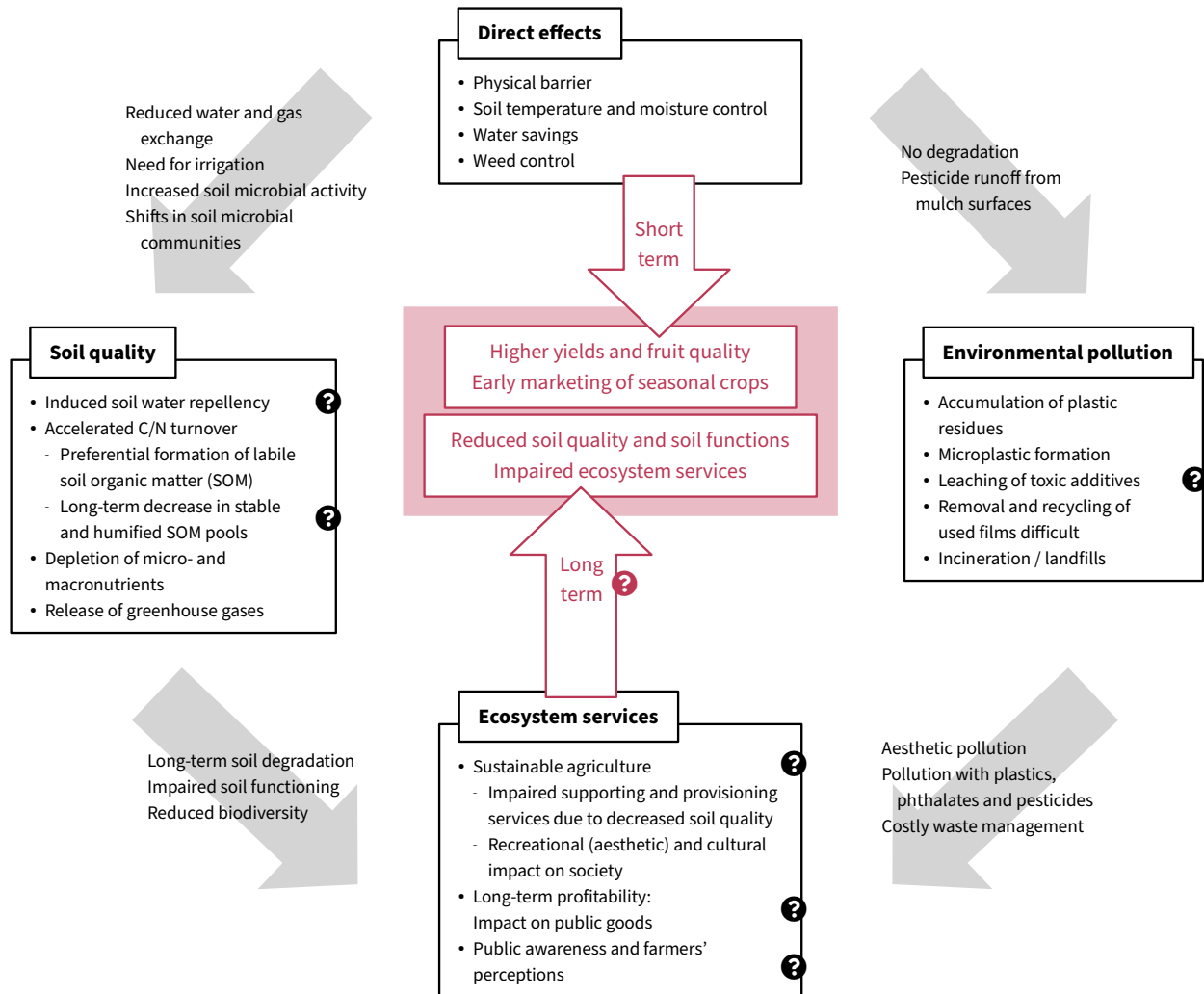


Figure 2.1: Schematic representation of the impacts of plastic mulch use on soil quality, pollution, and implications on agronomy and ecosystem services; question marks indicate need for research.

this regard, it remains especially important to raise public awareness and create a holistic understanding of non-market ecosystem services and their values to public welfare to sustain agricultural landscapes in the long term.

2.7 CONCLUSIONS

This literature review identified certain reasons for farmers to apply plastic mulches in agriculture, but it also identified a number of risks and less beneficial effects of plastic mulching with regard to waste treatment, life cycle balance, and impact on soil quality. This includes the persistence of unrecovered plastic mulch in soil, their potential to alter soil quality by shifting the edaphic biocoenosis, accelerating carbon and nitrogen metabolism, as well as potentially degrading SOM. This further includes inducing soil water repellency, increasing the risk of mycotoxin formation in soil and an enhanced release of climate relevant gases. Although several attempts have been made to extend the life cycle of plastic mulches and to reduce their input to soil by recovering and recycling used mulching films, in some cases the cost and effort of these options seem to outweigh their benefits from yield increases, water savings, and facilitated pest control. If, in addition, external

effects of mulching on (public) goods or resources like soil quality, biodiversity, or recreation are taken into account, a holistic ecosystem services assessment could make plastic mulching uneconomic and unsustainable.

Comprehensive research with the aim of gaining an extensive understanding of the processes governing the impacts of mulching on soil quality is needed. As most of these biogeochemical processes are not yet sufficiently understood, a final judgment on the implications of plastic mulching for the environment will require long-term field experiments combined with targeted process-orientated studies on a laboratory scale in order to be able to estimate and potentially avoid environmental risks such as soil degradation. This process understanding is of particular importance for the development of truly biodegradable mulches. In order to assess the contribution of plastic mulching to the pollution with plastic debris and to changes in SOM composition and quality, future research should focus on more detailed soil characterization techniques such as Py-GC/MS or thermogravimetric approaches as a basis for further impact assessments and life cycle analyses. Similarly, analytical methods which can detect, identify, and quantify plastic debris in soil, need to be developed.

The currently rather unquestioned application of plastic mulching may be attributed to the lack of long-term studies and attention in the mass media addressing the potential risks for the soil, biota, and society. Future research should analyze why and under which premises plastic mulching is accepted by farmers, the public, and further stakeholders of the agronomic sector and which long-term incentives drive farmers to apply plastic mulches. Deeper knowledge of these aspects would help to make both the agribusiness and society more environment-friendly.

3

QUANTITATIVE ANALYSIS OF PET PLASTIC DEBRIS IN SOIL VIA TGA/MS

Abstract The use of plastic materials in daily life, industry, and agriculture can cause soil pollution with plastic debris down to the micrometer range, namely, microplastics. The quantitative assessment of plastic debris in soil has been limited so far. Until now, microplastic analyses in soil require laborious sample cleanup and are mostly restricted to qualitative assessments. In this study, we applied TGA/MS to develop a method for the direct quantitative analysis of PET without further sample preparation. For this, soil samples containing $1.6 \pm 0.2\%$ C_{org} were spiked at $2.3\text{--}45.9 \text{ g kg}^{-1}$ PET plastic debris from recycled bottles. DL-Cysteine was used as an internal standard. Sample mixtures were pyrolyzed with a 5 K min^{-1} ramp ($40\text{--}1000 \text{ }^\circ\text{C}$), while sample mass loss and MS signal intensities of typical PET pyrolysis products were recorded. We found signal intensities linearly responding to PET concentrations. The most promising results were obtained with the internal standard-corrected PET pyrolysis product vinylbenzene/benzoic acid (105 m/z , adj. $R^2 = 0.987$). The limits of detection (LODs) and limits of quantification (LOQs) were 0.7 and 17.2 g kg^{-1} PET, respectively. Our results suggest that TGA/MS can be an easy and viable complement to existing methods such as TED-GC/MS or microspectroscopic techniques.

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See Parts of this Thesis and Author Contributions, page ix, for details.

3.1 INTRODUCTION

Microplastics are synthetic polymers with typical particle sizes smaller than 5 mm either disintegrated from larger plastic parts or originally produced in particulate form (Cincinelli et al., 2017). Microplastics have been recently recognized as a ubiquitous environmental contaminant in marine and fresh waters, sediments, and organisms (Karlsson et al., 2017; Rochman, 2018). However, the sources, pathways, and reservoirs of microplastics in terrestrial systems are still hardly known (Dris et al., 2016).

Microplastics could be introduced into soil via (1) air transport of non-managed plastic wastes, littering, and street runoff (Dris et al., 2016; Bläsing and Amelung, 2018), (2) disintegration of agriculture plastics such as mulch films, tarpaulins, tunnels, and pipes (Lambert et al., 2014), or (3) application of sewage sludge and reclaimed wastewater containing plastic microbeads or fibers (Bläsing and

Amelung, 2018; Zubris and Richards, 2005). In this respect, the presence of plastic fragments has become an important parameter to describe urban soils and Technosols (Rillig, 2012; Nizzetto et al., 2016). Particularly in transitional and developing economies, used agricultural plastic mulches and other plastic wastes may be incorporated into the soil of agricultural fields (Duis and Coors, 2016) and household gardens (van der Wal et al., 2011), where they are likely to become an environmental issue (Sintim and Flury, 2017). Plastic debris is assumed to further accumulate in the soil food web (Rillig, 2012), to function as sorbent for agrochemicals (Ramos et al., 2015), or adversely affect soil organisms (Kirstein et al., 2016), eventually decreasing soil stability and quality. Synthetic polyester fibers, namely PET, as used in this screening study, have already been found in sewage sludge (Zubris and Richards, 2005) and are continuously introduced into the environment by washing and wearing synthetic textiles (Pirc et al., 2016). Agricultural tarpaulins or discarded PET bottles are another source of plastic pollution in soil.

In order to assess the content of plastic debris in agricultural soil and adjacent freshwater sediments, analytical assays for the identification and quantification of plastic debris in complex environmental matrices are needed (Bläsing and Amelung, 2018). Microscopic techniques, mainly light microscopy, are currently the most used but pose extraordinarily high requirements on laboratory cleanliness and typically require labor-intensive preconcentration procedures (Woodall et al., 2015). If these requirements are not met, misinterpretation coming from false positive results is likely (Lachenmeier et al., 2015). Microspectroscopic techniques, such as FTIR spectroscopy with optional attenuated total reflection (ATR) or Raman microspectroscopy, represent alternative approaches. The latter may help to fulfill the analytical requirements of distinguishing particles or fibers of synthetic origin from natural matrix structures such as cellulose fibers or silicate particles. Primpke et al. (2017) presented an interesting method for the automated detection of plastic debris on membrane filters using advanced image analysis software. Such techniques have been used for more easily accessible and homogeneous atmospheric or aqueous matrices so far but not for soil (Ioakeimidis et al., 2016; Fischer et al., 2015; Comnea-Stancu et al., 2016), and they often produce only qualitative results (Bläsing and Amelung, 2018) because of interferences from SOM autofluorescence.

Another promising technique may be alkali depolymerization of PET and subsequent analysis of depolymerized building blocks bisphenol A and *p*-phthalic acid in sludge, sediments, and mussels via liquid chromatography/mass spectrometry (LC/MS) (Wang et al., 2017). However, both bisphenol A and *p*-phthalic acid are not specific for the analysis of one single polymer, extraction from soil may be incomplete, and leaching and mobilization of building block compounds from the polymer backbone into the environment may produce ambiguous results (Wang et al., 2017). Elert et al. (2017) achieved recovery rates of about 80% PET extracted from soil with hexafluoroisopropanol followed by SEC and reverse-phase liquid chromatography (LC).

In contrast, analytical techniques based on sample pyrolysis have the potential to overcome the aforementioned drawbacks of microscopic and extraction methods in terms of higher specificity, lower sample preparation efforts, and facilitation of semiquantitative to quantitative analyses. For example, by using Curie point Py-GC/MS, PET quantification in fish required less than 5 µg of substance when combined with prior enzymatic and chemical digestion (Fischer and Scholz-

Böttcher, 2017). However, high sand contents made an additional density separation step necessary, which is challenging considering the high density of PET. Here, Dümichen et al. (2015) were the first to successfully apply and validate a quantitative method for PE in soil. The authors established a two-step procedure involving pyrolysis of PE-spiked soil via thermogravimetric analysis (TGA) and capturing of pyrolysis gases followed by TED-GC/MS. The same method has also been applied for the determination of PET, so far only with qualitative results (Dümichen et al., 2017).

An alternative to this two-step approach is on-line TGA/MS, measuring simultaneously the masses of gases evolving during thermal treatment. Thermal treatment can either be oxidation (combustion) or pyrolysis in an inert Ar atmosphere. A defined portion of gaseous degradation products are transferred into a quadrupole MS via a heated capillary or a capillary-less orifice. The mass loss at a specific temperature is then related to the MS signal of gaseous pyrolysis products. Even without chromatographic separation, analytes with the same or similar pyrolysis products as the matrix may be distinguished from each other^[1] according to their distinct decomposition temperatures.

So far, TGA/MS has been successfully applied for characterizing combustion or pyrolysis products of soils (Pallasser et al., 2013; Edmondson et al., 2015; Tamimi et al., 2017), sediments (Findorakova et al., 2017), and polymers (Pagacz et al., 2015; Schindler et al., 2013). However, complex mixtures of plastic debris and soil have not yet been assessed. With this proof-of-principle work, we aimed to evaluate the potential of a capillary TGA/MS system to qualitatively and quantitatively determine PET in a spiked soil without any pre-separation of PET plastic debris from soil. We focused on the determination and quantification of characteristic pyrolysis products of PET such as benzoic acid and vinyl and alkylbenzenes (105 m/z fragment) and biphenyl (154 m/z fragment) (Dümichen et al., 2017; Dimitrov et al., 2013; Duemichen et al., 2014); the latter being formed by a radical reaction and intramolecular ring formation (Richter and Howard, 2000; Kawai et al., 2008). The formation of these pyrolysis products can then be related to their specific degradation temperatures as determined by TGA. DL-Cysteine was used as internal standard for normalizing the present detector signal and ionization state. By using a capillary TGA/MS, we wanted to provide an easy-to-use instrumental setup for plastic analysis. Since some studies have discussed the potential of the TGA/MS capillary to become blocked during polymer measurements (Schindler et al., 2013; Duemichen et al., 2014), particular attention was paid to monitoring and maintaining a working capillary throughout all our experiments. In this work, we study the possibilities of using the capillary TGA/MS device for a quicker and cheaper assessment of plastic debris in soil within the soil matrix and the influences of SOM on the detection limits.

3.2 EXPERIMENTAL

3.2.1 MATERIALS

Cryomilled PET dust obtained from mechanical shredding of bottle recycle^[2] (0.15–0.4 mm dominant particle size) was used as the microplastic sample. A PET standard^[3] and a PET water bottle sample^[4] were used to assess PET dust quality. For the preparation of calibration series, a standard loamy sand (75% sand, 16%

^[1] For instance plastic pyrolysis products from soil pyrolysis products.

^[2] PETKA CZ, Brno, Czech Republic.

^[3] CAS 25038-59-9, PlasticsEurope, Frankfurt, Germany.

^[4] EDEKA, Hamburg, Germany.

^[5] Landwirtschaftliche Untersuchungs- und Forschungsanstalt, Speyer, Germany.

^[6] CAS 3374-22-9, 98% purity, Carl Roth, Karlsruhe, Germany.

^[7] Q1000, TA Instruments, New Castle, USA.

^[8] TZero, TA Instruments, New Castle, USA.

^[9] Sartorius SE 02-OCE, Göttingen, Germany.

^[10] Netzsch, Selb, Germany.

^[11] STA 449 F3 Jupiter TGA analyzer, Netzsch, Selb, Germany.

^[12] QMS 403 C Aëolos, Netzsch, Selb, Germany.

^[13] SGE Analytical Science, Ringwood, Victoria, Australia.

silt, 9% clay, LUFA 2.2)^[5] with $1.6 \pm 0.2\%$ C_{org} content was used. DL-Cysteine^[6] served as the internal standard for TGA/MS pyrolysis measurements.

3.2.2 QUALITY ASSESSMENT OF THE PET DUST

In order to compare the potential difference in the physicochemical properties of the shredded microplastic sample and the PET standard, DSC^[7] was used to determine their melting temperature and melting enthalpy. The thermal history of PET samples was erased with a preheating run from 40 to 310 °C followed by a cooling run from 310 to -20 °C. For the subsequent measurement, the heating run was repeated from -20 to 310 °C. All runs were performed in hermetically sealed pans^[8] under a 50 mL min^{-1} N_2 flow and a thermal ramp of $\pm 10 \text{ K min}^{-1}$. All DSC analyses were performed in triplicate.

3.2.3 PREPARATION OF SPIKED SOIL SAMPLES

Two calibration series were prepared, each in duplicate. For both experiments, a microscale^[9] and 85 μL alumina TGA crucibles^[10] were used. All specimens were weighed directly into the TGA crucible and carefully mixed.

The first calibration series was performed without internal standard. To this end, between 42.98 and 50.79 mg of soil was spiked with 0.28–2.02 mg of milled PET bottle recycle in order to prepare five different PET concentrations in soil ranging from 5.6–41.8 g kg^{-1} . For the second calibration series, about 1% of DL-cysteine (0.87–1.08%; 0.41–0.52 mg) was added as internal standard to PET-spiked and blank soil. Here, seven different concentrations were prepared ranging from 2.3 to 45.9 g kg^{-1} PET (0.10–2.24 mg added to 44.18–46.83 mg of soil).

DL-Cysteine has not been used in TGA/MS as internal standard yet. In this work, it was selected to obtain an easily detectable and distinguishable pyrolysis product with lower molecular weight than the observed PET pyrolysis products. The amount of S in SOM is approximately two orders of magnitude lower than that in DL-cysteine (Blume et al., 2016). Pyrolysis of DL-cysteine provides a strong signal at 33 m/z corresponding to the SH^- ion (Choi et al., 1995), which was proven absent both in PET and SOM pyrolysis products, in a relatively narrow pyrolysis temperature range (Appendix, Figure A.1). Normalization of analyte signals to the signal of the internal standard is of considerable importance to obtain more stable peak responses during routine TGA/MS measurements. Particularly during long measurement series of various samples, non-standardized MS signals may vary with respect to current ionization and detector state (Netzsch Gerätebau, 2010).

3.2.4 TGA/MS ANALYSIS

All samples were subjected to a 5 K min^{-1} pyrolysis ramp from 40 to 1000 °C under a 20 mL min^{-1} Ar 5.0 gas flow in a two-fold evacuated Ar-filled TGA chamber^[11]. The TGA was coupled with an electron ionization quadrupole MS^[12] via a 2.2 m long, 75 μm wide, untreated fused silica capillary^[13] heated to 300 °C. The mass resolution as contribution to neighboring masses of 40/41 was < 50 ppm. The detector was set to on-line mode in order to directly detect preselected m/z ratios from 12 to 154. Dependent on the m/z ratios of interest, the following settings were used: For m/z ratios of 12–32 and 44, the secondary electron multiplier (SEM) was adjusted to 1400 V, a dwell time of 1 s, and a resolution of 50 au. For m/z 33–154,

an SEM voltage of 2400 V, a dwell time of 5 s, and a resolution of 250 au were applied. Both calibration series, with and without DL-cysteine as internal standard, were measured together with six blank soil samples.

LODs and LOQs [$\mu\text{g mL}^{-1}$] were calculated using Equations 3.1 and 3.2, respectively, in accordance with the German standard DIN 32645 (2008) as implemented in the R package “envalysis”^[14] (version 0.3.3).

$$\text{LOD} = \frac{\sigma_{\text{blank}}}{\alpha} \cdot t_{n-1;0.01} \sqrt{n^{-1} + m^{-1}} \quad (3.1)$$

$$\text{LOQ} = k \cdot \frac{\sigma_{xy}}{\alpha} \cdot t_{n-2;0.01} \sqrt{n^{-1} + m^{-1} + \frac{(\text{LOQ} - \bar{x})^2}{S_{xx}}} \quad (3.2)$$

Therein, σ_{blank} is the standard deviation (SD) of integrated peak areas from blank measurements, σ_{xy} is the residual SD, and α [$\text{mL } \mu\text{g}^{-1}$] is the slope of the calibration curve. t is the 99% percentile of the Student’s t distribution with $n - 1$ and $n - 2$ degrees of freedom, n as the total number of measurements, and m as the number of replicates. $k = 3$ is the recommended certainty factor for the LOQ; \bar{x} is the arithmetic mean of all standard concentrations, and S_{xx} [$\mu\text{g}^2 \text{ mL}^{-2}$] is the sum of squares of x . Note that calculating the LOQ is an iterative process with $\text{LOQ} = k \cdot \text{LOD}$ as initial value.

3.2.5 TRANSFER CAPILLARY CONTROL EXPERIMENTS

Although some authors use TGA/MS for pyrolysis of polymers without reporting problems (Pagacz et al., 2015), it has been discussed whether the heated capillary used for the transfer of the pyrolysis product from the TGA chamber to the MS detector may become blocked by condensing pyrolysis products during measurements (Schindler et al., 2013; Duemichen et al., 2014). In order to control the state of the transfer capillary, the following control experiments were conducted: after each spiked sample, a cleaning run with an empty crucible and a 10 K min^{-1} heating ramp from 40 to $1000 \text{ }^\circ\text{C}$ in a 50 mL min^{-1} synthetic air flow was followed by pyrolysis^[15] of calcium oxalate hydrate ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$)^[16]. Constant MS signals of calcium oxalate pyrolysis products ensured a consistently working capillary. Signals of $105 \text{ } m/z$ from cleaning runs and oxalate pyrolysis events were averaged and taken as the noise throughout the complete temperature range in order to assess a potential residual signal carried over from the capillary and originating from impurities remaining in the transfer capillary during spiked sample measurements and potential leaks during control experiments.

For the least concentrated PET sample, the signal-to-noise ratio (SNR) (Equation 3.3) was calculated on the basis of the mean m/z signal μ_{sample} over a temperature range of $300\text{--}650 \text{ }^\circ\text{C}$ divided by the SD of a cleaning run (σ_{clean}) containing either no sample or oxalate (Wells et al., 2011).

$$\text{SNR} = \frac{\mu_{\text{sample},300-650 \text{ }^\circ\text{C}}}{\sigma_{\text{clean},40-1000 \text{ }^\circ\text{C}}} \quad (3.3)$$

In addition, the capillary pressure was controlled before every measuring sequence to monitor constant throughput.

^[14] The package source is available at DOI: [10.5281/zenodo.1240305](https://doi.org/10.5281/zenodo.1240305).

^[15] Under the same conditions as spiked samples.

^[16] CAS 5794-28-5, Sigma-Aldrich, Steinheim, Germany.

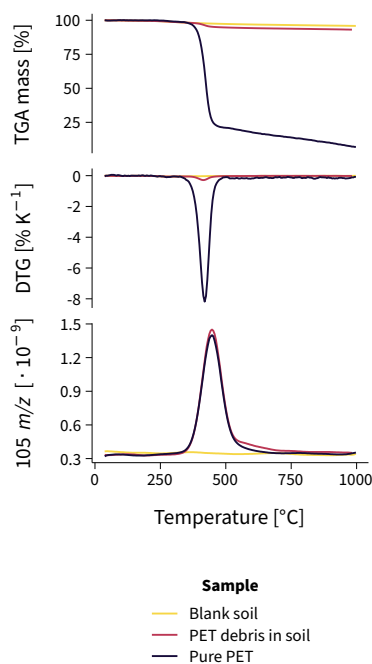


Figure 3.1: TGA and derivative thermogravimetry curves and normalized 105 m/z ratios of blank soil, pure PET (1.73 mg), and an exemplary mixture of 37.1 g kg^{-1} PET debris (1.74 mg) in soil.

3.3 RESULTS AND DISCUSSION

3.3.1 QUALITY ASSESSMENT OF THE PET RECYCLATE

The DSC measurements revealed a comparable melting temperature (T_m) and specific enthalpy of fusion ($\Delta H_{\text{fus}}^\circ$) for the PET recyclate ($T_m = 243.6 \pm 0.4^\circ\text{C}$, $\Delta H_{\text{fus}}^\circ = 48 \pm 3 \text{ J g}^{-1}$), the PET standard ($T_m = 243.1 \pm 0.1^\circ\text{C}$, $\Delta H_{\text{fus}}^\circ = 48 \pm 3 \text{ J g}^{-1}$), and the PET water bottle obtained from a common German retail chain store ($T_m = 246.5 \pm 0.2^\circ\text{C}$, $\Delta H_{\text{fus}}^\circ = 50 \pm 6 \text{ J g}^{-1}$; averaged heat flows are given in Figure A.2). Therefore, the PET recyclate was deemed qualitatively representative for further method development.

3.3.2 TGA/MS RESULTS OF PET-SPIKED SOILS WITH AND WITHOUT INTERNAL STANDARD

The degradation onsets of PET, blank soil, and the internal standard *D,L*-cysteine were 382, 208, and 205 $^\circ\text{C}$, respectively. Figure 3.1 shows the TGA curves, derivative thermogravimetry (DTG) curves, and 105 m/z ratios of blank soil, pure PET, plastic dust, and an exemplary 37.1 g kg^{-1} PET mixture with soil. The TGA curve of soil indicated a mass loss of $0.27 \pm 0.03\%$ between 40 and 150 $^\circ\text{C}$ typically ascribed to soil residual humidity. Above 208 $^\circ\text{C}$, degradation of SOM caused a mass loss of $1.5 \pm 0.1\%$ (calculated until 380 $^\circ\text{C}$). The pure PET degraded between 380 and 650 $^\circ\text{C}$ as indicated by a considerable mass loss and accompanied by a peak for 105 m/z . Such a peak was absent in blank soil without any PET. As for pure PET, soil samples spiked with microplastic PET lost its residual humidity between 40 and 150 $^\circ\text{C}$. SOM degraded above 208 $^\circ\text{C}$. The mass loss between 382 and 650 $^\circ\text{C}$ was attributed to the degradation of PET. *D,L*-Cysteine added as internal standard rapidly degraded between 205 and 250 $^\circ\text{C}$ (Figures 3.2 and A.3).

Irrespective of the internal standard, the 105 and 154 m/z fragments evolving from pyrolysis of PET in soil (Figure 3.2) corresponded to the mass loss of PET on the TGA curves. Although these signals have been reported as the most intensive signals occurring during PET thermal degradation (Dümichen et al., 2017; Dimitrov et al., 2013), they cannot be considered absolutely specific for PET in soil. To a certain extent, 105 and 154 m/z are also produced during the pyrolysis of SOM (Schulten and Leinweber, 1999) and other polymers that contain phthalate plasticizers. However, relating MS signals to the specific temperature range of PET degradation, namely 300–650 $^\circ\text{C}$, enabled us to reduce the false positive detection of PET degradation products and to correlate them with the nominal PET content in soil. It remains noteworthy that this approach may be restricted to our given setup. Interferences may occur when analyzing other soils containing complex mixtures of different polymers.

Apart from PET and SOM degradation products, the sharp mass loss at 205–250 $^\circ\text{C}$ corresponded to the degradation of *D,L*-cysteine added as internal standard (33 m/z). *D,L*-Cysteine signal intensities were linear in the anticipated concentration range of 0.25–1.78% in soil (Figures 3.2 and A.3).

Peaks of 105 and 154 m/z ratios integrated within 300–650 $^\circ\text{C}$ were used for linear calibration curves of PET pyrolysis products (Figure 3.3). Corresponding LODs, LOQs, adj. R^2 s, and relative standard errors (RSEs) are presented in Table 3.1. Within a linear range of 2.5–40 g kg^{-1} PET, the best goodness-of-fit measures, these were an adj. R^2 of 0.987 and an RSE of 3.21%, were achieved with the

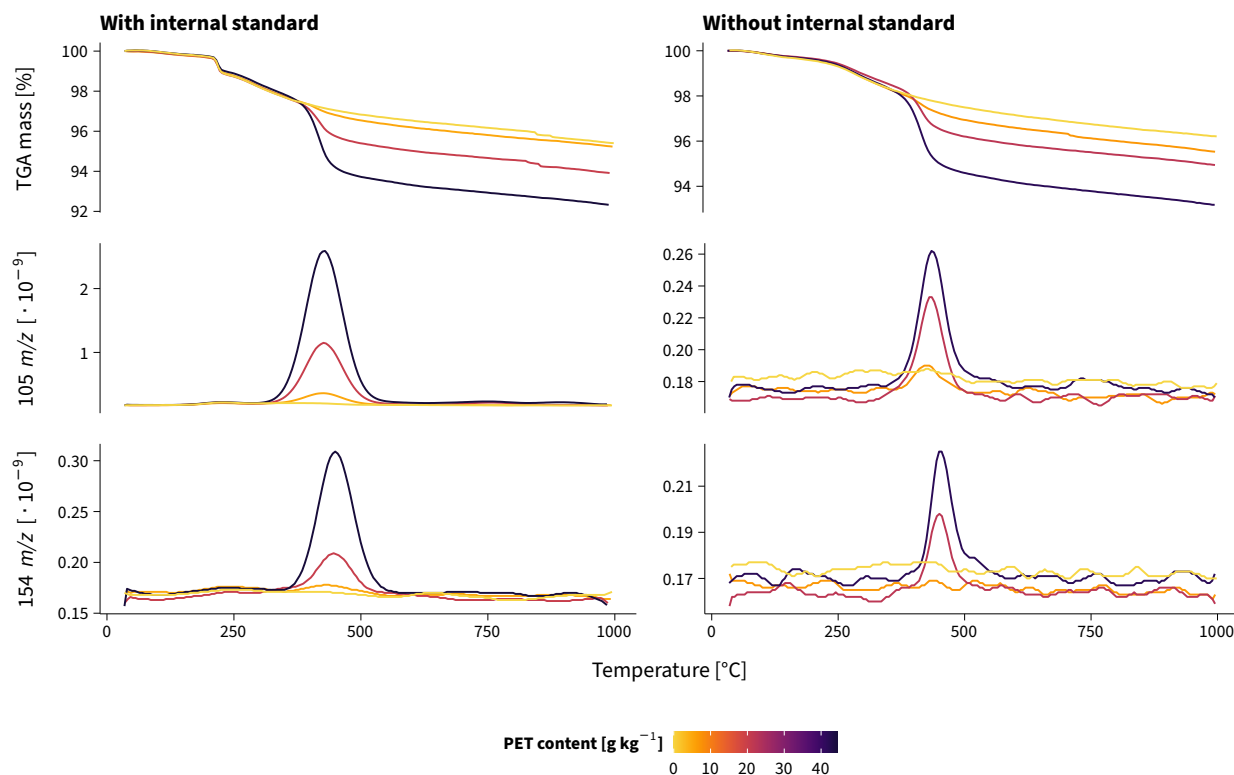


Figure 3.2: Exemplary TGA/MS curves (mass loss, together with 105 and 154 m/z ratios) of soil spiked at three different PET contents either with or without DL-cysteine as internal standard.

105 m/z signal after internal standard addition. The LOD and LOQ were 0.7 and 17.2 g kg^{-1} PET, respectively. For internal standard-corrected 154 m/z , the LOD was comparable to that of 105 m/z as a result of a low background noise. However, the MS signal responded less linearly with increasing PET concentrations. Without internal standard, the curve linearity, LODs, and LOQs were considerably worse.

In contrast to our study, Dümichen et al. (2017) used a common PE bag shredded to microplastic particles and an uncharacterized sandy topsoil sampled from an urban area. The authors analyzed various n-alkadienes as characteristic products of PE pyrolysis via TED-GC/MS. They spiked the soil with 15 to 150 g kg^{-1} PE concentrations and achieved linear calibration curves of integrated 55 m/z signals as a characteristic fragment for eight different n-alkadienes with an adj. R^2 ranging from 0.540 for 1,11-dodecadiene to 0.996 for 1,15-hexadecadiene. Their highest signal response was observed for 1,13-tetradecadiene, for which an adj. $R^2 = 0.988$ and an LOQ of 10 g kg^{-1} PE were determined. RSEs of slope estimates inferred from the calibration curves by Dümichen et al. (2015) varied from 2.97 to 12.41%. In this respect, our LOQ, adj. R^2 , and RSE obtained from 105 m/z after internal standard correction (17.2 g kg^{-1} PET) were generally comparable with those by Dümichen et al. (2015). Small differences in adj. R^2 s, LODs, and LOQs are proba-

m/z	Internal standard	adj. R^2	RSE [%]	LOD [g kg^{-1}]	LOQ [g kg^{-1}]
105	no	0.870	12.76	2.5	510.0
154	no	0.888	11.75	5.8	184.0
105	yes	0.987	3.21	0.7	17.2
154	yes	0.893	9.57	0.6	65.3

RSE = relative standard error of the slope estimate.

Table 3.1: TGA/MS calibration parameters; see Figure 3.3 for calibration curves.

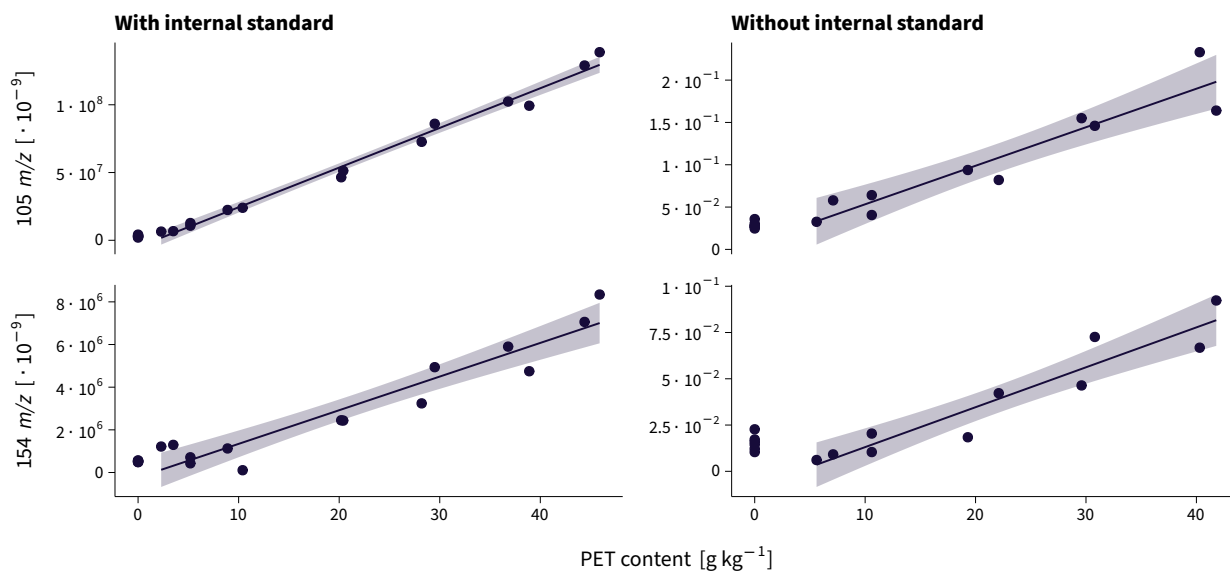


Figure 3.3: TGA/MS calibration curves of PET (105 and 154 m/z) in soil normalized to the sample mass when no internal standard was added or normalized to 33 m/z from the pyrolysis of DL-cysteine as internal standard; shaded bands represent the 95% CI of the linear model; calibration parameters are summarized in Table 3.1.

bly due to use of a different soil and polymer. In addition to that, we tried to mimic a potential environmentally relevant PET sample with the dust that originated from shredding of recycled PET bottles. Although checked by DSC, recycled PET dust may contain impurities from different polymer or paper microparticles. When pyrolyzed, such impurities may interfere with 105 or 154 m/z signals produced by pure PET. Together with PET concentrations up to six times lower than the PE contents used by Dümichen et al. (2015), a slightly higher variation in detector responses and, with that, a reduced goodness of fit of the calibration curves are deemed plausible. One option to further reduce detector variation could be to recalibrate the SEM voltage after every sample run, which is however, not practical for routine analyses. This is why we normalized the obtained signals to an internal standard, which increased the linearity of the calibration curves (Figure 3.3). Moreover, TGA/MS has so far mostly been used to analyze pure chemicals with known stoichiometry of decomposition reactions and low-molecular-weight pyrolysis products (Hotová and Slovák, 2016). Reactions of pyrolysis products potentially occurring in the heated capillary may therefore be another reason for less sensitive signal responses, which we assessed with regular capillary tests.

3.3.3 TRANSFER CAPILLARY CONTROL EXPERIMENTS

^[17] As the stronger of the m/z ratios analyzed.

Series of cleaning runs confirmed that no signal of 105 m/z ^[17] was detected in runs following soil analysis. Figure 3.4 shows worst case scenarios, this is cleaning run and oxalate run after the most concentrated spiked samples, where the probability of capillary blocking was the highest, both with and without DL-cysteine as internal standard. The results are in comparison with the best case scenarios, namely cleaning run and oxalate run after the least concentrated spiked samples and the 105 m/z signals of both least concentrated PET samples. Note that the baselines of the least spiked samples (2 g kg⁻¹ PET) vary in comparison to cleaning runs, because the cleaning runs were performed in synthetic air.

The SNRs of 105 m/z without internal standard correction ranged from 51 to 96 with respect to cleaning runs and from 90 to 128 when based on oxalate

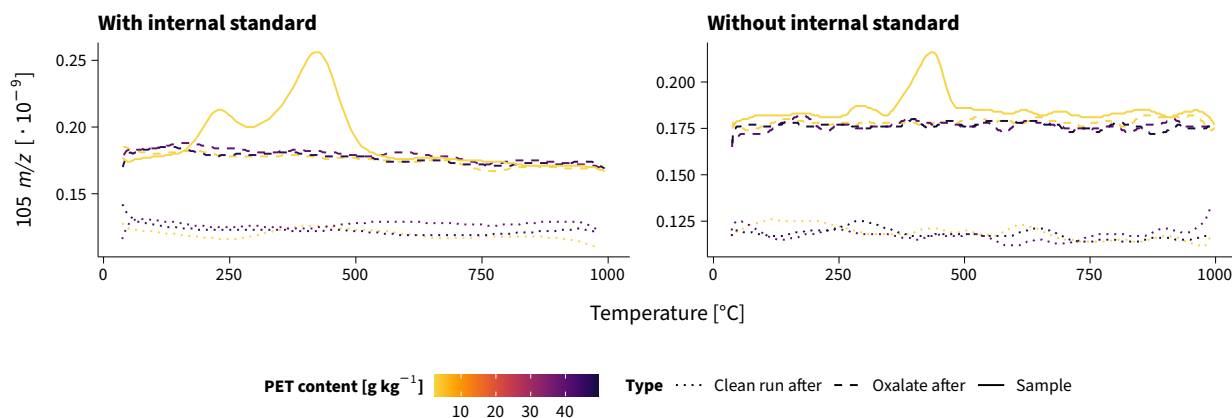


Figure 3.4: 105 m/z ratios of selected cleaning runs and calcium oxalate hydrate pyrolyses after measuring a highly concentrated PET sample ($>40 \text{ g kg}^{-1}$, worst case) and the least concentrated sample (2 g kg^{-1} , best case) in comparison to the same signal of the lowest spiked soil sample either with or without DL-cysteine as internal standard.

pyrolysis runs. With internal standard added, the SNRs were 26–354 and 45–315 for cleaning runs and oxalate pyrolysis runs, respectively. Figure 3.4 shows that during cleaning runs and oxalate pyrolysis, no interfering 105 m/z signals were found. With DL-cysteine added as internal standard, we found a small shoulder peak between 170 and 300 °C probably originating from 2-methylthiazolidine (103 m/z), a byproduct of cysteine pyrolysis (Fujimaki et al., 1969). The 103 m/z fragment may become visible due to the presence of heavier isotopologues and insufficient mass resolution of the TGA/MS. An additional indication for a working capillary was provided by the pressure measurements in the capillary performed before each experiment. The capillary pressure was within the normal range of $2 \cdot 10^{-5}$ to $8 \cdot 10^{-6}$ mbar. Capillary pressures below $8 \cdot 10^{-6}$ mbar would indicate a blocked capillary. Pressures above $2 \cdot 10^{-5}$ mbar may result from a break in the capillary (Figures A.4 and A.5). Therefore, it was assumed that the capillary had not become blocked during the analyses. Capillary conditions were further checked by observing the peaks of H_2O (18 m/z), CO (28 m/z), and CO_2 (44 m/z) resulting from stoichiometric calcium oxalate hydrate pyrolysis. For quantitative determination of pyrolysis products of plastic materials, we recommend introducing this capillary checking procedure in between sample measurements. In our case, the variation of obtained H_2O , CO , and CO_2 signals of the control calcium oxalate runs was within the common limits of the TGA/MS device used (Netzsch Gerätebau, 2010).

3.4 CONCLUSIONS

With this study, we showed for the first time the suitability of TGA/MS for the quantitative analysis of PET plastic debris in a standard loamy sand with $1.6 \pm 0.2\%$ C_{org} . We considerably improved signal sensitivities and linearity by using DL-cysteine as an internal standard. This broadens the application of TGA/MS, bringing new insight into the emerging field of microplastics research in soil science. Follow-up studies will need to show whether a similar analytical setup could be extended to standard soils with different C_{org} contents and real soil samples polluted with PET debris. However, high C_{org} contents, for instance from applied sewage sludge, or contamination with other polymers would probably interfere with PET or internal standard pyrolysis products. Such challenges could be further addressed using chemically assisted pyrolysis or deconvolution techniques combined with a

simple sample preparation method to reduce noise from the sample matrix. This would also enable us to further reduce LOQs to approach environmentally relevant PET contents.

Although recently published methods using TED-GC/MS (Dümichen et al., 2015), Py-GC/MS (Fischer and Scholz-Böttcher, 2017), and LC/MS (Wang et al., 2017) produced lower or equal LOQs than this study, TGA/MS measurements are generally cheaper and require only a minimal sample preparation effort. In addition, TGA/MS can be used with various heating rates and sample amounts up to 1 g (Jakab et al., 2003), which will be needed to account for the heterogeneity of soil samples. We therefore consider TGA/MS a valuable complement to existing analytical methods in terms of serving as a first assessment tool for plastic debris in soil in order to further elucidate if agricultural soils are a potential sink for plastic debris.

4

SELECTIVE QUANTIFICATION OF PE, PP, AND PS PLASTIC DEBRIS IN SOIL BY PY-GC/MS

Abstract The lack of adequate analytical methods for the quantification of plastic debris in soil challenges a better understanding of their occurrence and fate in the terrestrial environment. With this proof-of-principle study, we developed a simple and fast method for the selective quantification of the three most environmentally relevant polymers PE, PP, and PS in soil using Py-GC/MS. In order to facilitate the preparation of calibration series and to better account for the heterogeneity of the soil matrix, polymers were dissolved in TCB at 120 °C. Thereby, liquid sample aliquots from up to 4 g of solid sample became amenable to pyrolysis without further pretreatment. To evaluate the performance of this approach, three reference soils with 1.73–5.16% C_{org} were spiked at 50 and 250 mg kg⁻¹ of each polymer and extracted with TCB. Prior cleanup steps with methanol, flocculation with $KAl(SO_4)_2$, or Fenton digestion were tested for their suitability to reduce potentially interfering C_{org} . Calibration curves responded linearly (adj. $R^2 > 0.996$) with instrumental LODs of 1–86 ng corresponding to estimated method LODs of 1–86 mg kg⁻¹. The measurement repeatability was 3.2–7.2% relative standard deviation (RSD). Recoveries of 70–128% were achieved for plastic contents of 250 mg kg⁻¹ extracted with TCB without prior cleanup from soils with less than 2.5% C_{org} . A higher C_{org} particularly interfered with the quantification of PE. The addition of non-target polymers (PET, PVC, PMMA, and tire wear particles (TWP)) did not interfere with the quantification of the analytes highlighting the selectivity of the method. Further research is needed to determine low plastic contents in soils exceeding 2.5% C_{org} . With 1–3 h processing time per sample, our method has the potential for routine analyses and screening studies of agricultural systems to be complemented with microspectroscopic techniques for additional information on particle shapes and sizes.

This chapter is based on: Steinmetz, Z., Kintzi, A., Muñoz, K., and Schaumann, G. E. (2020a). “A Simple Method for the Selective Quantification of Polyethylene, Polypropylene, and Polystyrene Plastic Debris in Soil by Pyrolysis-Gas Chromatography/Mass Spectrometry”. *Journal of Analytical and Applied Pyrolysis* 147, p. 104803. ISSN: 0165-2370. DOI: [10.1016/j.jaap.2020.104803](https://doi.org/10.1016/j.jaap.2020.104803).

See Parts of this Thesis and Author Contributions, page ix, for details.

4.1 INTRODUCTION

The majority of plastic is produced, used, and disposed of on land, where it probably disintegrates into smaller debris such as microplastics (1 μm to 1 mm respectively 5 mm) or even nanoplastics (<1 μm) (Hartmann et al., 2019; Hurley and Nizzetto, 2018; Wagner and Reemtsma, 2019). Whereas previous research has mainly fo-

cused on studying plastic debris in the aquatic environment, it remains unknown how and in which quantities such particles may distribute in terrestrial systems and particularly in soil. Currently, atmospheric deposition, littering, sewage sludge or biosolid applications, and use of agricultural plastic films are being discussed as potential sources of terrestrial plastic pollution, with PE, PP, PS, and PET as the most relevant polymers of interest (Hurley and Nizzetto, 2018; Wang et al., 2019).

Developing a better understanding of the occurrence and fate of plastic debris in the terrestrial environment requires reliable, quantitative analytical methods for complex environmental matrices (Bläsing and Amelung, 2018; He et al., 2018; da Costa et al., 2018). So far, most studies have relied on optical detection by FTIR or Raman microspectroscopy (Renner et al., 2018). Both techniques require an extensive sample preparation to separate the plastic particles from sample matrix without losing the polymer analyte (Hurley et al., 2018). When analyzing more complex matrices such as soil or organic wastes, the sample preparation may easily take days or weeks (Löder et al., 2017). In addition, particle identification becomes prone to false positive detections, for example, by mistaking natural fibers or sand grains for plastic debris (Bläsing and Amelung, 2018). While this complicates a reliable quantification, microspectroscopic techniques provide valuable information about particle shapes and sizes. Scheurer and Bigalke (2018) were the first who successfully developed and applied a method for the quantification of plastic debris in soil using a combination of density separation and oxidative matrix digestion followed by FTIR microspectroscopy. With their procedure, the authors obtained recoveries of 93–98% and found a plastic content averaging 5 mg kg^{-1} in Swiss floodplain soil. However, plastic contents were estimated from particle counts ($0\text{--}600 \text{ particles kg}^{-1}$), sizes, and densities without stating LODs or LOQs. Similarly, Piehl et al. (2018) screened agricultural soil for plastic debris and found $0.3 \pm 0.4 \text{ particles kg}^{-1}$, but neglected debris smaller than 1 mm due to the challenging sample preparation.

In such cases, thermoanalytical techniques such as TGA/MS (Chapter 3; David et al., 2019), Py-GC/MS (Fischer and Scholz-Böttcher, 2017; Fischer and Scholz-Böttcher, 2019), or combinations of TGA with GC/MS namely TED-GC/MS (Dümichen et al., 2015; Duemichen et al., 2019) may demonstrate their inherent benefits. All these methods are based on thermal decomposition of polymer mixtures at temperatures $>500 \text{ }^\circ\text{C}$ and their quantification via characteristic indicator pyrolysates. Currently, instrumental LODs range from 3 to 200 ng for PS (Fischer and Scholz-Böttcher, 2019; Duemichen et al., 2019) and up to 0.5–50 μg for PE, PP, and PET (Chapter 3; Duemichen et al., 2019). In contrast to microspectroscopic methods, thermoanalytical techniques are assumed to be more robust against impurities from the sample matrix. Yet, interferences may occur when pyrolysis products in plastic and matrix are identical. In addition, thermoanalytical measurements are typically restricted to sample amounts $<100 \text{ mg}$, which puts high, hardly attainable requirements on sample homogeneity.

These challenges may be overcome by combining an adequate sample preparation with the selectivity of Py-GC/MS analyses. Therefore, we developed and validated a new Py-GC/MS method for the quantification of PE, PP, and PS by using TCB as a solvent both for the preparation of readily measurable polymer standards and for the extraction of plastic debris from different soil types. TCB is a typical eluent for SEC of polymers (Bivens, 2016) and has been assessed for quantitative ^1H nuclear magnetic resonance spectroscopy (^1H NMR) of polymers

(Peez et al., 2019b). Recently, Dierkes et al. (2019) took a comparable approach by extracting PE, PP, and PS with THF from various solid matrices using accelerated solvent extraction (ASE). Although the polymers needed to be reprecipitated in silica gel and could not be analyzed directly via Py-GC/MS. Unlike THF, TCB is not classified as teratogenic and has a more than 100-fold lower vapor pressure according to the respective material and safety data sheets. This makes TCB easy to handle in batch extraction setups. Moreover, sample preparation and extraction can be carried out in a single tube which reduces the contamination potential and facilitates scalability for routine analyses.

4.2 MATERIAL AND METHODS

4.2.1 PREPARATION OF POLYMER STANDARDS

The polymers used in this study were PE beads of 500 μm average particle size^[1], isotactic PP pellets^[2], and PS particles with an average particle size of 250 μm ^[3]. The PP pellets were ground using a commercially available coffee mill with stainless steel lining^[4] to pass a 1000 μm sieve. All polymer standards were prepared in TCB^[5] containing 0.015% butylated hydroxytoluene^[6] as antioxidant (Bivens, 2016). To this end, 50 mg of PE, PP, and PS were weighed individually and as an equal mixture of all three polymers into glass culture tubes^[7]. The tubes were equipped with a polybutylene terephthalate screw cap and a PTFE-coated sealing^[8]. The plastic particles were mixed with 5 mL of TCB and heated to 120 °C for 30 min to facilitate dissolution. After having cooled down to room temperature, the polymers formed a sol-like phase within the TCB that could easily be dispersed upon manual agitation before diluting the polymer standards. Dilution series of 5, 10, 20, 50, 100, and 150 $\mu\text{g mL}^{-1}$ were prepared using 10–100 μL positive displacement pipettes with glass capillaries^[9] and 2–5 mL volumetric glass flasks. Standard solutions were kept in 2 mL ND9 glass vials with PTFE-sealed caps.

4.2.2 EXTRACTION OF PLASTIC DEBRIS FROM SOIL

For the recovery experiment, three soils with different textures and C_{org} contents were selected (Table 4.1). RefeSol 06-A^[10] and LUFA 2.2^[11] as used in Chapter 3 served as reference soils from organically managed arable areas. In addition, a pristine forest soil was taken from a continuous observation site in Wallmerod (WR)^[12] (Meyer et al., 2018). None of the suppliers provided information on polymer background levels.

In order to assess the efficacy of TCB for extracting PE, PP, and PS from different soil types, soil triplicates of 4 g were weighed into glass culture tubes and spiked with 0.2 and 1.0 mg PE, PP, and PS using a microscale^[13]. With that, a nominal content of 50 and 250 mg kg^{-1} of each polymer was obtained. Soil without any plastic supplement served as control. One batch of LUFA 2.2 soil was further spiked with 0.2 mg of plastics not targeted in our analysis to evaluate whether

^[1] CAS 9002-88-4, Alfa Aesar, Kandel, Germany.

^[2] CAS 9003-07-0, Aldrich Chemistry, Taufkirchen, Germany.

^[3] CAS 9003-53-6, Goodfellow, Huntingdon, UK.

^[4] Cloer 7580, Arnsberg, Germany.

^[5] CAS 120-82-1, 99% purity, Alfa Aesar, Kandel, Germany.

^[6] CAS 128-37-0, $\geq 99\%$ purity, Merck, Darmstadt, Germany.

^[7] 16 \times 100 mm^2 , GL18, VWR, Darmstadt Germany.

^[8] Carl Roth, Karlsruhe, Germany.

^[9] Transferpettor micro, Brand, Wertheim, Germany.

^[10] Fraunhofer IME, Schmallenberg, Germany.

^[11] Landwirtschaftliche Untersuchungs- und Forschungsanstalt, Speyer, Germany.

^[12] Landesamt für Geologie und Bergbau, Rhineland-Palatinate, Germany.

^[13] Sartorius SE 02-OCE, Göttingen, Germany.

Soil	Texture	Clay [%]	Silt [%]	Sand [%]	pH	C_{org} [%]
RefeSol 06-A	Silty clay	47.2	41.3	11.5	7.39	2.5
LUFA 2.2	Loamy sand	8.6	15.7	75.7	5.6	1.73
WR	Clayey silt	25.0	70.0	5.0	5.0	5.16

Table 4.1: Overview of physicochemical soil properties.

^[14] PETKA CZ, Brno, Czech Republic.

^[15] Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany.

^[16] Aldrich Chemistry, Taufkirchen, Germany.

^[17] Bundesanstalt für Straßenwesen, Bergisch Gladbach, Germany.

^[18] CAS 67-56-1, 99.9%, Carl Roth, Karlsruhe, Germany.

^[19] CAS 7782-63-0, 20 g L⁻¹, pH 2, Carl Roth, Karlsruhe, Germany.

^[20] CAS 7722-84-1, 30%, Carl Roth, Karlsruhe, Germany.

^[21] CAS 7784-24-9, ≥98%, Carl Roth, Karlsruhe, Germany.

^[22] CDS Analytical, Oxford, US.

^[23] Thermo Fisher Scientific, Bremen, Germany.

^[24] Whatman QM-A, Kent, UK.

^[25] Miltex, Rietheim-Weilheim, Germany.

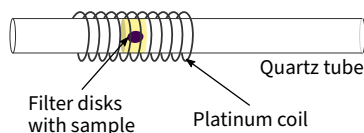


Figure 4.1: Schematic of a pyrolyzer quartz tube equipped with filter disks to absorb the liquid sample.

^[26] Hamilton 1701 N with 26s gauge, Bonaduz, Switzerland.

their pyrolysates interfere with PE, PP, and PS extraction and quantification. This non-target plastic mixture consisted of 19% PET from recycled bottles^[14], 11% PMMA ground from a commercial plexiglass^[15], 41% PVC^[16], and 29% TWP from a test rig^[17]. Content and composition of the non-target polymers were based on findings by Piehl et al. (2018) to reflect realistic conditions in agricultural soil.

Since natural soil polymers may also interfere with plastic quantification, additional sample cleanup procedures were tested for WR soil with a C_{org} of 5.16%. The selected cleanup procedures were intended to be fast (<2 h processing time for a 12-sample batch), easily scalable and reproducible, robust against external contamination, and compatible with the subsequent dissolution of polymers in TCB. To this end, soil C_{org} was either preextracted with methanol, oxidatively digested using Fenton reagent, or flocculated with $\text{KAl}(\text{SO}_4)_2$ prior to TCB extraction. The methanol cleanup was simplified from Fuller and Gautam (2016). In brief, spiked soils were topped off with 8 mL methanol^[18] and agitated for 60 min in a horizontal shaker at 150 rpm. Afterwards, the extracts were centrifuged at 1500 rcf for 15 min and the supernatant was discarded. The remaining methanol was evaporated at 60 °C under a gentle N_2 stream. The Fenton digestion was performed by adding 10 mL of aqueous $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ solution^[19] and 10 mL of H_2O_2 ^[20] to the spiked soil in accordance with Hurley et al. (2018). The reaction mixture was left for 60 min in an ice bath before slowly heating it to 60 °C to dry the sample and decompose remaining H_2O_2 . Humic substances were flocculated by mixing 4 mL of a 500 mg L⁻¹ aqueous $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ solution^[21] with the soil (Mandalakis et al., 2018). The mixture was shaken for 60 min at 150 rpm and evaporated under N_2 at 105 °C.

Finally, all soil samples were extracted with 8 mL TCB at 120 °C for 60 min. After having cooled down, the extracts were allowed to sediment before transferring the supernatant into ND9 vials using glass Pasteur pipettes. Procedural blanks and control soil without any plastic added followed all extraction steps to quantify a potential contamination.

4.2.3 PY-GC/MS ANALYSIS

Instrumental analyses were performed using a Pyroprobe 6150 filament pyrolyzer^[22] coupled with a Trace GC Ultra with DSQII MS^[23]. The pyrolyzer probe consists of a resistively heated platinum coil that holds an open ended quartz tube. The quartz tubes were filled with two quartz filter disks punched out of a high-purity microfiber filter^[24] using a 2 mm biopsy punch with plunger^[25]. The filter disks were positioned inside the quartz tube so that they align with the center of the platinum coil when placed into the pyrolyzer probe (Figure 4.1).

Prior to Py-GC/MS analysis, a sample aliquot of 2 μL was applied onto the filter disk inside the quartz tube using a gastight 10 μL syringe with PTFE plunger^[26]. The quartz tube was transferred into the pyrolyzer using stainless steel tweezers to avoid any contamination, for instance, from nitrile or latex gloves. The pyrolyzer interface was held at 300 °C and continuously flushed with 20 mL min⁻¹ He to evaporate remaining TCB (boiling point: 213 °C) and volatiles on-line while remaining below PE, PP, and PS degradation onsets of 310–350 °C (David et al., 2019). After 3 min, the sample was flash pyrolyzed (10 K ms⁻¹) at 750 °C for 15 s. The pyrolysis temperature was chosen following the manufacturer's recom-

mentation to overcome the heat resistance of the pyrolyzer quartz tube ensuring complete thermal degradation of the polymers. The pyrolysates were transferred to the GC/MS system via a passivated transfer line (350 °C). The split/splitless injector was operated at 300 °C with a split ratio of 1:10. The pyrolysates were separated on a 30 m × 0.25 mm capillary column (5% phenyl-arylene, 95% dimethylpolysiloxane, 0.25 μm film thickness)^[27] connected to a 2 m deactivated fused silica guard column^[28]. The He carrier gas flow was set at 1.3 mL min⁻¹. The gas chromatograph oven was programmed from 40 °C (2 min hold) to 300 °C at 8 K min⁻¹ (50 min run time). The transfer line connecting the gas chromatograph with the MS was kept at 280 °C, and the MS ion source (electron ionization, 70 eV) was heated to 230 °C. The fore pressure of the MS was checked to be <0.07 mbar. The background intensity of 28 *m/z* (atmospheric N₂) was supposed to be <5·10⁷ and the total ion current <10⁸. Values exceeding these criteria indicated a leak in the system.

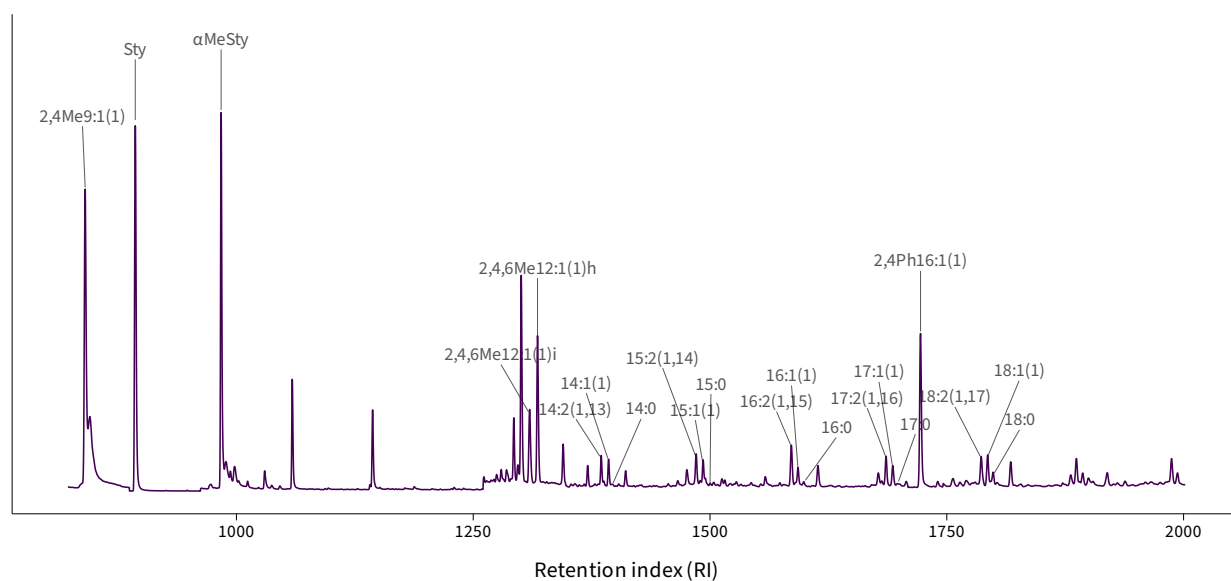
^[27] ZB-5MS, Phenomenex, Aschaffenburg, Germany.

^[28] Phenomenex, Aschaffenburg, Germany.

4.2.4 PYROLYSATE IDENTIFICATION AND CALIBRATION

Pyrolysates were first screened in scan mode (50–300 *m/z*) before switching to selected ion monitoring of specific *m/z* ratios (100 ms dwell time) as indicated in Figure 4.2 and Table 4.2 and reported in previous research (Tsuge et al., 2011; Fischer and Scholz-Böttcher, 2017; Dümichen et al., 2015). Total ion current pyrograms were evaluated using OpenChrom, version 1.4.0^[29] (Wenig, 2011) with the NIST08 database for peak identification. The identified pyrolysates (Table 4.2) were abbreviated based on a modified “lipid number” notation in the form of bC:D(p₁, p₂, ..., p_{D/2}), in which C is the total number of carbon atoms of the compound, D denotes the number of double bonds, and their respective position *p* is given in parentheses (Zelles, 1999). The prefix *b* specifies additional functional groups and their position in the carbon backbone, for example, 2Me for a methyl group or 2Ph for a phenyl moiety at the second carbon atom.

^[29] Lablicate, Hamburg, Germany.



The peaks were automatically integrated from the valley between the peaks to the horizontal baseline using a sliding window size of 3 scans and a minimum SNR

Figure 4.2: Sample pyrogram of a polymer mixture containing each 150 mg kg⁻¹ PE, PP, and PS. Sty is not at scale. See Table 4.2 for details.

Polymer	Pyrolysate	Full name	CAS	RI	<i>m/z</i>	
PE	14:2(1,13)	1,13-Tetradecadiene	021964-49-8	1385	82, 95	
	14:1(1)	1-Tetradecene	001120-36-1	1392	55, 69, 83 [‡]	
	14:0	Tetradecane	000629-59-4	1400	55, 69, 83 [‡]	
	15:2(1,14)	1,14-Pentadecadiene	021964-50-1	1485	82, 95	
	15:1(1)	1-Pentadecene	013360-61-7	1493	55, 69, 83 [‡]	
	15:0	Pentadecane	000629-62-9	1500	55, 69, 83 [‡]	
	16:2(1,15)	1,15-Hexadecadiene	021964-51-2	1585	82, 95	
	16:1(1)	1-Hexadecene	113032-42-1	1593	55, 69, 83 [‡]	
	16:0	Hexadecane	000544-76-3	1600	55, 69, 83 [‡]	
	17:2(1,16)	1,16-Heptadecadiene	021964-52-3	1686	82, 95	
	17:1(1)	1-Heptadecene	006765-39-5	1693	55, 69, 83 [‡]	
	17:0	Heptadecane	000629-78-7	1700	55, 69, 83 [‡]	
	18:2(1,17)	1,17-Octadecadiene	013560-93-5	1787	82, 95	
	18:1(1)	1-Octadecene	000112-88-9	1793	55, 69, 83 [‡]	
	18:0	Octadecane	000593-45-3	1800	55, 69, 83 [‡]	
	PP	2,4Me9:1(1)	2,4-Dimethyl-1-heptene	19549-87-2	841	70, 126
		2,4,6Me12:1(1)i	2,4,6-Trimethyl-1-nonene (isotactic)	55771-40-9	1307	69, 111
		2,4,6Me12:1(1)h	2,4,6-Trimethyl-1-nonene (heterotactic)	55771-40-9	1316	69, 111
PS	Sty	Styrene	100-42-5	895	78, 104	
	αMeSty	α-Methylstyrene	98-83-9	981	103, 118	
	2,4Ph16:1(1)	2,4-Diphenyl-1-butene	16606-47-6	1721	91, 208	
	2,4,6Ph24:1(1)	2,4,6-Triphenyl-1-hexene	18964-53-9	2438	91, 207	

RI = retention index; [‡] used for screening only.

Table 4.2: PE, PP, and PS pyrolysates analyzed for Py-GC/MS method development.

of 7. Calibration series of 5–150 $\mu\text{g mL}^{-1}$ mixed PE, PP, and PS standards were pyrolyzed together with 3–5 blanks (0 $\mu\text{g mL}^{-1}$ in TCB). LODs and LOQs were calculated using Equations 3.1 and 3.2 as described in Chapter 3. Instrumental LODs were calculated by multiplication of the respective LODs with the injection volume of 2 μL . Method LODs were estimated by dividing LODs by the extracted soil mass (4 g) and multiplying it with the extraction volume of 8 mL.

4.2.5 METHOD VALIDATION

At the beginning of each week, a fresh calibration series was prepared. Sample measurements of the following days were bracketed with 100 $\mu\text{g mL}^{-1}$ standards to correct for inter-day variations in peak intensities. Corrected peak areas were then used for quantification.

In line with IUPAC recommendations (Currie, 1995), the intra-day repeatability of the Py-GC/MS method was verified by measuring a sequence of 150 $\mu\text{g mL}^{-1}$ standards ($n = 10$) and determining RSDs of peak areas. A linear model was fitted to the data to check if the peak areas changed significantly during the day. Inter-day variability was estimated from two 150 $\mu\text{g mL}^{-1}$ standard samples repeatedly measured for 8 days.

In order to test whether PE, PP, and PS selectively decompose into their respective pyrolysates without interfering with each other, successive measurements of 150 $\mu\text{g mL}^{-1}$ mixed polymer standards were compared with standards containing each individual polymer. Furthermore, potential interferences from soil matrix and non-target plastics (PET, PMMA, PVC, and TWP) were assessed. Differences in peak areas of pyrolysates were statistically evaluated using analyses of variance with Bonferroni-adjusted Tukey tests for post-hoc multiple comparisons. Analyses of variance were checked for normality and homoscedasticity of residuals using quantile–quantile and residual vs. fitted plots. The same statistical tools were applied to compare the various extraction and cleanup methods for PE, PP, and PS from different soil types with one another. Data analysis was performed using

R statistical software (version 3.6.1)^[30]. Results are given as mean \pm SD.

^[30] All data and R code to reproduce data processing and statistical tests are publicly available at DOI: [10.6084/m9.figshare.11861664](https://doi.org/10.6084/m9.figshare.11861664).

4.3 RESULTS AND DISCUSSION

4.3.1 POLYMER QUANTIFICATION

From the initial screening set of 22 pyrolysates (Table 4.2), six compounds performed best in terms of linearity (adj. $R^2 > 0.996$) within the calibration range, LODs, and LOQs (Figure 4.3 and Table 4.3). LODs were below the lowest standard of $5 \mu\text{g mL}^{-1}$ for the PE n-alkadienes 15:2(1,14) and 17:2(1,16) detected via 82 and 95 m/z . 18:2(1,17) produced an LOD of $11.3 \mu\text{g mL}^{-1}$. The LOQs ranged between 25 and $54 \mu\text{g mL}^{-1}$. For PP, only 2,4Me9:1(1) was quantifiable (70 and 126 m/z) with an LOD and LOQ of 43.2 and $46.7 \mu\text{g mL}^{-1}$, respectively. Sty and αMeSty were the most indicative pyrolysates for PS and detected via 78 and 104 m/z and 103 and 118 m/z , respectively. Their adj. R^2 s, LODs, and LOQs were similar to PE pyrolysates.

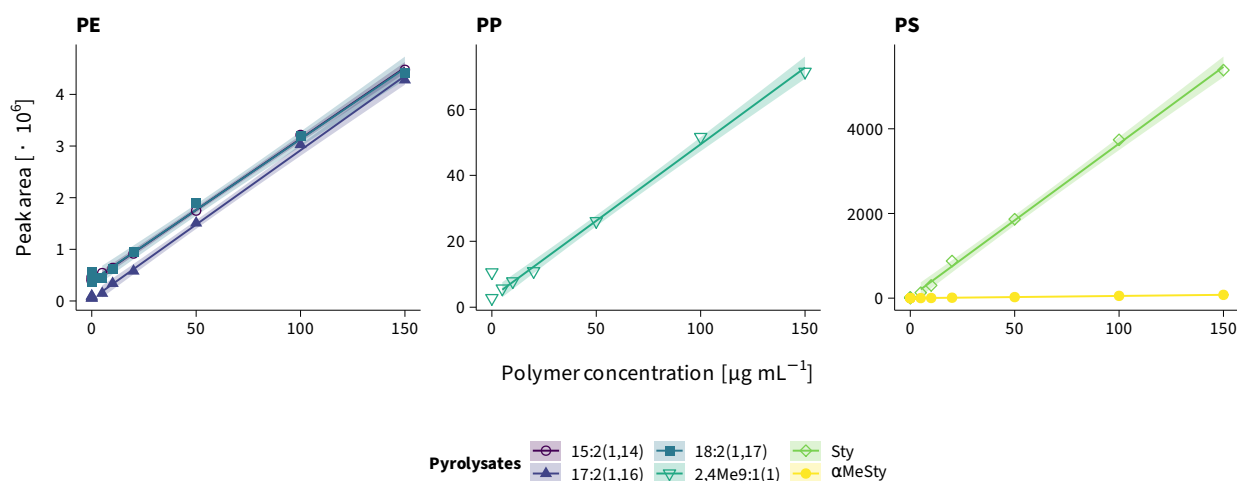


Figure 4.3: Py-GC/MS calibration curves of PE, PP, and PS standards in TCB; see Table 4.3 for parameters.

Taking into account the $2 \mu\text{L}$ injection volume, instrumental LODs were 1–86 ng. This is at least 2.5 times lower than most recent advances in PE, PP, and PS method developments with TED-GC/MS and microfurnace Py-GC/MS (Duemichen et al., 2019; Fischer and Scholz-Böttcher, 2019; Dierkes et al., 2019). Note that Dierkes et al. (2019) reported LOQs calculated from blanks, which is usually defined as LOD (Equation 3.1). While Duemichen et al. (2019) and Dierkes et al. (2019) used the same indicator pyrolysates for quantification as we did but on different m/z ratios, Fischer and Scholz-Böttcher (2019) chose n-alkanes, n-alkenes, and the PS trimer 2,4,6Ph24:1(1).

Polymer	Pyrolysate	Intercept	Slope	adj. R^2	LOD [$\mu\text{g mL}^{-1}$]	LOQ [$\mu\text{g mL}^{-1}$]
PE	15:2(1,14)	384 440	27 563	0.9992	4.8	25.7
	17:2(1,16)	40 501	28 782	0.9980	2.5	38.6
	18:2(1,17)	391 786	27 423	0.9962	11.3	53.4
PP	2,4Me9:1(1)	2 987 986	464 559	0.9971	43.2	46.7
PS	Sty	26 306 594	36 246 576	0.9975	0.5	43.3
	αMeSty	-860 185	527 700	0.9986	1.6	33.1

Table 4.3: Py-GC/MS calibration parameters of pyrolysates selected for quantification.

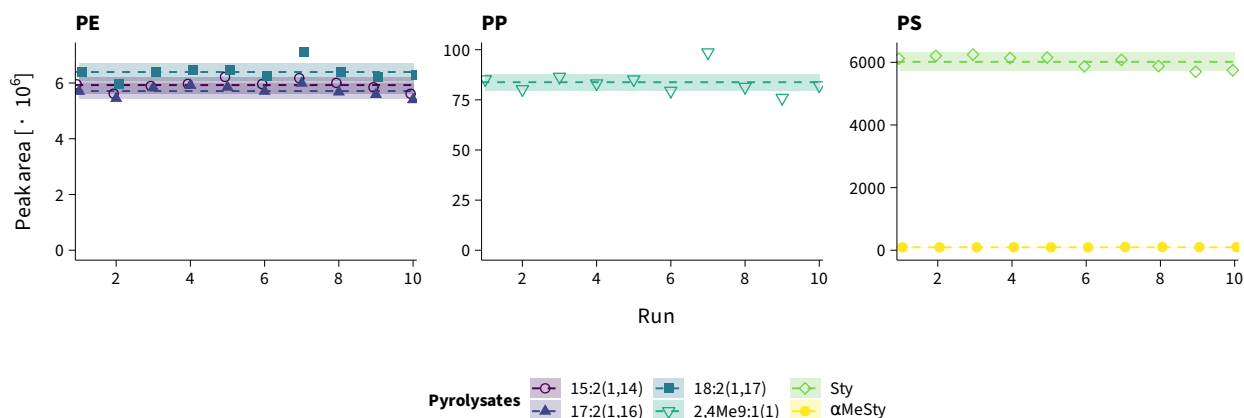


Figure 4.4: Repeatability of Py-GC/MS measurements ($n = 10$) with means (dashed lines) and $\pm 5\%$ RSD bands.

All these studies have in common that they relied on a very sensitive microscale to weigh several nanograms of solid polymer directly into pyrolyzer sample cups or to quantitatively transfer a representative aliquot of solid mixture. To facilitate the heat transfer of the pyrolyzer filament or microfurnace into the sample, the lowest sample amount possible is typically aimed for. However, the lower the amount to be weighed, the higher the relative weighing error becomes and the more challenging it is to obtain a homogeneous mixture. So far, this has been one of the major drawbacks of Py-GC/MS (Fischer and Scholz-Böttcher, 2019). When combining Py-GC/MS with prior dissolution of polymers in an appropriate solvent such as TCB, stock solutions can be easily handled, quantitatively diluted or preconcentrated, and transferred directly into the pyrolyzer quartz tubes. Dissolution in TCB therefore allows for constantly pyrolyzing the same but low amount of sample. Absorbing the TCB solution into the quartz filter disks inside the quartz tube further ensures the optimal alignment of the sample with the pyrolyzer filament and thereby enabling more accurate and reproducible pyrolyses down to the nanogram range. Trying to further improve LODs and LOQs by increasing sample injection volumes could therefore be at the expense of measurement accuracy.

4.3.2 REPEATABILITY

The RSDs of PE indicator pyrolysates were 3.4–4.5% without showing any trend of systematically increasing or decreasing peak intensities during a one-day series of $n = 10$ standard measurements (Figure 4.4, $p > 0.529$, linear model); this is intra-day variability. By contrast, inter-day variability was 15.2–17.9%. The PP pyrolysate 2,4Me9:1(1) produced a stable ($p = 0.728$, linear model) intra-day RSD of 7.2%, and an inter-day RSD of 10.4%. With 3.2 and 4.2% of intra-day variability, the RSDs of PS pyrolysates Sty and α MeSty were in the same range as PE. However, Sty showed a statistically significant tendency to decrease in signal intensity by 0.88% per measurement ($p = 0.002$, linear model), while α MeSty increased by 1.05% ($p = 0.020$, linear model). With respect to the RSDs of the measurement series, these changes are deemed negligible if peak intensities are corrected with bracketing standards measured in the beginning and at the end of each day. This also applies to the inter-day variabilities of Sty and α MeSty which were 13.9 and 16.5%.

Measurement repeatability was in line with comparable studies. PS analysis

via LC/MS with an atmospheric pressure photoionization source, for instance, resulted in an intra- and inter-day repeatability of 1.8–2.4% and 15.5–25.6%, respectively ($n = 5$) (Schirinzi et al., 2019). With TED-GC/MS, Duemichen et al. (2019) achieved RSDs ranging from 6 to 12% for various PP pyrolysates. The authors suggested using an internal standard to further optimize RSDs. Fischer and Scholz-Böttcher (2019) used androstane, deuterated anthracene, 9-dodecyl-1,2,3,4,5,6,7,8-octahydro anthracene, and cholanic acid for internal standardization of PE, PET, polycaprolactam, and PS. Since those internal standards are not polymers, they probably behave differently than the polymer analytes when heated to typical pyrolysis temperatures of 600–800 °C. Particularly polycyclic aromatic hydrocarbons such as anthracene are thermally stable and more likely to evaporate instead of thermally decomposing along with the polymer analytes. Accordingly, Fischer and Scholz-Böttcher (2019) reported that the deuterated anthracene might have interacted with the inner surface of the pyrolyzer which eventually decreased repeatability. Though expensive, deuterated plastics (Dierkes et al., 2019) or specialized polymers like poly(3,4-ethylenedioxythiophene) typically used in semiconductor industry could be promising alternatives since they decompose in the same temperature range as the polymer analytes (Jin et al., 2013). The use of an appropriate internal standards for routine Py-GC/MS analyses will be evaluated in future studies (Chapter 6).

4.3.3 SELECTIVITY OF INDICATOR PYROLYSATES

PE pyrolyzes into *n*-alkanes, *n*-alkenes, and *n*-alkadienes of decreasing chain length (Figure 4.2). In the pyrogram sections given in Figure 4.5, the first peaks of these triplets are the *n*-alkadienes used for quantification (retention indices (RIs) = 1486, 1686, and 1786, Table 4.2) followed by their respective *n*-alkenes (RIs + 7). Note that the *n*-alkanes (RIs = 1500, 1700, and 1800) were low in intensity due to *m/z* ratios optimized for *n*-alkadienes. Regardless of pyrolyzing a 150 $\mu\text{g mL}^{-1}$ PE standard individually or in a mixture with PP and PS, the *n*-alkadiene peaks aligned accurately with one another, while signals from PP or PS were negligible particularly for 15:2(1,14) and 17:2(1,16). 18:2(1,17) was slightly interfered by PP and PS although this was not statistically significant (Figure 4.6; $p = 1$, Tukey). For 15:2(1,14), however, triplicate measurements of the polymer mixture were on average about 15% lower than pure PE ($p < 0.001$, Tukey). In general, 17:2(1,16) showed the least interferences with background signals from pure PP and PS being comparable to blank measurements ($p = 1$, Tukey). The PP indicator pyrolysate 2,4Me9:1(1) at RI 841 was about 10% lower in intensity when pure PP was pyrolyzed compared to the polymer mixture ($p = 0.057$, Tukey). This suggests a minor interference from PE that may have originated from the peak shoulder at RI 845 and a slightly higher but statistically insignificant background noise from PE and PS ($p = 1$, Tukey). In comparison to that, Sty and αMeSty from PS pyrolysis were both selective in terms of showing no interference from PE and PP ($p < 0.001$, Tukey). For its lower variation compared to Sty, αMeSty may be favorably used for PS quantification.

To our knowledge, the possibility of polymers analyzed together and interfering with each other by formation of identical or chromatographically inseparable pyrolysates has so far only been described by Fischer and Scholz-Böttcher (2017). However, the authors neither tested potential interferences in their Py-GC/MS

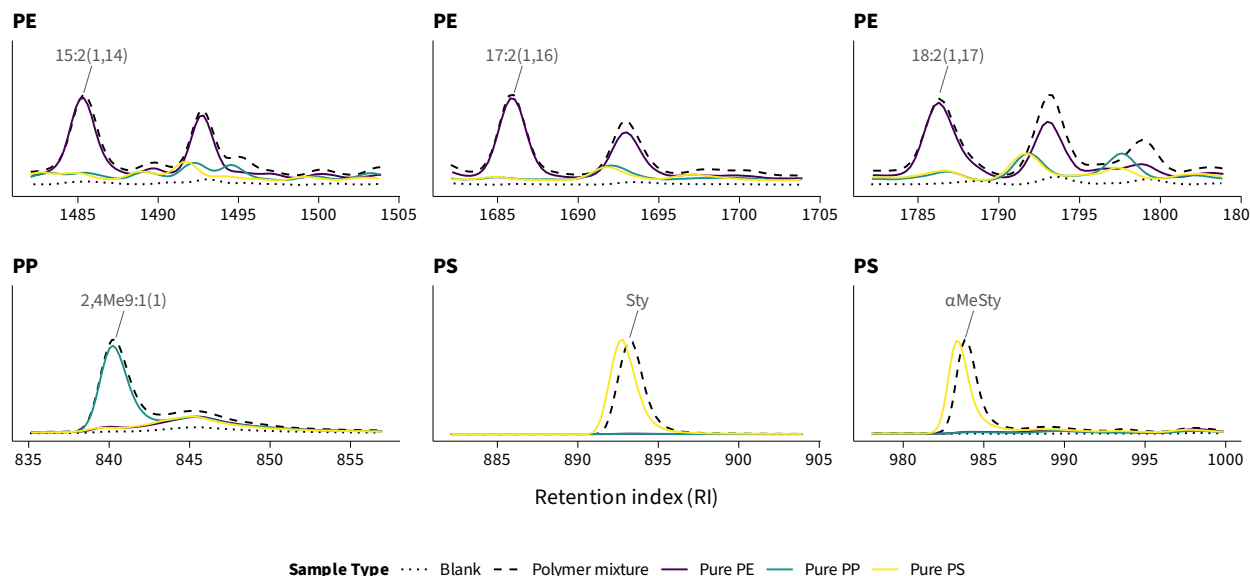


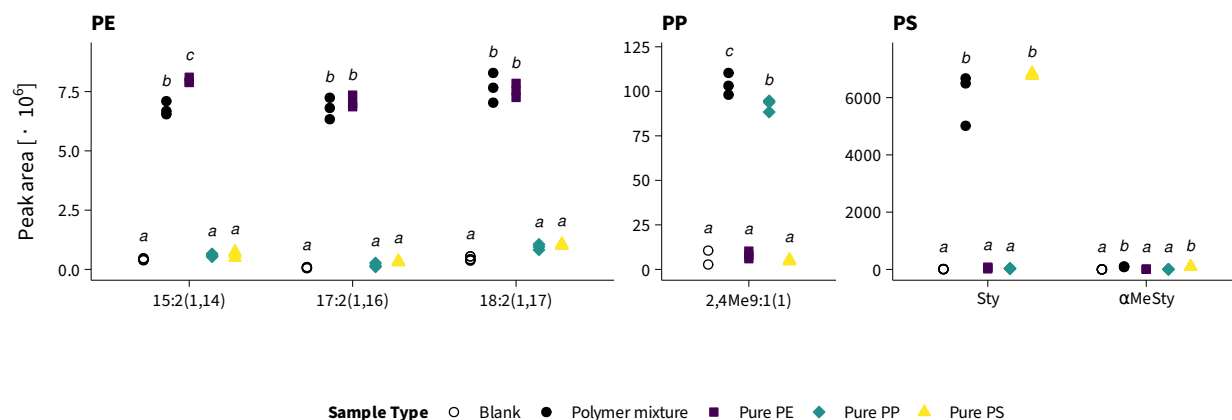
Figure 4.5: Pyrogram sections of PE, PP, and PS pyrolysates obtained by analyzing each individual polymer or a mixture of all three polymers ($150 \mu\text{g mL}^{-1}$).

setup nor suggested a certain approach to counteract them. With our experimental design, we were able to show that PE, PP, and PS can be selectively analyzed in a polymer mixture without interfering with each other by more than 10% at equal concentrations. Especially PP quantified via 2,4Me9:1(1) may be slightly overestimated when PE is present in large quantities. But since the PE pyrolysate 17:2(1,16) was particularly robust against background signals from PP or PS, it would be possible to correct the overestimated PP content for its PE share.

4.3.4 MATRIX INTERFERENCES

Extracting LUFA 2.2 and RefeSol 06-A with TCB, but without adding plastic, resulted in background signals equivalent to 70 ± 10 and $31 \pm 4 \text{ mg kg}^{-1}$ PE, respectively (Table 4.4). Interestingly, addition of the non-target plastics PET, PVC, PMMA, and TWP to LUFA 2.2 soil did not increase matrix interferences. With $700 \pm 200 \text{ mg kg}^{-1}$, the matrix-induced background signal in WR soil was about 10–20 times higher than in LUFA 2.2. For soils with a C_{org} content exceeding 2%,

Figure 4.6: Peak areas of PE, PP, and PS pyrolysates measured individually or in a mixture of all three polymers ($150 \mu\text{g mL}^{-1}$); different letters (in italics) indicate significant differences between sample types for each pyrolysate ($p < 0.05$, Tukey).



namely RefeSol 06-A and WR, a prior cleanup step with methanol doubled PE background levels. Similarly, Fenton digestion of WR soil resulted in matrix interferences equivalent to $1000 \pm 200 \text{ mg kg}^{-1}$ PE. Only flocculation with $\text{KAl}(\text{SO}_4)_2$ considerably reduced background levels to $400 \pm 200 \text{ mg kg}^{-1}$. Regardless of the extraction method and pretreatment, procedural blanks were below the estimated method LODs of 5 mg kg^{-1} . The PP background extracted with TCB was not detectable except for WR soil ($100 \pm 100 \text{ mg kg}^{-1}$). Similar to PE, PP levels doubled when applying a prior methanol cleanup step. However, $\text{KAl}(\text{SO}_4)_2$ flocculation and Fenton digestion were able to reduce matrix interferences below the LOD. PS background levels in LUFA 2.2 soil were below the method LOD of 3.2 mg kg^{-1} . In line with PE and PP, PS contents slightly increased with the C_{org} content of the soil. With respect to SDs, neither the methanol cleanup nor Fenton digestion changed the matrix-induced background considerably while $\text{KAl}(\text{SO}_4)_2$ decreased matrix interferences to non-detectable levels.

Polymer	Soil	Extraction procedure [mg kg^{-1}]			
		TCB only	Methanol cleanup	$\text{KAl}(\text{SO}_4)_2$ flocculation	Fenton digestion
PE	LUFA 2.2	70 ± 10			
	LUFA 2.2*	70 ± 7			
	RefeSol 06-A	31 ± 4	70 ± 20		
	WR	700 ± 200	1300 ± 100	400 ± 200	1000 ± 200
PP	LUFA 2.2	0 ± 200			
	LUFA 2.2*	0 ± 100			
	RefeSol 06-A	0 ± 0	32 ± 100		
	WR	100 ± 100	200 ± 100	0 ± 0	0 ± 0
PS	LUFA 2.2	2 ± 4			
	LUFA 2.2*	4 ± 3			
	RefeSol 06-A	20 ± 30	1 ± 1		
	WR	7 ± 3	12 ± 4	0 ± 4	8 ± 3

* with 50 mg kg^{-1} non-target polymers (19% PET, 11% PMMA, 41% PVC, and 29% TWP); indicator pyrolysates were 17:2(1,16) for PE, 2,4Me9:1(1) for PP, and α MeSty for PS.

Table 4.4: Matrix interferences of different soil types (mean \pm SD).

The matrix interferences identified in our study were generally comparable to those reported in previous thermoanalytical studies: Dierkes et al. (2019) detected matrix interferences equivalent to 140, 210, and 50 mg kg^{-1} PE in an artificial, inert matrix spiked with 3% of wood, leafs, or humic acids, respectively. The authors applied ASE with methanol and THF prior to Py-GC/MS quantification via 15:2(1,14). Similarly, Fischer and Scholz-Böttcher (2017) found their PE and PS pyrolyses affected by chitin, wood, wool, and cellulose, however, without quantifying potential interferences. For two natural soils with unreported C_{org} , $790\text{--}850 \text{ mg kg}^{-1}$ PE, 40 mg kg^{-1} PP, and $40\text{--}50 \text{ mg kg}^{-1}$ PS were detected (Dierkes et al., 2019). The question whether these levels came from matrix interferences or a contamination with plastic debris remained unresolved. By contrast, Dümichen et al. (2015) applied TED-GC/MS and found that soil matrix with an unspecified C_{org} did not induce any interferences. Since Dümichen et al. (2015) and Dümichen et al. (2017) determined PE in a concentration range approximately three orders of magnitude higher than we did, contrasting findings are most likely attributed to the higher sensitivity of our Py-GC/MS setup. A comparison with existing microspectroscopic methods (Scheurer and Bigalke, 2018; Piehl et al., 2018) remains difficult since results are typically reported as particle counts. Conversions from particle counts and sizes to mass concentrations are error-prone for the high uncertainties associated with the underlying assumptions on particle shapes and density distributions. That being said, background levels from FTIR analyses of

Swiss floodplains were estimated at 0–55 mg kg⁻¹ and averaged 5 mg kg⁻¹, which is 1.2–15 times lower than the matrix interferences identified in our study.

Besides a facilitated sample handling, dissolution of PE, PP, and PS in TCB offers the advantage of restricting the amount of other polymers and interfering matrix being dissolved along with the analytes and transferred into the Py-GC/MS system. Apart from our three target polymers, TCB is recommended as SEC solvent only for poly(ethylene-vinyl acetate), polythiophene, and other polyolefins (Bivens, 2016). In addition, only compounds thermally decomposing between 300 and 750 °C were passed to our GC/MS, which may have further reduced the potential for interferences.

In spite of that, we found particularly high matrix interferences for PE in WR soil, a pristine forest soil with 5.16% C_{org}. The two agricultural soils with <2.5% C_{org} showed considerably lower background signals. This is not surprising since up to 9% of soil C_{org} consists of (CH₂)_n chains of 25–30 units (Hu et al., 2000) as, for example, present in suberins, cutins, or microbial cell membranes. Based on the C_{org} of our reference soils, this fraction could potentially induce interferences equivalent to 1500–4500 mg kg⁻¹ PE. Just by using TCB as an extraction agent, we were able to reduce potential interferences by a factor of 5–20. In comparison with that, prior Fenton digestion or methanol cleanup rather mobilized than removed interfering matrix constituents, for instance by cell lysis, which was indicated by elevated PE background levels from both pretreatments. The differences between both pretreatments may be attributed to the oxidization potential of Fenton reagent that most likely made available but at the same time removed a larger fraction of interfering matrix constituents than methanol. Here, existing ASE applications with three rinsing cycles of 15 mL methanol per 1 g of sample at 100 °C (Fuller and Gautam, 2016; Dierkes et al., 2019) may be superior to our simplified batch setup. But matrix interferences from such extraction setups have not been quantified for organic rich soils yet. Besides that, it cannot be excluded that reference soils may have been contaminated with plastic debris on-site or during packaging and shipping, thereby, mistaking a potential plastic contamination for matrix interferences. This could only be assessed by characterizing SOM fractions from soil databases dating back to times before the introduction of today's consumer plastics. Based on these findings, further efforts should be made to reduce interferences from specific soil constituents, for instance by using an advanced flotation and filtration apparatus, molecular sieves, dispersive solid phase extraction, or on-line transesterification and evaporation of lipid-like substances with BF₃ or trimethylsulfonium hydroxide prior pyrolysis. Moreover, further research will need to test alternative solvent mixtures to extend the applicability of our Py-GC/MS approach to a wider range of polymer types.

4.3.5 PLASTIC RECOVERY FROM SOIL

As outlined above, matrix interferences equivalent to >400 mg kg⁻¹ PE exceeded the spiked polymer content by a factor of 2–4. In those cases, the calculation of matrix-corrected recoveries was not meaningful and data were thus excluded from further examination (Figure 4.7). PE recovered from LUFA 2.2 with TCB only ranged from 80 to 110%. The recoveries were independent of the spiking level, and the addition of non-target polymers did not influence the recovery of PE. For RefeSol 06-A, recoveries with TCB were slightly lower than in LUFA 2.2 (61 and

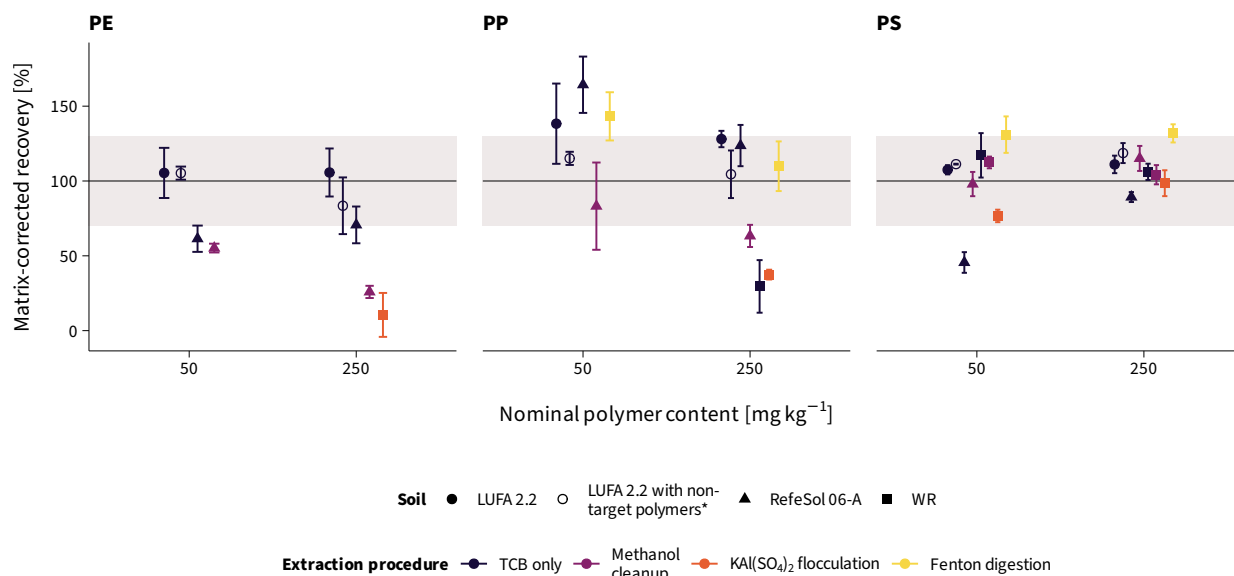


Figure 4.7: Recoveries of PE, PP, and PS from different soil types (mean \pm SD) corrected for matrix interferences (Table 4.4); the gray band marks the 70–130% range acceptable for recovery experiments; * 50 mg kg⁻¹ consisting of 19% PET, 11% PMMA, 41% PVC, and 29% TWP.

70%). The methanol cleanup decreased the recovery to 26 and 55%. Due to the high matrix interferences discussed in Section 4.3.4, PE recoveries from WR soil could only be evaluated for samples flocculated with KAl(SO₄)₂ prior to TCB extraction, and the recovery was very low (10 \pm 10%). Extracting PP from LUFA 2.2 and RefeSol 06-A soil using TCB yielded recoveries of 100–160%. At 50 mg kg⁻¹ spiking level, recoveries were higher and varied more than at 250 mg kg⁻¹. In line with PE, the methanol pretreatment decreased recoveries to 63 and 80%. In WR soil, only 30 \pm 20% of PP were recovered after KAl(SO₄)₂ flocculation. Prior Fenton digestion increased recoveries to 110 and 140%. PS recoveries ranged from 77 to 119%, except for the Fenton digestion of WR soil (130 \pm 10%) and TCB extraction of RefeSol 06-A at the lower spiking level of 50 mg kg⁻¹ (46 \pm 7%).

In summary, TCB extractions without any pretreatment performed best (70–128% recovery), particularly at 250 mg kg⁻¹ spiking level from soils with less than 2.5% C_{org}. PP contents were slightly overestimated due to the aforementioned interference with PE (Section 4.3.3). Although KAl(SO₄)₂ effectively immobilized interfering matrix constituents, it concomitantly reduced PE and PP recoveries. This was potentially due to matrix flocules entrapping plastic debris, hence making it inaccessible to TCB extraction. Similarly, low recoveries resulting from the methanol cleanup were most likely attributed to the discarding of supernatant methanol after rinsing, which probably also removed some plastic debris from the soil. Interestingly, prior Fenton digestion led to elevated recoveries, which contrasts Hurley et al. (2018) who found Fenton reagent performing best in terms of organic matter removal and preservation of plastic particles prior to FTIR imaging. However, our findings are in line with previous thermoanalytical studies that obtained recoveries of 80–130% when extracting PE, PP, and PS with dichloromethane (DCM) and THF from solid matrices after an initial methanol cleanup (Fuller and Gautam, 2016; Dierkes et al., 2019). In contrast to our study, Fuller and Gautam (2016) used about 20–100 times higher spiking levels (5 g kg⁻¹) and Dierkes et al. (2019) extracted 50 and 750 mg kg⁻¹ microplastics from an artificial sample containing 3% humic acids in sea sand. In such an artificial matrix, interferences are

less likely to occur than in natural soil with its large variety of substance classes like natural polymers, lipids, or proteins.

4.4 CONCLUSIONS

Dissolving the three most environmentally relevant polymers PE, PP, and PS in TCB for the direct quantification of liquid sample aliquots via Py-GC/MS facilitated the preparation of calibration curves, simplified and sped up sample handling, reduced the risk of contamination, and allowed for the selective extraction of plastic debris from several grams of solid matrix. The latter enabled us to account for the heterogeneity of soil while minimizing interferences from non-target polymers and soil matrix. Yet, one organic-rich forest soil inflated matrix interferences so that the method currently remains limited to agricultural soil with less than 2.5% C_{org} . Further method development is necessary to reduce such matrix interferences in order to comply, for example, with the EU Decision 2002/657/EC (2002) for residual analysis. Follow-up studies will also need to assess to what extent the solubility of plastic debris in TCB may be affected by the degree of polymer crosslinking, varying molar weights, or changes in particle crystallinity and surface properties that are likely to occur during plastic aging in soil.

Once this is resolved, our new Py-GC/MS method may be applied for routine analyses and screening studies to better understand the occurrence and fate of plastic debris in agricultural systems, for instance, to scrutinize whether agricultural plastic films function as source for plastic debris in soil. After an initial screening, selected hotspots or points of interest could be analyzed by complementary FTIR or Raman microspectroscopy for additional information about particle shapes and sizes.

5

ANALYTICAL TECHNIQUES FOR PLASTIC DEBRIS IN SOIL

Abstract Although most plastic pollution originates on land, current research largely remains focused on aquatic ecosystems. Studies pioneering terrestrial research on plastic debris and microplastics have adapted analytical methods from aquatic research without acknowledging the complex nature of soil. Meanwhile, novel methods have been developed and further refined. However, methodical inconsistencies still challenge a comprehensive understanding of plastic occurrence and fate in and on soil. This chapter aims to disentangle the variety of state-of-the-art sample preparation techniques for heterogeneous solid matrices to identify and discuss best-practice methods for soil-focused polymer analyses. We show that soil sampling, homogenization, and aggregate dispersion are often neglected or incompletely documented. Plastic preconcentration is typically performed by separating inorganic soil constituents with high-density salt solutions. Not yet standardized but currently most used separation setups involve overflowing beakers to retrieve supernatant plastics, although closed-design separation funnels probably reduce the risk of contamination. Fenton reagent may be particularly useful to digest SOM if suspected to interfere with subsequent quantification of plastic debris. A promising new approach is extraction of target polymers with organic solvents. However, insufficiently characterized soils still impede an informed decision on optimal sample preparation. Further research and method development thus requires thorough validation and quality control with well-characterized matrices to enable robust routine analyses for terrestrial plastic debris.

This chapter is based on: Thomas, D., Schütze, B., Heinze, W. M., and Steinmetz, Z. (2020). “Sample Preparation Techniques for the Analysis of Microplastics in Soil—A Review”. *Sustainability* 12.21, p. 9074. ISSN: 2071-1050. DOI: [10.3390/su12219074](https://doi.org/10.3390/su12219074).

See Parts of this Thesis and Author Contributions, page ix, for details.

5.1 INTRODUCTION

A world without plastics seems difficult to imagine given the versatile possibilities for plastics use in all areas of our modern society. Since the advent of plastics mass production in the 1950s, plastics have found their way into everyday consumer products including packaging, mobility, building and construction, and agriculture (Geyer et al., 2017; Kawecki and Nowack, 2019). As a consequence, the global plastic production has increased exponentially from 2 Mt in 1950 to 359 Mt in 2018 (PlasticsEurope, 2019; Geyer et al., 2017). The most produced polymers in terms of market shares are high- and low-density PE (36%), PP (21%), PVC (12%), PET (10%), polyurethane (8%), and PS (8%) (Geyer et al., 2017). Biodegradable plastics like PLA or PBAT have a combined market share of 1.3% (Burgstaller et al.,

2018) but are gaining increasing attention as potential alternatives for conventional polymers.

Current estimates indicate that the extensive use of plastics has already piled up about 5 Gt of plastic waste in the environment, which is equivalent to 60% of all plastic ever produced (Geyer et al., 2017). Thompson (2006) suggested that 10% of the produced plastic is entering the world's oceans leaving an unknown sink of 50%; that is 2.5 Gt. In line with this, plastic release into terrestrial systems has been hypothesized to be 4–23 times higher than that into aquatic systems (Horton et al., 2017). Accumulating plastic debris may adversely affect the soil structure and water dynamics (de Souza Machado et al., 2019; de Souza Machado et al., 2020) as well as the fitness of soil biota including earthworms (Boots et al., 2019), nematodes (Lei et al., 2018), and plants (Rillig et al., 2019; Büks et al., 2020). Nonetheless, only a few attempts have been made so far to better understand the extent of plastic pollution and fate in terrestrial ecosystems for an informed risk assessment. Soil, in particular, has been largely neglected as highlighted by He et al. (2018), who only found 4% of studies published on plastic debris actually focusing on soil. Consequently, terrestrial environments most likely play a key role in the world's plastic problem while remaining largely understudied.

Although scarcely quantified but regularly reviewed, plastics are assumed to enter the terrestrial environment via sewage sludge or biosolid application, use of agricultural plastic films, littering, and atmospheric deposition (Chapter 2; Hurley and Nizzetto, 2018; Wang et al., 2019; Bianco and Passananti, 2020). While plastic items may be distributed and transported by air and water erosion (Bergmann et al., 2019), bioturbation (Huerta Lwanga et al., 2017a; Rillig et al., 2017b), or plowing (van den Berg et al., 2020), they fragment into smaller debris due to physical abrasion, exposure to sunlight, or biological degradation (Briassoulis et al., 2015a; Cai et al., 2018). Plastic fragments are typically categorized by size into macroplastics (>5 mm), large microplastics (1–5 mm), microplastics (1 μm to 1 mm), and nanoplastics ($\leq 1 \mu\text{m}$) (Braun et al., 2018; Hartmann et al., 2019). In addition, primary and secondary plastic can be distinguished in terms of particles being produced as such or resulting from fragmentation, respectively. Further classification criteria address the particles' shape, chemical constitution, and material properties (Hartmann et al., 2019). However, the scientific community has not yet established a consensual definition of polymeric properties despite the urgent need for a unified terminology defining criteria on the size, shape, color, and origin of plastics to facilitate the communication and comparability of data (Hartmann et al., 2019).

The lack of harmonization is moreover immanent in the plethora of current approaches for plastic analysis of soil samples. Whereas Bläsing and Amelung (2018) still concluded that plastic pollution in soil remained virtually unknown due to utterly lacking analytics, most recent reviews (Möller et al., 2020; Dioses-Salinas et al., 2020) outdo each other with new methods and microplastic findings. However, the majority of reported methods was initially developed for aquatic samples and potentially underestimates the complex nature of soil matrix that keeps sample preparation and polymer analysis challenging.

Analyzing soil requires careful consideration of the soil profile, soil type, and soil constituents like soil solutes, silicates, (swellable) clay minerals, and SOM in varying quantities, grain and aggregate sizes, and densities (Blume et al., 2016). SOM is a dynamic, highly heterogeneous mixture of plant- and animal-derived

litter at various stages of decomposition. The labile SOM fraction contains easily degradable molecules like peptides, lipids, and carbohydrates, whereas the more stable fraction consists of more complex, polymeric macromolecules (Bronick and Lal, 2005). Some of these soil constituents are suspected or have already been reported to interfere with polymer analysis so that they need to be removed or at least reduced during sample preparation (Chapter 4; Löder et al., 2017; Fischer and Scholz-Böttcher, 2017). Inorganic fractions such as silicates or clay are often physically removed by density separation, while organic fractions are wetchemically oxidized^[1]. Apart from their purification efficiency, the selected methods further need to preserve the polymer analytes, which becomes particularly relevant for the analysis of nanoplastics or biodegradable polymers^[2]. For both, reliable and quantitative analytical tools are still to be developed (Wang et al., 2018; Wahl et al., 2021).

Previous reviews gave an extensive overview of potential occurrences of plastic debris in terrestrial systems (Hurley and Nizzetto, 2018; Zhu et al., 2019; Dioses-Salinas et al., 2020; Wu et al., 2020a; Meixner et al., 2020) and reflected on the suitability of generic methods for soil plastic analysis (Bläsing and Amelung, 2018; Möller et al., 2020). Our review, in contrast, specifically aims at critically discussing and evaluating current sample preparation techniques for the microplastic analysis of soil. Since soil-specific sample preparation methods are still scarce, we also assessed methods for other solid matrices like sediment or suspended organic matter for their transferability to soil with particular emphasis on their potential applicability and robustness against matrix interferences from various soil constituents.

To this end, we searched Web of Science, CAS SciFinder, Scopus, and Google Scholar literature databases for search terms including “microplastic” or “plastic debris” in conjunction with “soil”, “biosolid”, “sediment”, or “organic matter”. Based on these findings and supplemented with cross references, we selected 229 original research articles, 37 reviews, 15 books or book chapters, and 25 reports, theses, and guidelines for further evaluation. The reviewed preparation steps included soil drying and sieving, dispersion of soil aggregates, density separation, SOM removal, and extraction with organic solvents. Further, we give a brief overview of suitable options for microplastic analysis after soil sample preparation. We conclude with suggestions for best-practice sample preparation techniques and innovative ideas promoting the development of novel, refined methods for a soil-focused microplastic analysis.

5.2 FROM THE FIELD TO THE LAB

5.2.1 SAMPLING STRATEGIES

The selection of an adequate sampling strategy is the most crucial step in environmental analysis. The choice of the sampling approach is determined by the research question and involves considerations of the hypothesized analyte distribution in the field, potential sources, or site geomorphology. As recently reviewed by Möller et al. (2020), common soil sampling strategies in accordance with ISO 18400-102 (2017) are equally applicable to microplastics and include hotspot or suspect sampling, systematic grid or transect sampling (as conducted by Piehl et al., 2018), stratified sampling, and random sampling (Corradini et al., 2019b). The sampling area and sampling procedures are to be documented with field notes and

^[1] See He et al. (2018) for a general introduction to analytical methods for microplastics in soil.

^[2] See Fojt et al. (2020) for a recent review on biodegradable plastics in soil.

photographs. Sampling depths should be defined a priori and reflect the soil profile and management practices like plowing (Sponagel et al., 2005; ISO 18400-102, 2017). For agricultural fields, for instance, the Federal Soil Protection and Contaminated Sites Ordinance of Germany stipulates a minimum sampling depth of 30 cm (BBodSchV, 1999). Yet, the majority of agricultural screening studies for microplastics have so far limited their sampling depth to the topmost 5 cm (Liu et al., 2018; Piehl et al., 2018).

Sampling guidelines by the US Department of Agriculture (Schoeneberger et al., 2012) and the US Environmental Protection Agency (US EPA, 2020) further recommend taking control samples of the same soil type from an area nearby that is not affected by the contaminant of concern. While this may be challenging for microplastics that ubiquitously enter soil via atmospheric deposition (Bergmann et al., 2019), this would offer the advantage of quantifying microplastic background levels, controlling contamination potentially introduced during sampling, or better understanding matrix interferences. The risk of contamination may be reduced by using sampling equipment and containers that are free of plastics (Piehl et al., 2018; Scheurer and Bigalke, 2018). Plastic sledgehammers or nitrile gloves should thus be avoided (Witzig et al., 2020).

The number of samples per site depends on the spatial extent of the investigated area. In order to cover the spatial variation of an exemplary field with 0.05–1 ha, German legislation (BBodSchV, 1999) recommends subdividing each field into at least three subplots. For each subplot, one composite sample consisting of 15–50 subsamples ha^{-1} should be drawn (ISO 18400-102, 2017). While composite sampling has already been adopted by numerous microplastic field studies to increase sample homogeneity and representativity (Ramos et al., 2015; Huerta Lwanga et al., 2017b; Scheurer and Bigalke, 2018), others took single samples only (Piehl et al., 2018; Liu et al., 2018; Corradini et al., 2019b).

Minimal, yet representative sample quantities are typically guided by the soil's largest grain size. In accordance with ISO 17892-4 (2016) and ISO 18400-102 (2017), a sample quantity of at least 500 g is required for a fine soil with particles sizes smaller than 2 mm. This is in line with existing microplastic screening studies of agricultural and floodplain topsoils that involved sample quantities of 300 g to several kilograms per plot (Scheurer and Bigalke, 2018; Liu et al., 2018; Piehl et al., 2018). By contrast, Huerta Lwanga et al. (2017b) only took 50 g of garden soil for the investigation of plastic transfer along a terrestrial food web. Larger sample quantities are generally advisable in order to acknowledge the heterogeneous distribution of discrete microplastic particles in soil. However, sample quantities of several kilograms usually increase both the sampling and analytical effort. Furthermore, removing large quantities of fertile agricultural soil for sampling purposes may be contrary to sustainability efforts and economic interests of farmers and land owners. Here, stochastic particle distribution models (Hammersley, 1972) may help to find optimum, representative sample quantities for a given soil texture and the expected microplastic particle sizes and concentrations.

5.2.2 SOIL CHARACTERIZATION

Methods for the determination of basic soil characteristics like soil texture, bulk density, aggregate stability, pH, redox potential, SOM or organic and inorganic carbon contents, and cation exchange capacity are detailed in several guidelines,

such as ISO 11277 (2020), ISO 11272 (2017), and DIN EN 15935 (2020). For microplastic analysis, knowledge of the SOM content, carbonates, and soil texture is particularly relevant as these parameters may influence sample preparation and subsequent microplastic quantification. For example, Corradini et al. (2019b) related decreasing recovery rates after density separation to elevated SOM contents. In addition, microplastics were recovered at higher rates from sandy soils than from loess or clay (Zhang et al., 2018). However, both studies did not provide information on how soil parameters were obtained. In contrast to Zhang et al. (2018), Scheurer and Bigalke (2018) found no correlation between the soil texture and microplastic concentration in floodplain soil, but it remained unresolved to what extent potential microplastic relocation processes in the field may have masked microplastic recovery after sample preparation. This suggests that the description of sampling sites and soil characteristics needs to be more comprehensive in order to facilitate interstudy comparisons and to identify additional, yet uninvestigated, factors like pH or ionic strength potentially affecting sample preparation.

5.3 SAMPLE PREPARATION

5.3.1 (FREEZE) DRYING

Drying soil prior to analysis is imperative to obtain a comparable, water-free reference for microplastic contents or particle numbers. Independent of the analyte, ISO 11464 (2006) recommends soil drying at 40 °C until weight is constant. Yet, drying conditions and procedures for subsequent microplastic analysis are still contrasting. Whereas van den Berg et al. (2020) adhered to ISO 11464 (2006) and dried the soil at 40 °C for 72 h, Liu et al. (2018) chose 70 °C for 24 h. However, temperatures above 40 °C may affect the polymers' physical and structural properties by glass transition, melting, or degradation. For instance, the glass transition temperatures of polybutylene terephthalate, PMMA, and PA are 40, 50, and 50–75 °C, respectively (Beyler and Hirschler, 2002). Natural rubber and ethylene-vinyl acetate may start melting at temperatures of 30–65 °C (Beyler and Hirschler, 2002). Temperatures of about 60 °C typically initiate degradation of biodegradable polymers like PLA and PBAT (Burgstaller et al., 2018). This is why freeze drying has been recommended as a more gentle alternative (Enders et al., 2020a). On the one hand, freeze drying has been reported to break cell walls and soil aggregates and thereby facilitate further sample preparation (Enders et al., 2020a). On the other hand, temperatures below the glass transition temperature increase polymer brittleness. Frost wedging may further fragment microplastic particles and release additional cellular organic matter. In addition, freeze drying is more time-consuming than oven or air drying and often constrained by the size of the freeze dryer.

5.3.2 HOMOGENIZATION, SIEVING, AND SORTING

Prior to further sample processing, soil is recommended to be adequately homogenized manually or by using automatic sample dividers. Laboratory subsamples and retention samples should be at least 200 g (ISO 11464, 2006). After homogenization, ISO 11464 (2006) further specifies sieving to fine soil ≤ 2 mm (Zubris and Richards, 2005; Zhang et al., 2018). All subsequent soil analyses are performed on fine soil, and analyte contents are based on fine soil as common reference for

interstudy comparisons. This contrasts the common definition of microplastics of ≤ 1 and ≤ 5 mm (Hartmann et al., 2019; Braun et al., 2018). Accordingly, Piehl et al. (2018) sieved soils to 1 and 5 mm. Liu et al. (2018), Huang et al. (2020), and Zhou et al. (2020) included all fractions below 5 mm. In such cases, large microplastics may cover smaller particles and lead to systematic underestimation during spectroscopic analysis. We thus suggest sieving to 1, 2, and 5 mm in compliance with standard mesh sizes of commercially available test sieves. Use of a sieving cascade may reduce the work load. However, it is currently poorly understood how excessive sieving might enhance the fragmentation of particles, in particularly aged, biodegradable, or freeze-dried plastics.

5.3.3 DISPERSION OF SOIL AGGREGATES

As microplastics may be incorporated into soil aggregates and thus not be easily separable from other soil constituents (Zhang et al., 2018), additional preparative steps are required to promote the disintegration of soil aggregates and dispersion of grains. Although specified by ISO 11464 (2006), grinding of soil samples for subsequent microplastic analysis will increase particle fragmentation and may induce melting by frictional heat. A simple alternative is initial shaking of soil samples in a dispersion agent such as aqueous sodium hexametaphosphate solution (Garcés-Ordóñez et al., 2019; Vermaire et al., 2017; Zhou et al., 2020). Additionally, ultrasonication has been applied to soils suspended in deionized water (Zhang and Liu, 2018; Zhang et al., 2018) or in a salt solution prior to density separation (Liu et al., 2018). However, adequate sonication levels strongly depend on the soil type, in particular on the aggregate stability (Cerli et al., 2012), and progressive sonication may increase the amount of light-density SOM potentially interfering with density separation. Moreover, it has not yet been systematically assessed if or to what extent chemical dispersion agents or ultrasonication may cause interferences or enhance microplastic fragmentation, respectively. Further method development is thus needed to scrutinize potential adverse effects on microplastic analysis to transfer established methods from soil science to terrestrial microplastics research.

5.3.4 DENSITY SEPARATION

Separation Principle The most common technique to preconcentrate or isolate microplastics from soil is density separation. Density separation exploits the buoyancy of plastic particles in solutions with a higher density than that of plastics ($\rho = 0.9\text{--}1.6\text{ g cm}^{-3}$), while the soil mineral fraction (for instance silica, $\rho > 2.0\text{ g cm}^{-3}$) remains at the bottom (Enders et al., 2020b; Liu et al., 2020). To date there is no standardized density separation procedure for microplastic extraction from soils. In principle, the soil sample is mixed with a density solution, and floating plastic particles are collected after a certain amount of time. However, studies vary greatly in terms of sample amounts, applied density solutions, and the technical setup.

Density Solutions Various density solutions have already been used for isolating microplastic from soil, including deionized water, NaCl, NaBr, NaI, CaCl₂, ZnCl₂, and sodium heteropolytungstate solutions. Additionally, ethanol, potassium formate, ZnBr₂, sodium tungstate dehydrate, and sodium polytungstate (SPT) solutions have been tested for sediments but not yet for soil (Table 5.1). Apart from density solutions, the applied ratios of soil to density solution vary

Density Solution	Density [g cm ⁻³]	Evaluated Polymer Type(s)	Sample Type	Remarks	Reference
Ethanol (96%)	0.8	Light-density SOM	Plant material	Flotation of light-density SOM; no microplastic separation	Herrera et al. (2018)
Deionized water	1.0	PE, PP	Clay soil, loess, and sandy soil	Not suitable for high-density polymers	Zhang et al. (2018)
NaCl	1.2	PE, PP, PS, PA, PC, PMMA, ABS	Farmland soil, marine sediment	Not suitable for high-density polymers	Liu et al. (2018) and Nuelle et al. (2014)
NaBr	1.4–1.6	PE, PP, PS, PET, PVC, PA, PMMA	Agricultural and floodplain soil, sediment		Liu et al. (2019) and Quinn et al. (2017)
CaCl ₂	1.3–1.5	PE, PP, PS, PET, PVC, PC, PA, PU, ABS	Organic-rich topsoil	Ca ²⁺ may cause flocculation of SOM	Scheurer and Bigalke (2018)
Potassium formate	1.5–1.6	PE, PP, PS, PET	Lakeshore sediments	No validation performed	Xiong et al. (2018)
ZnCl ₂	1.5–1.7	PS	Biosolids, soil	Expensive [†] , corrosive, and harmful to the environment, may alter microplastics and cause foaming	Wang et al. (2018)
ZnBr ₂	1.7	PE, PP, PS, PET, PVC, PA	Sediment	Expensive [†] , corrosive, and harmful to the environment	Quinn et al. (2017)
NaI	1.6–1.8	PE, PP, PS, PET, PVC, PA, PU	Agricultural soil, sediment	Expensive [†] , harmful to the environment	Claessens et al. (2013), Quinn et al. (2017), Nuelle et al. (2014), and Huang et al. (2020)
SPT	1.4–1.8	PE, PET, PVC, PA	(Beach) sediment	Expensive [†]	Enders et al. (2020b) and Frère et al. (2017)
Sodium tungstate dihydrate	1.4	PE, PP, PS, PET, PVC, PC, PA, PU, PMMA, EVA	Sediment	Expensive [†]	Frias et al. (2018)

[†] >100 Euros kg⁻¹ (Campanale et al., 2020).

Table 5.1: Density solutions for the separation of plastic debris from solid matrices.

greatly between 1:2 (Chen et al., 2020a) and 1:25 (Zubris and Richards, 2005). While soil-to-solutions ratios are often determined by the sample size and technical setup, they may be decisive for microplastic recovery. However, this has not yet been addressed.

Deionized water ($\rho = 1.0 \text{ g cm}^{-3}$) and saturated NaCl solution ($\rho = 1.2 \text{ g cm}^{-3}$) are suitable for separating low-density polymers like PE, PP, and PS from soil mineral matrices, while being cheap, easily available, and not harmful to the environment (Masura et al., 2015; Zhang et al., 2018; Liu et al., 2018; Zubris and Richards, 2005; Renner et al., 2019). Scheurer and Bigalke (2018) reasoned that Na⁺ may further promote dispersion of soil aggregates, which could increase the extraction efficiency. While low-density microplastics can be specifically targeted using deionized water or NaCl solution, the extraction of denser particles is not possible. This particularly applies to PET ($\rho = 1.3\text{--}1.6 \text{ g cm}^{-3}$) and PVC ($\rho = 1.1\text{--}1.6 \text{ g cm}^{-3}$) (Scheurer and Bigalke, 2018; Van Cauwenberghe et al., 2015).

To this end, saturated CaCl₂ solution ($\rho = 1.3\text{--}1.5 \text{ g cm}^{-3}$) has been proposed due to its low cost (<100 Euros kg⁻¹) and environmental friendliness (Stolte et al., 2015; Scheurer and Bigalke, 2018). However, some unidentified, most likely organic floccules were observed after separation from soil (Scheurer and Bigalke, 2018). The authors suggested that divalent Ca²⁺ caused flocculation of organic substances through ion bridging. Thus, CaCl₂ solutions cannot be recommended for the separation of microplastic in SOM-rich samples.

While NaBr solutions ($\rho = 1.4\text{--}1.6 \text{ g cm}^{-3}$) did not result in significant improvement of microplastic recoveries from sediment (Quinn et al., 2017), Liu et al. (2019) found that NaBr outperformed both NaCl and CaCl₂ at separating various plastic types, sizes, and shapes from a range of different soil samples. One

reason for this discrepancy was probably the difference in the adjusted densities between both studies: Quinn et al. (2017) used 1.4 g cm^{-3} , whereas Liu et al. (2019) prepared a 1.6 g cm^{-3} solution. This raises the often neglected question of how density solutions are prepared and how this affects extraction efficiencies, once more underlining the need for a uniform protocol for the preparation of density solutions.

Potassium formate solutions ($\rho = 1.5\text{--}1.6 \text{ g cm}^{-3}$) were used for separating microplastics from sediments (Stock et al., 2019; Xiong et al., 2018) but have not been tested for soils so far. With regards to its density, it is reasonable to expect incomplete recovery of higher-density polymers. Yet, its environmental friendliness (ECHA, 2020a) would make it a solution worth testing.

A comprehensive comparison of different density solutions in sediment revealed that recovery rates of various microplastic types generally increased with the density of the solutions (Quinn et al., 2017). This trend was independent of the particle size and may therefore equally apply to soil. For denser polymers like PET or PVC, current studies therefore recommend high-density salt solutions such as ZnCl_2 ($\rho = 1.5\text{--}1.7 \text{ g cm}^{-3}$) or NaI ($\rho = 1.6\text{--}1.8 \text{ g cm}^{-3}$) (Mahon et al., 2017; Horton et al., 2017; Zhang et al., 2018). With prices $>100 \text{ Euros kg}^{-1}$ (Campanale et al., 2020), these salt solutions are 4–10 times more expensive than NaCl and both classified as environmentally harmful (ECHA, 2020b; ECHA, 2020c). Moreover, ZnCl_2 is corrosive and may thus degrade microplastics (He et al., 2018). In addition, Zobkov and Esiukova (2017) observed strong foaming when applying ZnCl_2 solution to organic-rich sediments. Although the cause was not further investigated, excessive foaming may be problematic for restricted container volumes and pose difficulties for retrieving the supernatant. By contrast, NaI solution may cause blackening of some filter papers, which may require an additional transfer step to a clean filter (Quinn et al., 2017).

A promising solution is sodium heteropolytungstate ($\rho = 1.5 \text{ g cm}^{-3}$), which was successfully used for separating microfibers from soil and earthworm deparates (Prendergast-Miller et al., 2019). Similar solutions, including sodium tungstate dihydrate ($\rho = 1.4 \text{ g cm}^{-3}$) (Frias et al., 2018) and SPT ($\rho = 1.4\text{--}1.8 \text{ g cm}^{-3}$) (Ballent et al., 2016; Enders et al., 2019; Enders et al., 2020a; Corcoran et al., 2009), were used for sediment samples but have not yet been applied to soil. Enders et al. (2020a) provided a detailed guidance protocol for an entire microplastic ($10 \mu\text{m}$ to 5 mm) extraction pipeline with SPT solution as separation agent. Nevertheless, SPT is costly ($>100 \text{ Euros kg}^{-1}$) (Campanale et al., 2020), and a systematic validation including recovery tests for soil samples is still missing. This impedes comparing the general performance of SPT with more commonly used salt solutions.

In order to maximize separation efficiency and reduce the consumption of higher-density solutions, multiple-step separation procedures have been introduced either by using the same solution several times (Liu et al., 2018; Huang et al., 2020) or by applying lower- and high-density solutions sequentially (Nuelle et al., 2014; Hurley et al., 2018; Corradini et al., 2019b; van den Berg et al., 2020; Dekiff et al., 2014; Zhou et al., 2018). Typically, deionized water (van den Berg et al., 2020; Hurley et al., 2018) or NaCl solution (Nuelle et al., 2014; Dekiff et al., 2014; Zhou et al., 2018; Frère et al., 2017) are used first. In a second step, residues may be subjected to NaI solution to extract high-density polymers. Frère et al. (2017) chose sodium tungstate for sediment samples instead and completely recovered PET, PVC, and PA particles (5 mm). Corradini et al. (2019b) even performed a three-

step density separation for sewage sludge and soil samples with deionized water, NaCl, and ZnCl₂ solution, which increased recovery for all plastics examined, but most significantly for PVC. However, recovery rates were not provided in detail.

Although not examined so far, low-density solutions may be equally valuable for reducing SOM ($\rho < 1.6 \text{ g cm}^{-3}$) (Cerli et al., 2012) in the soil matrix without altering polymers. For example, ethanol (96%, $\rho = 0.8 \text{ g cm}^{-3}$) has been suggested for separating plastics from less dense biological material (Herrera et al., 2018). While such an intermediate treatment step may facilitate and reduce material consumption for further sample preparation, the risk of losing light-density plastics needs to be carefully evaluated. When deciding on several density separation steps, potential tradeoffs between improved separation efficiency and increased risks of contamination or loss of microplastics need to be taken into account.

In general, density solutions have proven their suitability for separating microplastics from the soil matrix. Solutions with higher densities like NaBr, NaI, ZnCl₂, or SPT ($\rho = 1.6\text{--}1.8 \text{ g cm}^{-3}$) extract a wide range of polymers at the expense of potentially co-extracting SOM ($\rho < 1.6 \text{ g cm}^{-3}$) (Cerli et al., 2012) and thus require additional purification. By contrast, lower-density solutions (deionized water, NaCl; $\rho = 1.0\text{--}1.2 \text{ g cm}^{-3}$) may be preferred when targeting specific polymers or for reducing costs, operational effort, or environmental impact. Therefore, the suitability of a specific solution needs to be assessed on a case-by-case basis in accordance with the research question, the soil composition, and polymers of interest.

Recycling of Salt Solutions According to the principles of green chemistry, the quantity, hazardousness, and disposal of chemicals should be reduced as much as possible (Anastas and Eghbali, 2009). Thus, recycling is imperative for expensive solutions and solutions of environmental concern used for density separation. Several recycling attempts have already been described for NaBr, NaI, ZnCl₂, potassium formate, and SPT. Kedzierski et al. (2017) showed that NaI solutions used for density separation of sediments can be recycled up to 10 times by evaporation without decreasing the separation efficiency. Another approach evaluated ZnCl₂ recycling via membrane filtering (0.45 μm) (Rodrigues et al., 2020). Over five filtration cycles, microplastic recovery remained above 95%. Potential changes in density or pH were not reported. Stock et al. (2019) recycled potassium formate by filtering, however, without assessing recoveries. Liu et al. (2019) constructed an automatic flow system that allowed for immediate recycling and continuous use of density solution. This substantially reduced the needed amount of NaBr solution and recovery rates remained >90%. Recycled solutions may be stored either as solution (Liu et al., 2019; Rodrigues et al., 2020) or as extracted salt (Kedzierski et al., 2017). Although most authors reported cost and material reductions, it remains important to note that recycling and storage require additional working time, materials, space, and energy.

Instrumental Setups The simplest technique for density separation is direct mixing of sample and solution by manual shaking or stirring and subsequent settling in an appropriate sample container (Mahon et al., 2017; Dekiff et al., 2014; Zhang et al., 2018; Liu et al., 2019). However, automated and controlled shaking in overhead (Quinn et al., 2017) or platform systems (van den Berg et al., 2020), magnetic (Huang et al., 2020) or electric stirring (Imhof et al., 2012) may be preferred to

increase reproducibility and method standardization.

Containers used for density separation vary greatly, ranging from beakers and separation funnels to more complex setups. Glass beakers are used most widely (Quinn et al., 2017; Klein et al., 2015; Liu et al., 2018; Zobkov and Esiukova, 2017; Huang et al., 2020; Zhou et al., 2020), followed by bottles (Hurley et al., 2018), Erlenmeyer flasks (Wang et al., 2018), and centrifuge tubes (Corradini et al., 2019b). In some studies, separation devices were self-built (Imhof et al., 2012; Renner et al., 2019). Depending on the container of choice, a 5 g (Corradini et al., 2019b) to up to 6 kg (Imhof et al., 2012) sample can be processed, requiring 20 mL to 12 L density separation solution, respectively. Although rarely specified, the height of the container may be important as it determines the distance between the denser and lighter fraction and thereby the separation efficiency (Mahat, 2017). Furthermore, container materials should be free of plastics to avoid contamination or sticking of plastic particles to the inner surface of the container.

To further promote separation, Enders et al. (2020a) designed a spiral conveyor rotating inside a separation funnel to constantly transport the sample upwards. Thereby, the sample disperses more efficiently, which facilitates microplastic separation from the heavier soil matrix. Nuelle et al. (2014) proposed an air-induced overflow system, exposing the sample to turbulences by continuous air-bubbling potentially benefiting the separation of lighter particles from denser matrix. The method was efficient at reducing the amount of sediment for further treatment steps. A more advanced setup was developed by Renner et al. (2019) using larger air bubbles for dispersion and finer ones as adhesive surfaces for separating microplastics from the matrix. The setup also minimized dead spaces to ensure that no plastic particles would be retained in the container. The method seems promising as >90% of microplastic spikes were recovered from sand samples within 20 min. Although the authors propose its suitability for soil samples, an evaluation is still pending. Notably, when Scheurer and Bigalke (2018) combined stirring with continuous air-bubbling for soil samples, the method did not result in a significantly higher extraction efficiency. One possible challenge for the applicability of air bubbling systems to soil is that very fine textured, clayey soils or soils with very dense minerals may form a sludge at the bottom of the vessel, blocking the air inlet. Instead, Scheurer and Bigalke (2018) used centrifugation to reduce the processing time. While others also centrifuged soil samples in density solutions (van den Berg et al., 2020; Corradini et al., 2019b), only Scheurer and Bigalke (2018) reported recoveries ($\geq 93\%$).

In general, separation protocols vary not only in terms of the density separation procedure but also in treatment times (10 s to 2 h) (Nuelle et al., 2014; van den Berg et al., 2020) and settling times (5 min to 24 h) (Han et al., 2019; Scheurer and Bigalke, 2018). For adjusting these procedural parameters, plastic and soil mineral particle sizes as well as the SOM content and soil aggregate stability may provide a reference to evaluate suitable settling times (Wang et al., 2018).

Sample Collection After the separation procedure, microplastics floating on the solution surface need to be collected and isolated for further treatment and analysis. A simple and low-cost approach is to collect microplastics by decanting (Besley et al., 2017; Huang et al., 2020; Zhang et al., 2018; Scheurer and Bigalke, 2018). Since microplastics have the tendency to adhere to the inside of container walls (Nakajima et al., 2019), repeated density separations may be necessary to ensure the complete

transfer of all microplastics. However, this results in prolonged processing times and increases the risk of contamination. Floating SOM is particularly challenging for the decanting method.

Microplastics can also be further retrieved by suction. First applications involved pipettes to collect synthetic fibers from sludge and soil (Zubris and Richards, 2005; Prendergast-Miller et al., 2019). Scheurer and Bigalke (2018) used a vacuum pump to aspirate the topmost layer of the density solution with the microplastics and transferred them to a second vessel for collection. The inherent risk is that particles floating directly on the surface are not collected and are lost for analysis as tubes need to be submerged for vacuum pumping. Rinsing of tubes may also increase the demand of solution media. Adding surfactants such as polysorbate 80 (Enders et al., 2020a) may reduce adhesion to separation equipment. However, this has not been tested for soil so far.

Most of the recently developed systems are based on overflow of the supernatant through the continuous addition of density solution (Nuelle et al., 2014; Zhou et al., 2020; Vermeiren et al., 2020; Wang et al., 2018; Liu et al., 2018; Liu et al., 2019; Han et al., 2019). With this, microplastics may adhere not only to inner but also to the outer container walls, which complicates particle collection. Moreover, such open constructions are extremely prone to contamination.

By contrast, separation funnels^[3] have an outlet at the bottom of the apparatus that is used to drain the settled mineral fraction before collecting the supernatant (Wang et al., 2018; Nuelle et al., 2014; Mahon et al., 2017). Separation funnels are prone to clogging if the outlet is too narrow. This particularly applies to very fine or very coarse soil. Clogging may be mitigated by either adjusting the diameter of the outlet valves (Enders et al., 2020a) or carefully stirring up the sediment. However, the latter would favor particle adhesion to stirrers and might cause the resuspension of fine soil. Nevertheless, separation funnels offer the advantage of using a single container, which reduces dead spaces as well as the risk of contamination and analyte loss.

To further facilitate sample collection, density separation apparatuses were customized in such a way that a bottom chamber containing the dense material can be physically separated from a top chamber with the extracted microplastics, for instance, by use of a ball valve (Imhof et al., 2012; Zobkov and Esiukova, 2017; Coppock et al., 2017; Mahat, 2017). Depending on the chamber geometry and the type of ball valve, dead spaces may retain microplastics leading to reduced recoveries. Furthermore, fine clay particles may block the valve after long-term use.

Finally, microplastics are typically collected on membrane filters for subsequent analysis. Depending on the target particle size and analytical approach, decisions need to be made regarding the filter mesh width and material (Minténig et al., 2017; Löder et al., 2015). A first systematic evaluation of different filter materials was conducted by Löder et al. (2015) who found Al oxide and polycarbonate (PC) filters the least interfering with identification via FTIR spectroscopy. However, using filters made from plastic, such as PC (Löder et al., 2015) or nylon (Liu et al., 2018), may exclude these polymers from further analysis. While glass fiber filters come in as being useful for particle collection (Huang et al., 2020; Chen et al., 2020a), they were reported unsuitable for spectroscopic methods (Löder et al., 2015). Cellulose-based filters may be chosen instead (Zhou et al., 2020; Corradini et al., 2019b; van den Berg et al., 2020), but interactions with density solutions may alter filter properties (Quinn et al., 2017). Thus, potential interferences of altered

^[3] See Enders et al. (2020a) for illustrations.

filter material during analysis need to be tested. Although not always specifically stated, the filter mesh size determines the lower size limit for plastic detection. Reported mesh widths are often larger than 5 μm (Huang et al., 2020; Zhou et al., 2020). Consequently, the usage of filters for sample collection implies a systematic loss of the smallest microplastic fraction ($\leq 5 \mu\text{m}$), and the complete nanoplastic fraction ($< 1 \mu\text{m}$). This is particularly relevant for thermoanalytical methods, which are theoretically capable of capturing these fractions. Moreover, there is a potential tradeoff between minimizing mesh sizes and the filtration capacity, especially for soils high in light-density SOM where filters may easily get clogged.

5.3.5 SOM REMOVAL

With $\rho < 1.6 \text{ g cm}^{-3}$ (Cerli et al., 2012) the density of SOM is similar to that of microplastics ($\rho = 0.9\text{--}1.6 \text{ g cm}^{-3}$) (Enders et al., 2020b) and can thus be only partially removed by density separation. SOM removal is important as SOM constituents may interfere with subsequent microplastic analysis. Four groups of digestion agents for organic matter removal can be distinguished: (1) alkaline KOH or NaOH solutions, (2) acids including HNO_3 and H_2SO_4 , (3) oxidants like H_2O_2 or Fenton reagent, and (4) enzymes, for example proteinase K (Table 5.2) (Dehaut et al., 2016). Different digestion agents may be applied sequentially to optimize removal efficiencies.

Reagent	Sample Type	Evaluated Polymers	Extraction Time [d]	Temp. [°C]	SOM Removal Efficiency [%]	Deteriorated Polymers	Reference
KOH	Loamy sand	PE, PP, PS, PET, PA, PC, PMMA	1	60	30±20	PC	Hurley et al. (2018)
NaOH	Loamy sand	PE, PP, PS, PET, PA, PC, PMMA	1	60	70±20 (1 M), 60±40 (10 M)	PET, PC	Hurley et al. (2018)
HNO_3	Flood-plain soil	PE, PP, PS, PET, PVC, PA, PC, PU, ABS	2	90	Higher than NaOH, H_2SO_4 , H_2O_2	ABS, PA, PET	Scheurer and Bigalke (2018)
H_2SO_4	Flood-plain soil	PE, PP, PS, PET, PVC, PA, PC, PU, ABS	1, 4, and 7	90	Lower than with HNO_3	Not tested	Scheurer and Bigalke (2018)
H_2O_2	Loamy sand	PE, PP, PS, PET, PA, PC, PMMA	1	60	100±10	PS	Hurley et al. (2018)
H_2O_2	Agricultural soil	PE, PP, PS, PET, PVC, PA, PC, PMMA, ABS	1	60	Not reported	Not reported	Liu et al. (2019)
H_2O_2	Sediment	PE, PP, PS, PET, PVC, PA, PC, PU, ABS	7	RT	Not reported	PET, PVC, PC, PA, PUR, PP, PE	Nuelle et al. (2014)
H_2O_2	Loamy sand	PS, PP, PE, PET, PA, PC, PMMA	1	70	100±10	PA, PS	Hurley et al. (2018)
Fenton reagent	Loamy sand	PE, PP, PS, PET, PA, PC, PMMA	1	40	100±10	None	Hurley et al. (2018)

Table 5.2: Suitability of digestion agents for the removal of SOM for microplastic analysis.

Alkaline solutions are typically used for denaturation of proteins in biota. When applied to a floodplain loamy sand containing 5.8% SOM, however, NaOH (1 and 10 M) and KOH (1.8 M) solutions only removed 35–68% SOM (Hurley et al., 2018). The researchers suggested that humins and alkali-insoluble compounds could not be degraded and removed from the sample. In addition, NaOH resulted in a severe PET and PC mass loss of up to 30%, while KOH partially degraded PC. Alkaline treatments may even more severely affect biodegradable plastics. Kühn et al. (2017), for instance, reported complete loss of a PLA bag after purification with 1 M KOH.

Similarly, HCl and HNO_3 have been discussed as potential digestion agents for SOM (Bläsing and Amelung, 2018). Concentrated HNO_3 (65%) completely

removed SOM (>30%) from a floodplain soil whereas 96% H₂SO₄ and 13% potassium hypochlorite left 3 and 6% of organic residues, respectively (Scheurer and Bigalke, 2018). However, acrylonitrile butadiene styrene, PA, and PET were partly degraded or fragmented into smaller particles (Scheurer and Bigalke, 2018).

The majority of studies addressing the removal of SOM used H₂O₂ for sample preparation (Table 5.2). This may be attributed to the fact that H₂O₂ has been successfully applied to sediments in previous studies (Nuelle et al., 2014; Imhof et al., 2012). In line with this, Hurley et al. (2018) removed 96–108% SOM from a loamy sand with 30% H₂O₂ at 70 °C. However, PA particles were destroyed and PS particles partly degraded. Experiments at room temperature revealed changes in color and size for PE, PP, PET, PVC, PC, PA, and polyurethane after 7 d (Nuelle et al., 2014). While effective for removing vegetal litter, degrading effects on microplastics were also mentioned for a three-stage method developed by Duan et al. (2020). Therein, H₂O₂ (30%) was consecutively added at temperatures of 70 and 100 °C and left for digestion for 1–7 h. With regards to previous findings (Hurley et al., 2018), polymer degradation was probably related to the elevated reaction temperatures. Thus, temperature and time should be carefully adjusted in order to preserve the polymer analytes. In addition, the SOM removal efficiency most likely depends on the composition of the examined soil. Fe^{III} and Mn (sesqui)oxides, for instance, were indicated to catalyze the disproportionation of H₂O₂ into water and oxygen before an oxidation reaction was initiated (Petigara et al., 2002). Interactions with clay minerals, carbonate coatings, or occlusion in soil aggregates may further protect SOM from oxidation (Mikutta et al., 2005), which calls for more potent and selective SOM removal agents.

Fenton reagent, an acidified solution (pH 3–5) of H₂O₂ and a Fe²⁺ catalyst, produces hydroxyl and hydroperoxyl radicals at high yields. Hydroxyl radicals are particularly effective in degrading SOM (100±10% removal efficiency) already at room temperature. Additional cooling (≤40 °C) is advisable since the reaction is extremely exothermic (Hurley et al., 2018). In contrast to treatments with H₂O₂ at elevated temperature, Hurley et al. (2018) did not observe any detrimental effect on polymer sizes and masses after Fenton digestion, which may be attributed to the lower reaction temperatures (≤40 °C). This may further explain why Vermeiren et al. (2020) only recovered 90% PE after Fenton digestion of organic-rich sediments without monitoring the reaction temperature. Although promising, Fenton digestion has not yet been widely applied for soil sample preparations, but it should be further pursued.

Enzymatic digestion makes use of a variety of different enzymes for the selective degradation of potentially interfering matrix constituents without altering polymer analytes (Liu et al., 2020). These enzymes include proteinase K (Cole et al., 2014), trypsin (Courtene-Jones et al., 2017), lipase and amylase (Railo et al., 2018), corolase (Lavers et al., 2019), protease, cellulase, and chitinase (Löder et al., 2017). So far, no protocol on the enzymatic purification of soil samples for microplastic analysis has been published. Only a Swedish report by Sweden Water Research (Ljung et al., 2018) lists commercial cellulase, esterase, and xylanases as enzymes potentially suitable for soil sample preparation, however, without reporting removal efficiencies or recovery rates. Enzymes targeting specific SOM constituents therefore still need to be investigated. However, even the enzymatic digestion of wastewater samples is often incomplete so that several enzymes need to be applied successively and in conjunction with oxidative treatments (Löder

et al., 2017; Mintenig et al., 2017). Such multi-step protocols may be costly and easily take more than two weeks per sample (Löder et al., 2017). Furthermore, long and complicated sample preparation methods probably increase the risk of contamination, for instance, during additional filtering steps.

In terms of removal efficiencies and microplastic recoveries, oxidizing agents like Fenton reagent and H_2O_2 are currently considered the most suitable for SOM removal. However, biodegradable plastics and nanoplastics are still largely understudied and will require a reevaluation of sample preparation methods to avoid systematic underestimations. It is still not fully understood to what extent soil constituents like Mn oxides or clay minerals may interfere with oxidative techniques. Since most studies investigated agricultural soils, it is unclear if current methods are readily transferable to soils with a different SOM composition like chernozems or kastanozems. A thorough soil characterization, and thereby a better understanding of potential matrix interferences, may help the advancement of soil-specific sample preparation methods.

5.3.6 EXTRACTION WITH ORGANIC SOLVENTS

In addition to density separation and SOM digestion, the use of organic solvents for the extraction of microplastics from solid matrices has gained growing attention within the scientific community (Table 5.3). Fabbri et al. (2000) first extracted 1 g kg^{-1} PVC and PS debris from beach sand with DCM using a Soxhlet apparatus. PVC recovery was 85% while PS was evaluated qualitatively. In recent years, further technical and analytical developments have lowered recoverable concentrations by a factor of 20–50 (Chapter 4; Peez et al., 2019a; Dierkes et al., 2019) and made a broader spectrum of polymers amenable to extraction. Current methods not only include the commonly used polymers PE, PP, PS, PET, PC, and PMMA (Fuller and Gautam, 2016; Okoffo et al., 2020) but also biodegradables like polybutylene sebacate and PBAT (Siotto et al., 2013; Nelson et al., 2019). In addition, methods have been simplified to batch extraction setups (Chapter 4; Elert et al., 2017) and automated to increase sample throughput and reproducibility, for example using ASE (Fuller and Gautam, 2016; Okoffo et al., 2020) or microwave-induced extraction (MWE) techniques (La Nasa et al., 2021).

What all these methods have in common is that they require the careful adjustment of extraction conditions, including the selection of an appropriate organic solvent, extraction temperature, and time, to enable the quantitative dissolution or suspension of a predefined set of target polymers. While solvents like TCB and xylenes have been shown to selectively dissolve polyolefins at temperatures between 120 and 140 °C (Chapter 4; Ceccarini et al., 2018), hexafluoroisopropanol (HFIP) already dissolves PET at 45 °C (Elert et al., 2017). Higher temperatures (180 °C) and pressures (up to 100 bar), as typically applied by ASE and MWE, broaden the analytical window. However, the harsher the extraction conditions get, the more likely it is that extracted polymers cannot be stabilized in solution when cooling down. This may be circumvented by precipitating the polymers in an inert matrix such as quartz sand for further sample processing (Dierkes et al., 2019). Less selective extraction conditions may cause interferences from co-extracted matrix constituents (Chapter 4), which need to be tackled by additional clean-up steps with methanol, Fenton oxidation, or density separation prior to polymer extraction (Dierkes et al., 2019; Peez et al., 2019a). In this respect, soil is a particularly

Method	Sample Type	Mass [g]	Polymer Type	Spiked conc. [g kg ⁻¹]	Extraction Solvent(s)	Volume [mL]	Temperature [°C]	Time [h]	Recovery [%]	Reference
ASE	Municipal waste, soil	2	PE, PP, PS, PET, PVC	5–25	DCM	80	180	0.25	85–94	Fuller and Gautam (2016)
ASE	Roadside and potting soil	1	PE, PP, PS	0.05–0.75	THF	35	185	1	77–123	Dierkes et al. (2019)
ASE	Agricultural soil	2.5–5	PBAT	1	Chloroform/methanol (9:1)	40–50	120	0.5	100	Nelson et al. (2019)
ASE	Biosolids	1	PE, PP, PS, PET, PVC, PC, PMMA	0.02–0.1	DCM	80	180	0.25	85–128	Okoffo et al. (2020)
Batch extraction	Agricultural soil	0.5	PS	5	THF	2	45	24	100	Elert et al. (2017)
Batch extraction	Agricultural soil	0.5	PET	20	HFIP	2	45	24	80	Elert et al. (2017)
Batch extraction	Sediment	2.5	PET	0.8	Chloroform/TFA (4:1)	1	RT	2–4	91–108	Peez et al. (2019a)
Batch extraction	Agricultural soil	4	PE, PP, PS	0.05–0.25	TCB	8	120	1	70–128	Chapter 4
MWE	Beach sand	1	PS	0.05	DCM	1	80	1	97	La Nasa et al. (2021)
Kumagawa apparatus Soxhlet	Beach sand	160	PE, PS	0.36–0.82	(1) DCM, (2) xylenes [†]	90	(1) 37, (2) 135–140 [†]	3–6	95–97	Ceccarini et al. (2018)
Soxhlet	Sediment, suspended matter	10	PVC	1	DCM	300	>40	16	85	Fabbri et al. (2000)
Soxhlet	Agricultural soil	150	PBS	4	Chloroform	NA	>61	8	83	Siotto et al. (2013)

ASE = accelerated solvent extraction; MWE = microwave-induced extraction; DCM = dichloromethane; HFIP = hexafluoroisopropanol; TCB = 1,2,4-trichlorobenzene; TFA = trifluoroacetic acid; THF = tetrahydrofuran; [†] numbers in parentheses indicate sequential extraction steps.

Table 5.3: Recoveries of various extraction methods with organic solvents from soil and other solid matrices.

challenging matrix for its diverse and heterogeneous nature. Humic acids, plant suberins and cutins, cellulose, and lignin are currently being discussed as main sources for interferences (Chapter 4; Dierkes et al., 2019; Okoffo et al., 2020). Chapter 4 linked interferences with the quantification of PE to a soil C_{org} content exceeding 2.5%, whereas Dierkes et al. (2019) identified wood and leaf material as potential sources for interferences with PS and PE quantification, respectively. Both studies applied Py-GC/MS after solvent extraction. By contrast, Peez et al. (2019a) suspected carbonates co-extracted from invertebrates with chloroform/trifluoroacetic acid (Table 5.3) of interfering with PET analysis via quantitative ¹H NMR spectroscopy. Sediments (Peez et al., 2019a) and agricultural soil extracted for PBAT quantification (Nelson et al., 2019) were not affected. Consequently, matrix interferences should be closely investigated for soil samples suspected to contain soil invertebrates.

5.3.7 RECENT DEVELOPMENTS

The search for more robust and cost-effective, yet selective, sample preparation procedures for heterogeneous solid matrices has fueled further method development. Felsing et al. (2018), for example, constructed an electrostatic separator that recovered 99% of microplastics from sandy substrates. However, the applicability of this approach was assumed to largely depend on the size distribution of microplastic particles and the texture of the investigated matrix (Enders et al., 2020b). If applied

to soil, soil aggregates, SOM, and plant litter may further interfere with electrostatic interactions. Similarly, Grbic et al. (2019) attempted to recover microplastics by magnetic extraction through the binding of Fe nanoparticles to the microplastics' surface. However, matrix particles impeded the interaction of nanoparticles with microplastics, and microplastics fragmented during the separation procedure.

Another approach exploited the hydrophobicity of microplastics by recovering >96% microplastics with canola oil (Crichton et al., 2017). In follow-up experiments, castor oil (Mani et al., 2019) and olive oil (Scopetani et al., 2020) were tested, obtaining recovery rates of 99% and >90%, respectively. Enders et al. (2020b) further suggested *n*-pentane as a preliminary cleanup step before matrix digestion to accelerate the sample preparation process. Although Scopetani et al. (2020) emphasized that the distinct advantage of their method is its independence from polymer densities, Mani et al. (2019) was unable to suspend PS particles from a fluvial solid matrix. Furthermore, the use of separation funnels led to clogging of the funnel outlet and, thus, impractical separation of water and oil. To circumvent this, Scopetani et al. (2020) constructed cylinders made from PTFE and froze the suspension to -40°C to decant the oil fraction. Further method refinement will be necessary to elaborate on the extraction of microplastics coated with SOM or biofilms that might hinder the contact between oil and polymer. An oxidative treatment may help to address this.

5.4 OPTIONS FOR SUBSEQUENT MICROPLASTIC QUANTIFICATION

5.4.1 MICROSCOPY

The analysis of larger plastic particles (mostly $>500\ \mu\text{m}$) is traditionally performed by manual selection under a stereomicroscope. The procedure enables the non-destructive determination of particle numbers, sizes, and shapes at low cost. The degree of sample preparation can be flexibly adjusted to the complexity of the matrix. Even more so than in aquatic samples, plastic recovery from soil varies with sample purity and the operator's knowledge of the particles' visual features (Lusher et al., 2020; Filella, 2015; Zhang et al., 2020). For example, Corradini et al. (2019a) only considered plastic debris with "shiny surfaces, strong colors, and sharp geometrical shapes" after density separation of agricultural soil. Fibers with smooth sides and strong colors were classified as synthetic based on their visual appearance only. Additional fluorescent staining with Calcofluor white, Evans blue, and Nile red dyes may help to distinguish microplastics from the surrounding matrix (Helmberger et al., 2020; Nel et al., 2021). Particularly in heterogeneous solid matrices such as soil, visual sorting for identification is expected to exhibit error rates of 20–70% (Bläsing and Amelung, 2018) and should therefore be complemented with spectroscopic methods like FTIR–ATR or thermoanalytical approaches (He et al., 2018).

5.4.2 SPECTROSCOPY

FTIR and Raman (micro)spectroscopy permit the simultaneous analysis of chemical and physical properties of microplastics such as the polymer type, particle shapes, and sizes down to a resolution of 20 and $1\ \mu\text{m}$, respectively^[4]. Both mi-

^[4] See Anger et al. (2018) and Xu et al. (2019) for comprehensive reviews on instrumental analytics.

cross-spectroscopic techniques are commonly applied for particles $<500\ \mu\text{m}$ and require the sample to rest on a flat filter disk. With regard to typical disk diameters of 13–47 mm, spatial measurement increments of several micrometers protract acquisition times and render complete filter scans nearly impossible. Instead, specific areas of interest are preselected manually by automated pattern recognition or by randomized subsampling (Anger et al., 2018; Xu et al., 2019). Manual selection of suspected microplastic particles is particularly error-prone since white and transparent items may be easily missed on a bright filter background (Lares et al., 2019). Even automated approaches may over- or underestimate particle counts when microplastics are unevenly distributed on the filter disks after sample preparation (Anger et al., 2018). Error rates and measurement times may be decreased when using a FTIR microspectrometer with a focal plane array where a grid of detector elements allows for chemical mapping of larger areas on the filter and may provide multiple measurements for the same particle (Simon et al., 2018). However, even with focal plane array–FTIR microspectroscopy a single 47 mm filter may still take up to 10 h for acquisition (Minténig et al., 2017). Further challenges are associated with the sensitivity of FTIR and Raman microspectroscopy to interferences from water, atmospheric CO_2 , SOM, and concealment by clay particles that require rigorous matrix removal during sample preparation (Anger et al., 2018; Xu et al., 2019). Although crucial for the determination of particle morphologies, the time-consuming measurements might still restrict the applicability of microspectroscopic methods for the analysis of microplastics in soil, particularly for screening and monitoring studies.

5.4.3 THERMOANALYSIS

It has been continuously argued that microplastic mass contents are more robust and better suited to interstudy comparisons and modeling than particle counts. That may be because microplastic masses are often less affected by the sample treatment and less prone to bias from size selectivity (Simon et al., 2018; Braun et al., 2018). The non-uniform distribution of particles shapes, sizes, and densities in environmental samples further challenges a reliable extrapolation from particles sizes and densities to particle masses (Braun et al., 2018). Therefore, a range of mass-sensitive thermoanalytical methods is increasingly applied complementarily or in conjunction with FTIR and Raman imaging. These methods include TGA/MS (Chapter 3; Boyron et al., 2019), TED-GC/MS (Dümichen et al., 2017), and Py-GC/MS (Fischer and Scholz-Böttcher, 2017; Fischer and Scholz-Böttcher, 2019). For an extensive review on thermoanalytical techniques, we refer to La Nasa et al. (2020).

As thermoanalysis is based on the thermal decomposition of the polymer analyte at temperatures $>500\ ^\circ\text{C}$ and quantification via characteristic pyrolysis products, determination of the particle size and morphology is impossible if not done in advance (Nguyen et al., 2019; Dümichen et al., 2017). With recent method refinements (Chapter 4; Dierkes et al., 2019) and novel hyphenations of thermoanalytical sample introduction with FTIR or time-of-flight detectors (Sullivan et al., 2020), instrumental analytics have become sufficiently sensitive for the quantification of microplastics in the low mg kg^{-1} to $\mu\text{g kg}^{-1}$ range. A recent interlaboratory comparison of thermoanalytical methods further showed that thermoanalytical setups involving chromatographical separation were able to reliably identify and quantify

PE, PP, PS, and PET in an organic sediment (Becker et al., 2020). TGA/MS proved itself particularly useful for the assessment of total polymer contents. Method harmonization and interlaboratory reproducibility were identified as crucial points. If microplastics are not extracted with organic solvents (see also Section 5.3.6), one major challenge of applying thermoanalytical techniques to soil is the preparation of a homogeneous aliquot of less than 100 mg for sample introduction. This typically requires cryomilling and a very sensitive microscale to maintain sufficient measurement repeatability (Chapter 4; Dierkes et al., 2019). Furthermore, interferences may occur when pyrolysis products in plastic and matrix are identical. This may particularly apply to lignins interfering with PS quantification (Fischer and Scholz-Böttcher, 2017) and lipids and waxes from plant cuticles leading to a false positive detection of PE (Chapter 4). As discussed in Section 5.3.7, further research will be needed to scrutinize the sources of matrix interferences in soil for the advancement of analytical methods for microplastic analysis.

5.4.4 FURTHER TECHNIQUES

In the last few years, well-established LC methods like LC/MS (Schirinzi et al., 2019), SEC, and GPC (Elert et al., 2017) have been rediscovered for microplastic analysis^[5]. Although particularly sensitive and highly reproducible, LC/MS is restricted to polymers like PS that are readily soluble in organic eluents at room temperature (Schirinzi et al., 2019). By contrast, high-temperature GPC and SEC systems are able to analyze a wide range of different polymers and provide additional information on the polymer's molecular weight, but their UV and refractive detectors typically require polymer concentrations in the mg mL⁻¹ range (Elert et al., 2017). Their applicability for real-world soil samples may thus be limited, and interferences from soil constituents may be more likely.

Another promising new technique is quantitative ¹H NMR spectroscopy initially developed by Peez et al. (2019a) for the quantification of PET in environmental samples. Furthermore, PE and PS (Peez et al., 2019b), PVC, acrylonitrile butadiene styrene, and PA (Peez and Imhof, 2020), as well as polybutylene sebacate and PBAT (Nelson et al., 2019) have been shown to be amenable to this approach. LODs are currently in the low mg kg⁻¹ range. Matrix interferences from sediment (Peez et al., 2019a) and agricultural soil (Nelson et al., 2019) were negligible if samples were oxidatively pretreated or extracted via ASE, respectively. Similar to LC, however, quantitative ¹H NMR spectroscopy requires the polymers to be dissolved in an appropriate solvent prior to analysis, as outlined in Section 5.3.6. The use of deuterated solvents reduces the ¹H NMR background noise but may easily increase solvent costs by a factor of 1000. In addition, the solubility of polymers in organic solvents is often specific so that the analysis of polymer mixtures needs to be performed for each polymer or certain subgroups separately.

Further noteworthy approaches include electron microscopy with energy-dispersive X-ray spectroscopy (Watteau et al., 2018), time-of-flight/secondary ion mass spectrometry (Du et al., 2020), and near infrared (NIR) spectroscopy (Paul et al., 2019; Corradini et al., 2019a). The methods enable fast, qualitative screenings of microplastic particles and surface characteristics after oxidative treatment or density separation. Quantifying PE, PET, and PVC via NIR, however, only yielded LODs in the lower g kg⁻¹ range, which may be suitable for identifying microplastic hotspots in soils near point sources, but may not be applicable to

^[5] See Drzeżdżon et al. (2019) for an extensive review on alternative, less established methods for microplastic analysis.

more diffuse pollution scenarios. Moreover, the interpretation of NIR spectra is complicated and depends strongly on the soil matrix (Corradini et al., 2019a), which calls for further method development.

5.5 SUGGESTIONS FOR BEST-PRACTICE SAMPLE PREPARATION

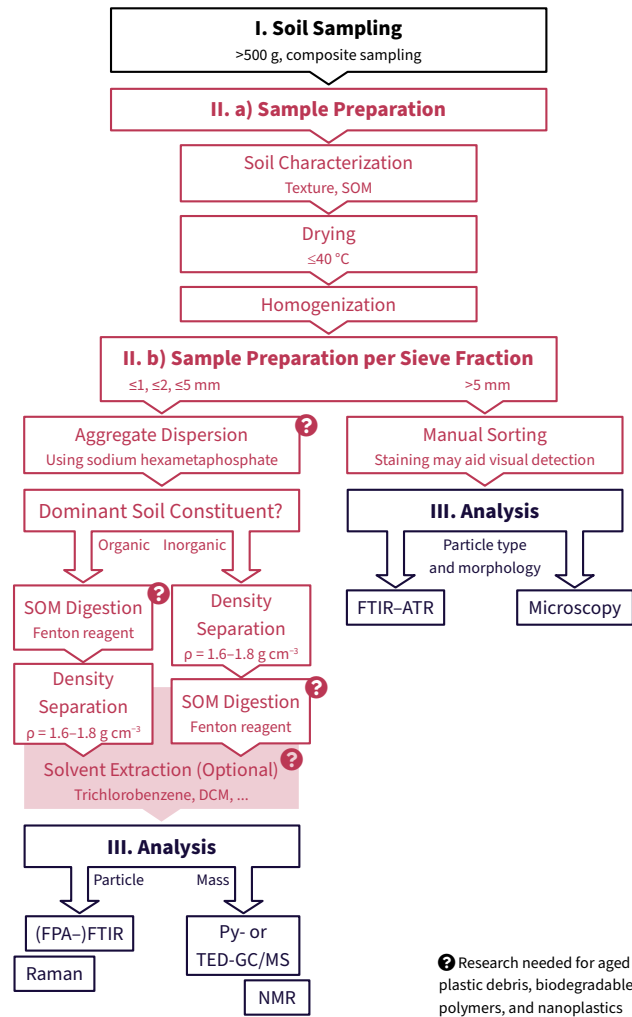
Figure 5.1 summarizes state-of-the-art preparation methods for microplastic analysis of soil samples and suggests best practices. Current research on microplastics in terrestrial and soil systems provides limited information on the study area, soil, and sampling procedure. Based on established soil sampling guidelines, future studies are suggested to implement representative sampling schemes involving a sufficient number of composite samples for a given sampling area (Section 5.2.1). Sample quantities should be >500 g to acknowledge the heterogeneous distribution of microplastic particles in soil. Total sample quantities may need to be negotiated with local farmers or land owners to assure sustainable management of soil resources. Local stakeholders can further help to obtain valuable information on site geomorphology, land use history, and agricultural management practices. As a complement, the studied soil should at least be characterized for its texture, SOM content, and carbonate content to enable an informed assessment of microplastic recoveries and interstudy comparisons (Section 5.2.2).

Sample preparation involves drying below 60°C , ideally $\leq 40^{\circ}\text{C}$, to avoid any deterioration of microplastic particles (Section 5.3.1). This may be particularly important for preserving biodegradable polymers. Whether freeze drying might fragment microplastics by frost wedging is unknown to date. After sufficient homogenization, soil should be sieved to 1, 2, and 5 mm to comply both with established soil texture classifications and microplastic definitions (Section 5.3.2). Further sample preparation is performed per sieve fraction. While manual sorting of macroplastics often suffices for the sieve fraction >5 mm, finer fractions (≤ 1 , ≤ 2 , and ≤ 5 mm) may require dispersing soil aggregates to retrieve occluded microplastics (Section 5.3.3). However, it still needs to be assessed whether soil sieving and dispersion methods like agitation with sodium hexametaphosphate solution or ultrasonication may fragment aged or biodegradable microplastics as well as nanoplastics.

If inorganic minerals are dominant in the investigated soil, the microplastic fraction should be preconcentrated by density separation (Section 5.3.4). Selecting a specific density separation setup involves careful consideration of the targeted polymers and particle sizes, recoveries, cost efficiency, ease of operation, and environmental concerns. To extract all major polymer types, aiming for determination of total plastic contents in soil, high-density solutions ($\rho = 1.6\text{--}1.8\text{ g cm}^{-3}$) such as NaBr or SPT are recommended. Solutions with lower densities like saturated NaCl solution may be useful for target analyses, particularly of PE, PP, and PS. In any case, separation methods should be validated by recovery experiments that involve spiking known polymer types and particle sizes to a realistic, well-characterized soil matrix. In addition, potential sources of contamination need to be closely monitored, for instance, by using procedural blanks and closed containers. In this respect, separation funnels may be a promising alternative to open vessels that are currently the most common equipment for microplastic separation.

Additional SOM removal (Section 5.3.5) is necessary if analytical interferences

Figure 5.1: Suggestions for best-practice sample preparation for microplastic analysis of soil.



from SOM are expected. Ideally, SOM removal agents should efficiently digest or degrade SOM while preserving microplastic analytes. Current literature recommends Fenton reagent, which allows for efficient SOM oxidation at controlled temperatures ($\leq 40\text{ }^{\circ}\text{C}$) and thus has minimal impact on microplastics. An alternative may be selective extraction of polymers in organic solvents like DCM or TCB at elevated temperature (Section 5.3.6) while keeping interfering SOM in the precipitate. By doing so, physical properties of the particles will be lost. Nonetheless, such approaches may become increasingly relevant due to the growing demand for quantitative methods for biodegradable plastics, which are more sensitive to degradation during sample preparation than conventional polymers.

The major options for subsequent microplastic analysis are visual microscopy for particles $>500\text{ }\mu\text{m}$ (Section 5.4.1), FTIR or Raman (micro)spectroscopy for smaller particles (Section 5.4.2), mass-based thermoanalytical methods (Section 5.4.3), and quantitative ^1H NMR spectroscopy (Section 5.4.4). If particle numbers, sizes, and morphology are of specific interest to the research question, spectroscopic methods are favorable. For quantifying plastic pollution in terms of mass, which has been argued to be more comparable, thermoanalytical methods and ^1H NMR spectroscopy may be preferred. The associated LODs in terms of microplastic size need to be stated, also taking previous sample preparation steps into account.

Terrestrial microplastics research is a quickly evolving field characterized by an

extraordinarily high diversity of newly developed or refined analytical approaches. While this challenges future standardization, active method development offers great opportunities for innovations and microplastic analyses tailored to specific research questions. However, harmonization needs to start with uniform communication of microplastic quantities in particles kg^{-1} for microplastic counts and in μg or g kg^{-1} for mass-based results (Braun et al., 2018). Furthermore, quality control measures should be implemented at an early stage of method development. This includes (1) controlling contamination by working plastic-free and including blank measurements, (2) thorough documentation of the studied soil, sample preparation, and analytical methods, and (3) method validation with recovery tests and an assessment of analytical limitations. In this respect, the best practices for terrestrial microplastic analysis still need to be established. Because of the complexity and heterogeneity of soil, soil sample preparation for microplastic analysis must be adapted to the specific properties and composition of the examined soil. This will not only help to ensure efficient matrix removal while conserving microplastics, it will also advance the field towards a better understanding of processes and interactions of microplastic particles with SOM and other soil constituents.

6

SCREENING FOR PLASTIC DEBRIS IN PLASTIC-COVERED SOIL

Abstract Agricultural plastic covers made from PE and PP provide increased yields and an improved crop quality. However, such covers are suspected of partially breaking down into smaller debris and thereby contributing to soil pollution with microplastics. To scrutinize this, we randomly sampled 240 topsoil cores (0–5 cm) from eight fields which were covered with fleeces, perforated foils, and plastic mulches for less than two years. Samples from the field periphery (50 m perimeter) served as a reference. Visual plastic debris >2 mm was analyzed by FTIR. Smaller, soil-associated plastic debris was dispersed from 50 g of fine soil (≤ 2 mm) using sodium hexametaphosphate solution and density-separated with saturated NaCl solution. The collected PE, PP, and PS debris was selectively dissolved in a mixture of TCB and *p*-xylene at 150 °C and quantified by Py-GC/MS. We counted six PE and PS fragments >2 mm in two out of eight fields. By contrast, Py-GC/MS detected PE, PP, and PS contents in the fine soil of six fields (6% of all samples). In three fields, PE levels of 3–35 mg kg⁻¹ were potentially associated with the use of thinner and less durable perforated foils (40 μ m thickness). This was slightly more pronounced at field edges where the plastic covers are turned and weighed down. By contrast, 50 μ m thick PE films were not shown to emit any plastic debris. PP contents of 5–10 mg kg⁻¹ were restricted to single observations in the field centers of three sites. At one site, we found expanded PS particles >2 mm that concurred with elevated PS levels (8–19 mg kg⁻¹) in the fine soil. Both PP and PS were distributed indistinctly across sites so that their source remained unresolved. In addition, the extent to which plastic contents of up to 7 mg kg⁻¹ in the field periphery of some sites were attributed to wind drift from the covered fields or from external sources needs to be investigated in future studies. Our results suggest that the short-term use of thicker and more durable plastic covers should be preferred over thinner or perforated films to limit plastic emissions and accumulation in soil.

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See Parts of this Thesis and Author Contributions, page ix, for details.

6.1 INTRODUCTION

The use of plastic covers has become common agricultural practice for improving yields and crop quality, managing harvest times, and increasing pesticide and water use efficiency (Chapter 2; Lamont, 1993). The most used materials are PE films and

PP fleeces of various thicknesses made to last for up to 10 years (Bertling et al., 2021). However, wind, heavy machinery, or UV irradiation are likely to disintegrate parts of the covers into debris smaller than 1–5 mm (Scarascia-Mugnozza et al., 2011), termed microplastics (Hartmann et al., 2019). In recent years, this supposition has raised a discussion about agricultural plastic covers acting as a potential source of plastic debris in the terrestrial environment and particularly in soil (Chapter 2; Hurley and Nizzetto, 2018). Yet, the actual contribution of agricultural plastic covers to soil pollution with plastic debris has remained incompletely understood and rarely discriminated from other potential sources like aerial deposition or littering.

These knowledge gaps are probably because the few studies that have analyzed plastics in and on soil so far mostly relied on optical detection by FTIR spectroscopy or visual microscopy. Both techniques deliver particle counts, are relatively sensitive to matrix interferences, and thus require extensive sample preparation when applied to heterogeneous matrices with a similar particle structure to the plastic particles of interest (Chapter 5). For those reasons, Piehl et al. (2018) and Harms et al. (2021) excluded plastic debris <1 mm from their FTIR analysis of agricultural topsoil (0–5 cm). The investigated sites were not covered with plastic, yet the soil contained 0.3 to 6 particles kg^{-1} of 1–5 mm size. These findings contrast Zhang and Liu (2018) who detected 95% of plastic debris <10 mm (up to 40 000 particles kg^{-1}) in the size fraction of 0.05–1 mm after more than 25 years of permanent greenhouse cultivation. Topsoil previously covered with plastic revealed plastic counts of 60 up to 1000 particles kg^{-1} correlating with the 5–24 years of continuous plastic coverage (Huang et al., 2020). PE and PP are typically found the most (Harms et al., 2021; Kim et al., 2021). However, there are still studies which neither state particle sizes and analysis cutoffs nor assess the polymer composition of the retrieved particles (for example, Zhang et al., 2018; Beriot et al., 2021). Moreover, mass-based information is still missing but urgently needed for the monitoring and regulation of plastics in the environment.

With this study, we aimed to understand the mass distribution of plastic debris associated with fine soil (≤ 2 mm) better and to scrutinize the extent to which agricultural plastic covers emit plastic debris into their surroundings. In contrast to other studies, we screened fields covered with plastic for less than two years, which reflects typical land use and crop rotations in Germany (Harms et al., 2021). To this end, we randomly sampled topsoil within and around eight commercially managed agricultural fields covered with fleeces, perforated foils, and plastic mulches. PE, PP, and PS debris ≤ 2 mm was quantified by solvent-based Py-GC/MS (Chapter 4). To better account for the heterogeneous distribution of plastic debris in soil, we further refined and validated a new sample preparation procedure involving soil aggregate dispersion and density separation that allowed for the analysis of up to 50 g soil. The analyses were complemented by FTIR–ATR for plastic debris > 2 mm. We hypothesized that a directed gradient of plastic debris from the field center to its periphery (50 m field perimeter) supports the assumption of plastic covers contributing to an increased soil pollution with plastic debris. On the contrary, an undirected gradient would suggest another source of pollution such as littering. A uniform distribution may be an indicator for aerial deposition. In addition, we expected field margins (5 m perimeter) to be hotspots for plastic debris due to mechanical stress subjected to the plastic covers by weighing them down with soil or sandbags.

6.2 METHODS

6.2.1 STUDY AREA

The screening study was conducted in cooperation with local farmers in commercially managed horticultural fields in the Palatinate region in southwestern Germany. The study area has a mild and dry climate with mean annual temperatures of 10–13 °C and a total annual precipitation of 600±100 mm (Agrarmeteorologie Rheinland-Pfalz, 2020).

Sites 1–3 were located near Offenbach an der Queich^[1] and cultivated with strawberries (*Fragaria × ananassa*). Site 1 was fully covered with white fleece (100 µm thickness) and overlain by an additional 40 µm thick perforated foil (750 punch holes m⁻²) for one growing season; namely for the last four months. Site 2 had plastic-mulched ridges (black, 50 µm thickness) and bare furrows established two years previously. On top of this, the complete field was covered with white fleece (100 µm thickness) for the growing season. Site 3 was mulched like site 2 but without any additional fleece cover (Figure 6.1a).

^[1] GPS coordinates: 49° 12' N, 8° 11' E.

Sites 4 and 5 were located near Schifferstadt^[2] and cultivated with lettuce (*Cichorium endivia*) and cabbage (*Brassica oleracea* var. *gongylodes*), respectively. Both fields were completely covered with white fleece (40 µm thickness) and a top layer of white perforated foil (50 µm thickness, 750 punch holes m⁻², Figure 6.1b) for the growing season.

^[2] GPS coordinates: 49° 24' N, 8° 21' E.

Sites 6–8 were situated in Landau in der Pfalz^[3]. The rhubarb cultivation (*Rheum rhubarbarum*) was fully covered with white perforated foil for the growing season. The foil on site 6 had 250 punch holes m⁻² and was 50 µm thick. At site 7, the number of punch holes was similar to site 6, but the film thickness was only 40 µm. By contrast, the foil on site 8 (40 µm thickness) had 750 punch holes m⁻² (Figure 6.1c).

^[3] GPS coordinates: 49° 11' N, 8° 10' E.



Figure 6.1: Exemplary photographs of site 3, 4, and 8 field edges covered with (a) mulch, (b) fleece and perforated foil, and (c) perforated foil, respectively.

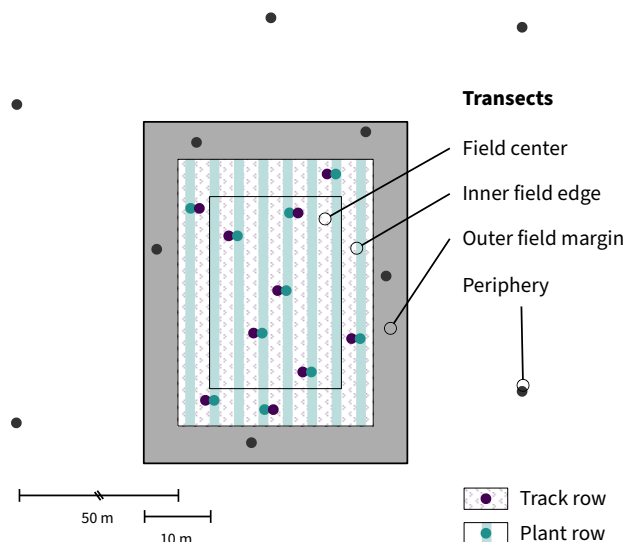
6.2.2 SAMPLING STRATEGY

To systematically screen these agricultural fields for plastic debris, each site was subdivided into four transects as shown in Figure 6.2. The field center and the inner field edge, defined as a 5 m strip around the field center, were cultivated and covered with plastic film. In these transects, plant rows (ridges) and track rows (furrows) were sampled separately. The outer field margin was marked by the 5 m perimeter around the cultivation. The field periphery (50 m perimeter around the cultivation) served as a reference.

Prior to retrieval of the plastic covers in spring 2018, small portions of the plastic cover were grab-sampled for subsequent characterization. Soil samples were taken <1 week after retrieval of the plastic covers. The sampling spots were predefined by

projecting a $1 \times 1 \text{ m}^2$ grid onto each transect and randomly selecting five squares without replacement (30 per site). At each of these spots, topsoil (0–5 cm depth) was sampled using a stainless steel core cutter (5 cm diameter). The soil cores were immediately transferred to uncoated paper bags and air-dried in there to reduce the risk of contamination.

Figure 6.2: Sampling scheme for one exemplary site; soil samples (filled dots, $n = 5$ per transect) were randomly selected. At the cultivated field centers and inner field edges, plant and track rows were sampled separately. The outer field margin and the field periphery were uncultivated.



6.2.3 SOIL CHARACTERIZATION AND CHEMICAL ANALYSIS OF PLASTIC COVERS

The soil texture at each site was estimated from composite subsamples using the hydrometer method described in ASTM D422-63 (2007). The electrical conductivity (EC) and pH were measured in deionized water and 0.01 M CaCl_2 aqueous solution, respectively. Soil C and N were determined by dry combustion elemental analysis^[4].

^[4] Vario MICRO Cube, Elementar, Germany.

The grab-sampled plastic covers were characterized by qualitative TED-GC/MS and Py-GC/MS, DSC, TGA, and FTIR-ATR analysis. TED-GC/MS and Py-GC/MS were applied to assess volatile additives or other polymer-associated compounds as well as the overall polymer composition of the agricultural plastic covers. To this end, a $1 \times 1 \text{ mm}^2$ piece was cut out of each plastic cover and placed into a pyrolyzer quartz tube of a Pyroprobe 6150 filament pyrolyzer^[5] coupled with a Trace GC Ultra with DSQII MS^[6]. For the TED-GC/MS analysis, the pyrolyzer interface was flash heated (10 K ms^{-1}) to $300 \text{ }^\circ\text{C}$ for 15 s to volatilize any polymer-associated compounds. A passivated transfer line ($350 \text{ }^\circ\text{C}$) transferred the volatiles to the split/splitless injector ($300 \text{ }^\circ\text{C}$, split ratio 1:75) of the GC/MS system. The compounds were chromatographically separated in a 1.3 mL min^{-1} He flow on a $30 \text{ m} \times 0.25 \text{ mm}$ capillary column (5% phenyl-arylene, 95% dimethylpolysiloxane, $0.25 \text{ } \mu\text{m}$ film thickness)^[7]. The oven program was: $40 \text{ }^\circ\text{C}$ (2 min hold), 8 K min^{-1} ramp to $300 \text{ }^\circ\text{C}$ (5 min hold). The GC/MS transfer line was kept at $280 \text{ }^\circ\text{C}$, and the MS ion source (70 eV) was heated to $230 \text{ }^\circ\text{C}$. The MS monitored $50\text{--}280 \text{ m/z}$ at a scan rate of 500 s^{-1} . After TED-GC/MS, the sample was pyrolyzed at $750 \text{ }^\circ\text{C}$ for 15 s applying the same GC/MS settings. All chromatograms were evaluated using OpenChrom, version 1.4.^[8] (Wenig and Odermatt, 2010), with the NIST08 database for peak identification.

^[5] CDS Analytical, Oxford, US.

^[6] Thermo Fisher Scientific, Bremen, Germany.

^[7] ZB-5MS, Phenomenex, Aschaffenburg, Germany.

^[8] Lablicate, Hamburg, Germany.

DSC and TGA measurements were conducted in accordance with Chapter 3. In brief, DSC was applied between -50 and 250 °C (10 K min^{-1} ramp, 50 mL min^{-1} N_2 flow)^[9] to determine the melting and crystallization temperatures of the agricultural plastic films. For the determination of polymer degradation onsets and evolved gases, plastic samples were subjected to TGA^[10]. The heating ramp was 5 K min^{-1} from 40 to 1000 °C under a 20 mL min^{-1} Ar flow. The degradation onset was determined by the temperature at which the polymer starts to thermally decompose ($<1\%$ mass loss).

Complementary FTIR–ATR analyses were performed between 4000 and 650 cm^{-1} at a resolution of 4 cm^{-1} using a Cary 630 spectrometer^[11]. Peaks were identified with Open Specy, version 0.9.2 (Cowger et al., 2021).

6.2.4 SOIL SAMPLE PREPARATION AND VISUAL PRE-SCREENING

All soil cores were sieved to fine soil (≤ 2 mm) and manually homogenized as suggested in Chapter 5. Visual plastic items retained by the sieve (>2 mm) were picked, photographed^[12], and analyzed via FTIR–ATR as described in the previous section.

Plastic debris ≤ 2 mm was density-separated from the soil matrix using saturated NaCl solution. To this end, 50 g of fine soil was first weighed into 1 L separation funnels with PTFE stop cock^[13] and agitated at 150 rpm with 125 mL of sodium hexametaphosphate^[14] solution (40 g L^{-1}) for 2 h to disperse any soil aggregates. In a second step, 90 g of NaCl^[15] and 125 mL of ultra-pure water were added to obtain a density solution of 1.2 g cm^{-3} . The mixture was shaken for another 2 h and left for sedimentation for at least 16 h. The sedimented soil was released from the separation funnel by gentle stirring of the suspension using the curved end of a bicycle spoke. Afterwards, the supernatant was collected in pleated cellulose filters with a particle retention of 4 – 12 μm ^[16]. The filter cakes were transferred into glass culture tubes^[17] and dried at 60 °C.

Based on Chapter 4, the culture tubes were topped off with 8 mL of a $1:1$ mixture (v+v) of *p*-xylene^[18] and TCB^[19] (see Table C.1 for solubility tests of a difficultly soluble ultra high-density PE). In addition, the mixture contained 100 mg L^{-1} butylated hydroxytoluene^[20] to prevent polymer oxidation. The tubes were sealed with a PTFE packing^[21], vortexed, and heated at 150 °C for 1 h to facilitate the extraction of the polymer analytes from the filter cake. After cooling down to room temperature, the supernatant was spiked with deuterated PS (PS-d5)^[22] for internal standardization using positive displacement pipettes with glass capillaries^[23]. The extracts were stored in 2 mL ND9 glass vials with inserts and PTFE-sealed caps^[24].

6.2.5 QUANTIFICATION OF PLASTIC DEBRIS IN SOIL

PE, PP, and PS debris in fine soil (≤ 2 mm) was quantified via Py-GC/MS as detailed in Chapter 4. In brief, 2 μL sample aliquots were injected into pyrolyzer quartz tubes equipped with two microfiber filter disks^[25] using a 10 μL syringe with PTFE plunger^[26]. Each sample was measured once as described in Section 6.2.3. However, the pyrolyzer interface was first held at 300 °C to purge remaining solvents and volatiles on-line. After 3 min, the sample was flash pyrolyzed (10 K ms^{-1}) at 700 °C for 15 s and transferred to the GC/MS system. The MS selectively monitored 70 and 126 m/z for the PP pyrolysate 2,4-dimethyl-1-

^[9] Q1000, TA Instruments, New Castle, US.

^[10] STA 449 F3 Jupiter with QMS 403 C Aeolos, Netzsch, Selb, Germany.

^[11] Agilent, Santa Clara, California, US.

^[12] Leica S9i, Wetzlar, Germany.

^[13] Carl Roth, Karlsruhe, Germany.

^[14] CAS 68915-31-1, $\geq 99\%$ purity, Carl Roth, Karlsruhe, Germany.

^[15] CAS 7647-14-5, $\geq 99.8\%$ purity, Carl Roth, Karlsruhe, Germany.

^[16] Whatman 589/2, GE Healthcare, Buckinghamshire, UK.

^[17] 16×100 mm², GL18, VWR, Darmstadt Germany.

^[18] CAS 106-42-3, $>98\%$ purity, Fluka Analytical, München, Germany.

^[19] CAS 120-82-1, 99% purity, Alfa Aesar, Kandel, Germany.

^[20] CAS 128-37-0, $\geq 99\%$, Merck, Darmstadt, Germany.

^[21] Carl Roth, Karlsruhe, Germany.

^[22] PolymerSource, Quebec, Canada.

^[23] Transferpettor micro, Brand, Wertheim, Germany.

^[24] Wicom, Heppenheim, Germany.

^[25] Whatman QM-A, Kent, UK.

^[26] Hamilton 1701 N with 26s gauge, Bonaduz, Switzerland.

heptene (2,4Me9:1(1), RI = 841), 104 and 118 m/z for the PS pyrolysates styrene (Sty, RI = 895) and α -methylstyrene (α MeSty, RI = 981), respectively, and 82 and 95 m/z for PE n -alkadienes like 1,21-docosadiene (22:2(1,21), RI = 2187). The internal standard styrene-d5 (Sty-d5, RI = 892) was acquired at 109 m/z .

6.2.6 METHOD VALIDATION

The reference polymers used for external standardization and recovery experiments were analytical grade PE beads^[27], PP fragments^[28], and PS beads^[29] (see Chapter 4 for details).

The Py-GC/MS system was calibrated weekly against external standards (5–200 $\mu\text{g mL}^{-1}$ PE, PP, and PS dissolved in *p*-xylene/TCB at 150 °C) following the protocol outlined in Chapter 4. Calibration curves were evaluated for signal sensitivity (slope) and linearity (adj. R^2). Daily sample measurements were bracketed with 100 $\mu\text{g mL}^{-1}$ standards to correct for inter-day variations. The intra-day repeatability was determined by consecutive injections of 100 $\mu\text{g mL}^{-1}$ standards ($n = 12$). The internal standard PS-d5 added after sample extraction was used for continuous repeatability checks of sample measurements.

To evaluate the plastic recovery from soil, triplicates of two agricultural reference soils were spiked at 2 and 20 mg kg^{-1} of each polymer. The used reference soils were a loamy sand (8% clay, 16% silt, 76% sand) with a C_{org} content of 1.7% (LUFA 2.2)^[30] and a silty clay (47% clay, 41% silt, 12% sand) with 2.5% C_{org} (RefSol 06-A)^[31]. Instrumental and method LODs and LOQs were calculated from standard deviations (SDs) of signal intensities of low analyte concentrations (2 $\mu\text{g mL}^{-1}$) and blank reference soils ($n = 3$), respectively, in accordance with Chapter 4, DIN 32645 (2008), and Magnusson and Örnemark (2014). The selectivity against other potentially interfering non-target polymers was estimated from peak intensities of PE, PP, and PS pyrolysates in LUFA 2.2 soil spiked at each 40 mg kg^{-1} of the PET, PMMA, PVC, and TWP described in Chapter 4. In addition, a matrix-matched calibration was performed in LUFA 2.2 soil extracts in accordance with Magnusson and Örnemark (2014) to assess the effect of soil matrix on the calibration parameters.

6.2.7 QUALITY CONTROL

To prevent the risk of contamination, all laboratory equipment coming into direct contact with the sample or the extract solution was made of glass, metal, paper, or PTFE. PE, PP, or PS equipment was completely avoided. The worn laboratory coats were of 100% cotton. In addition, all samples and extracts were kept in closed vessels or covered with aluminum foil. The vessels were only opened under a fume hood.

The sample extraction was monitored with weekly procedural blanks that underwent the complete extraction procedure as the samples but without soil addition. Plastic contents in our procedural blanks were exclusively below the LOD.

6.2.8 DATA EVALUATION

Data processing and statistical analyses were conducted using R (version 4.1.0)^[32] with “data.table”, “magrittr”, and “envalysis”^[33] as main libraries. The results are given as mean \pm SD. Measurement repeatabilities are stated as percentage RSD.

^[27] CAS 9002-88-4, 500 μm average particle size, Alfa Aesar, Kandel, Germany.

^[28] CAS 9003-07-0, isotactic, $\leq 1000 \mu\text{m}$, Aldrich Chemistry, Taufkirchen, Germany.

^[29] CAS 9003-53-6, 250 μm average particle size, Goodfellow, Huntingdon, UK.

^[30] Landwirtschaftliche Untersuchungs- und Forschungsanstalt, Speyer, Germany.

^[31] Fraunhofer IME, Schmallenberg, Germany.

^[32] All data and R code to reproduce data processing and statistical tests are publicly available at DOI: [10.6084/m9.figshare.14742849](https://doi.org/10.6084/m9.figshare.14742849).

^[33] The package source is available at DOI: [10.5281/zenodo.4585730](https://doi.org/10.5281/zenodo.4585730).

Matches from the Open Specy FTIR library are reported as Pearson's r .

The potential matrix effect on the calibration was evaluated using signal suppression/enhancement (SSE) ratios (Eq. 6.1) which compare the slope of a calibration curve [$\text{mL } \mu\text{g}^{-1}$] prepared in solvent (α_{solv}) with that of the matrix-matched calibration (α_{matrix}) (Magnusson and Örnemark, 2014).

$$\text{SSE} = \frac{\alpha_{\text{matrix}} - \alpha_{\text{solv}}}{\alpha_{\text{solv}}} \quad (6.1)$$

6.3 RESULTS AND DISCUSSION

6.3.1 SOIL PROPERTIES

According to FAO (2014) classification, the investigated soils were identified as Anthrosols. The dominant soil textures were silty clay and clayey silt (Table 6.1), with sites 1, 3, and 4 showing the highest clay contents ($>30\%$) compared to the remaining sites. Sites 1–3 and sites 6–7 had C_{org} contents of 1.1–1.3% and 1.4–1.5%, respectively. The lowest C_{org} contents (0.9%) were found at sites 4 and 5. Soil N was $\leq 0.2\%$ across all sites. The soil pH was slightly acidic (6.6–7.0), and the EC ranged from 118 to $536 \mu\text{S cm}^{-1}$. The highest EC values were observed at sites 6 and 7.

Site	Cover (bottom to top)	Location	Clay [%]	Silt [%]	Sand [%]	Texture [‡]	C_{org} [%]	C_{total} [%]	N_{total} [%]	pH	EC [$\mu\text{S cm}^{-1}$]
1	Fleece (PP), perforated foil (PE)	Offenbach	34	53	13	Tu3	1.3	1.3	0.1	6.6	200
2	Mulch (PE), fleece (PP)	Offenbach	10	77	13	Ut2	1.1	1.3	0.1	6.8	138
3	Mulch (PE)	Offenbach	36	64	0	Tu3	1.2	1.4	0.1	6.8	147
4	Fleece (PE), perforated foil (PE)	Schifferstadt	32	67	1	Tu4	0.9	1.1	0.1	6.7	118
5	Fleece (PE), perforated foil (PE)	Schifferstadt	24	76	0	Ut4	0.9	1.1	0.1	6.9	236
6	Perforated foil (PE)	Landau	25	75	0	Ut4	1.4	1.6	0.2	6.8	510
7	Perforated foil (PE)	Landau	21	79	0	Ut4	1.5	1.6	0.2	6.9	536
8	Perforated foil (PE)	Landau	15	85	0	Ut3	1.4	1.6	0.2	7.0	289

[‡] In accordance with Sponagel et al. (2005); Tu = silty clay, Ut = clayey silt.

Table 6.1: Soil properties of experimental sites.

6.3.2 AGRICULTURAL PLASTIC COVERS

The fleeces that covered sites 1 and 2 were identified as PP as indicated by multiple C–H stretch deformations at $2950\text{--}2838 \text{ cm}^{-1}$ as well as CH_2 and CH_3 bends at 1455 and 1377 cm^{-1} , respectively (Open Specy FTIR library match: $r \geq 0.96$, see Figure B.1a for an exemplary FTIR spectrum). A shapeless broad peak between 1860 and 1660 cm^{-1} indicated the presence of carbonyl groups (Grause et al., 2020). The indistinct band between 1200 and 900 cm^{-1} may be attributed to C–O stretching in alcohols, acids, or ethers originating from a contamination with SOM or plastic aging (Fu et al., 2021). Complementary DSC showed crystallization temperatures at 114 and $116 \text{ }^\circ\text{C}$ and melting temperatures at 158 and $160 \text{ }^\circ\text{C}$. Between 381 and $400 \text{ }^\circ\text{C}$, the polymers started to decompose into methylalkenes characteristic of PP (Tsuge et al., 2011, Figure B.2a for an exemplary pyrogram).

By contrast, the fleece from sites 4 and 5 was made of PE ($r = 0.96$). The respective FTIR spectrum showed indicative CH_2 stretching between $2919\text{--}2915 \text{ cm}^{-1}$ (asymmetric) and $2851\text{--}2845 \text{ cm}^{-1}$ (symmetric, Figure B.1c). The crystallization and melting temperatures were 96 and $108 \text{ }^\circ\text{C}$, respectively. The degradation onset was $408 \text{ }^\circ\text{C}$ and triggered the formation of PE-specific triplets of n -alkadienes,

n-alkenes, and n-alkanes (Figure B.2c). All other covers, namely mulches and perforated foils from sites 2–8, were made of PE ($r \geq 0.86$, Figure B.1b,d,e). The carbonyl band at $1860\text{--}1660\text{ cm}^{-1}$ was visible in all samples but was most pronounced for the PE mulch from sites 2 and 3. However, crystallization temperatures ($100\text{--}113\text{ }^{\circ}\text{C}$) and melting temperatures ($110\text{--}122\text{ }^{\circ}\text{C}$) of the PE mulch were slightly higher than those of the PE fleece. The degradation onsets of the mulches and perforated foils ranged from 384 to $397\text{ }^{\circ}\text{C}$.

The qualitative analyses of volatile polymer additives and other polymer-associated compounds thermally desorbing from the agricultural films at $300\text{ }^{\circ}\text{C}$ revealed three omnipresent substances (NIST08 matches $>75\%$, see Figure B.3): These were propyl dodecanoate^[34], oleonitrile^[35], and 9-octadecenamamide^[36] (see Figure B.2 for exemplary chromatograms). In addition, the PP fleeces from sites 1 and 2 as well as the PE perforated foils from sites 4–8 contained traces of a di-*tert*-butylphenol^[37] which is an indicator for antioxidants (Hahladakis et al., 2018). Propyl dodecanoate and oleonitrile are lubricants probably added to agricultural plastic covers for easier spreading out on site. 9-Octadecenamamide is a known degradation product of hindered amine light stabilizers like Chimassorb 944 (Haider and Karlsson, 2001). No pesticides were detected in the plastic covers, probably due to the limited sensitivity of the qualitative analysis and/or their low thermal stability.

Complementary FTIR–ATR and Py-GC/MS confirmed that both plastic mulches and perforated foils were exclusively made of PE. The fleeces were of PE and PP, although PP is more common (Hamouz et al., 2011). All PE covers melted within the range of $109\text{--}125\text{ }^{\circ}\text{C}$ and degraded $>318\text{ }^{\circ}\text{C}$ as expected for virgin low-density PE (Beyler and Hirschler, 2002). Interestingly though, melting temperatures of the PP fleeces were 5 to $10\text{ }^{\circ}\text{C}$ lower than those of virgin PP ($165\text{--}170\text{ }^{\circ}\text{C}$) (Beyler and Hirschler, 2002; Tocháček et al., 2019). The degradation onset was not affected by this and comparable to virgin PP ($>315\text{ }^{\circ}\text{C}$) (Beyler and Hirschler, 2002). Decreasing melting temperatures may indicate the presence of additives or other impurities but could also be a first sign of polymer aging as similarly observed after 5–20 months of temperate weathering (Tocháček et al., 2019). This is consistent with the carbonyl groups identified via FTIR which are indicative for the photo-oxidation of polyolefins (Grause et al., 2020). In our study, fleeces and perforated foils were on the fields for about four months. The mulches were applied two years previously. The incipient aging concurred with the release of antioxidant di-*tert*-butylphenol from the PP backbone as indicated by TED-GC/MS. As di-*tert*-butylphenol was also released from PE perforated foils, it remains unresolved whether the presence of di-*tert*-butylphenol was material-specific or indeed triggered by polymer aging.

6.3.3 VISUAL PLASTIC ITEMS ON SITE

We visually identified 30 suspect items ($>2\text{ mm}$) during soil sieving. Subsequent FTIR–ATR analysis revealed six items as plastics. These were a black PE film ($r = 0.92$, Figure 6.3a) and four PS fragments ($r \geq 0.91$, Figure 6.3b) at the field center of site 5 (see Figure B.4 for the respective FTIR spectra). The PS showed characteristic peaks at 3024 , 1492 , and 694 cm^{-1} originating from aromatic C–H stretch and bend deformations. In the field center of site 6, a green PE film ($r = 0.92$, Figure 6.3c) was found. All other items were of natural origin including

^[34] CAS 3681-78-5 or CAS 10233-13-3.

^[35] CAS 112-91-4.

^[36] CAS 301-02-0.

^[37] For instance CAS 96-79-4.

invertebrate shells, stones or wood fragments, and cellulose fibers that were identified by Open Specy as chitin, resin dispersion, and cotton, respectively ($r \geq 0.82$, Figure 6.3d–f).

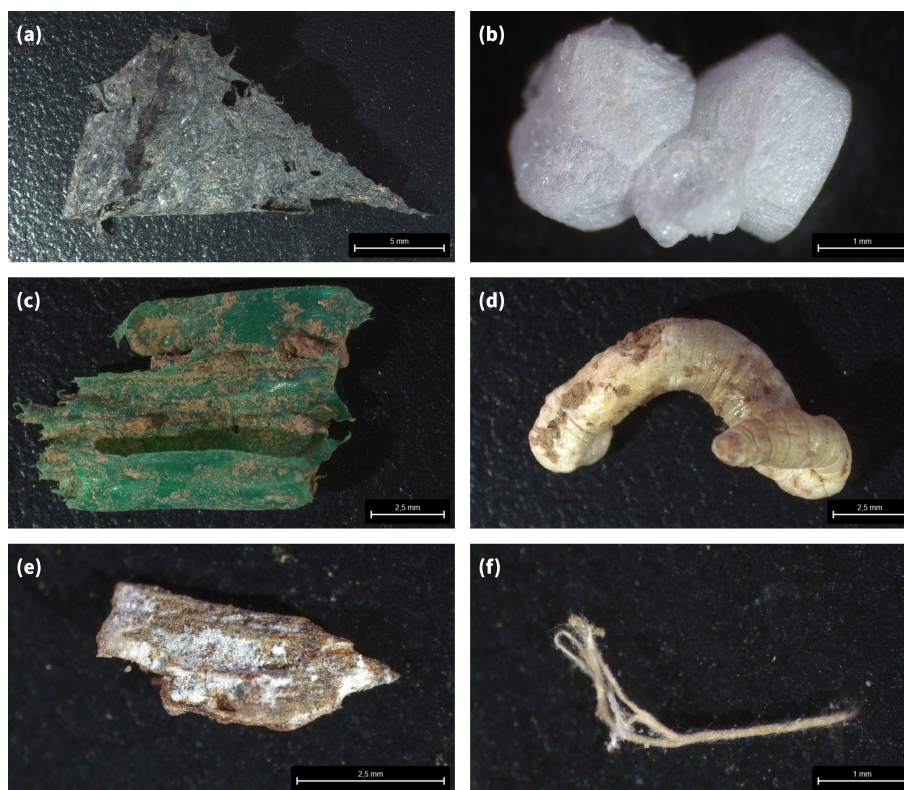


Figure 6.3: (a) PE film and (b) PS fragment from the field center of site 5, (c) PE film and (d) chitin shell from the field center of site 6, and (e) resin or natural fragment and (f) cotton fiber from the field edge of site 7; see Figure B.4 for the respective FTIR spectra.

In this respect, it is important to note that the visual identification of suspect items largely depends on the operator's experience and may thus lead to excessive over- or underestimation of particle numbers (Chapter 5). Furthermore, counting suspect items >2 mm in a 100 cm^3 soil core is hardly representative. We thus refrained from extrapolating our findings to particles kg^{-1} and intended visual identification to serve as a qualitative complement to subsequent Py-GC/MS quantification. Interestingly though, the plastic debris >2 mm was exclusively found at sites 5 and 6. None of the black and green PE or white PS fragments matched the applied white PE fleece and perforated foil in color or polymer type. This suggests an external source of plastic debris, for instance, from adjacent streets or other fields or residues from previous land use (Harms et al., 2021).

6.3.4 PY-GC/MS METHOD PERFORMANCE

The pyrolysates chosen for quantifying PE, PP, and PS were 22:2(1,21), 2,4Me9:1(1), and Sty, respectively, as they performed the best in terms of signal linearity (adj. $R^2 > 0.995$), instrumental LODs ($<10 \text{ ng}$), and measurement repeatability (RSD $<10\%$, Table 6.2). The *n*-alkadiene 22:2(1,21) was preferred over the respective *n*-alkene or *n*-alkane because of its higher selectivity for PE (Chapter 4). LUFA 2.2 exerted a negligible matrix effect of 16, -3, and -2% SSE on the selected PE, PP, and PS pyrolysates (see Figure B.5 for calibration curves). Method LODs were $0.7\text{--}1.2 \text{ mg kg}^{-1}$ in RefeSol 06-A and $1.9\text{--}3.3 \text{ mg kg}^{-1}$ in LUFA 2.2. The respective method LOQs ranged from 2.5 to 9.5 mg kg^{-1} (Table 6.3). A LUFA 2.2 soil

containing each 40 mg kg⁻¹ of potentially interfering, non-target PET, PMMA, PVC, and TWP did not induce significant false positive detections of PE, PP, or PS.

Table 6.2: Instrumental validity criteria of the Py-GC/MS method.

Polymer	Pyrolysate	adj. R ²	LOD* [ng]	RSD [%]
PE	17:2(1,16)	0.9912	9.0	11.3
	18:2(1,17)	0.9785	9.2	9.8
	19:2(1,18)	0.9965	5.6	11.3
	20:2(1,19)	0.9788	6.4	11.9
	21:2(1,20)	0.9897	10.0	12.8
	22:2(1,21)	0.9952	5.8	9.5
	23:2(1,22)	0.9709	7.2	11.2
PP	2,4Me9:1(1)	0.9997	4.6	8.9
PS	Sty	0.9980	6.6	3.5
	αMeSty	0.9866	19.4	11.5

* Instrumental limit of detection; RSD = relative standard deviation.

Polymer	Pyrolysate	LOD* [mg kg ⁻¹]	LOQ* [mg kg ⁻¹]	Interference† [mg kg ⁻¹]	Recovery	
					at 2 mg kg ⁻¹ [%]	at 20 mg kg ⁻¹ [%]
<i>LUFA 2.2</i>						
PE	22:2(1,21)	1.9	9.5	0.9±0.3	133±9	105±3
PP	2,4Me9:1(1)	2.9	2.9	0 ±0	70±10	93±5
PS	Sty	3.3	6.2	0 ±0	52±2	86±4
<i>RefeSol 06-A</i>						
PE	22:2(1,21)	1.2	9.5		30±20	50±10
PP	2,4Me9:1(1)	0.8	2.5		30±20	62±1
PS	Sty	0.7	6.2		0±0	12±5

* Method limits of detection and quantification; † introduced from 40 mg kg⁻¹ non-target polymers.

Table 6.3: Validation criteria of the extraction method.

The extraction of 20 mg kg⁻¹ plastic debris from LUFA 2.2 soil yielded recoveries of 86–105% (Table 6.3). PE was recovered the best whereas PS showed the lowest value. Recovering plastic debris at levels close to the method LOD (2 mg kg⁻¹) and below the respective method LOQs led to an overestimation of recovered PE (133±9%) while underestimating PP (70%) and PS (50%). Recoveries from RefeSol 06-A were generally lower: Whereas we still recovered 50 and 62% of the 20 mg kg⁻¹ PE and PP, respectively, recoveries dropped to 30±20% at the lower spiking level. Hardly any PS was recovered from RefeSol 06-A (<12%) irrespective of the spiking level.

As reviewed in Chapter 5, several studies have already evaluated their extraction procedures for various plastic debris from solid matrices using organic solvents like DCM or THF. In combination with quantitative Py-GC/MS, however, matrix interferences and false positive detections from organic matrix constituents or other non-target polymers should be closely monitored (Dierkes et al., 2019; Chapter 4). By combining density separation and solvent extraction with *p*-xylene/TCB, we obtained method LODs from blank LUFA 2.2 and RefeSol 06-A and interferences from non-target polymers equivalent to <3.3 mg kg⁻¹ PE, PP, and PS, which highlights the selectivity of our method. Dispersing soil aggregates with sodium hexametaphosphate prior to density separation further enabled the quantification of plastic debris potentially occluded in or masked by soil aggregates. The required filtration step, however, systematically excluded particles <4 μm that were not retained by the applied filter.

Inconsistent recoveries at a spiking level below the method LOQs of 2.5 to

9.5 mg kg⁻¹ challenged the sensitivity and robustness of our solvent-based approach. This particularly applied to the <30% PE, PP, and PS we recovered from RefeSol 06-A. While this clearly defines the quantitative limits of the method, our working range is still 10–100 times lower than that of previous applications involving solvent-based Py-GC/MS. Dierkes et al. (2019) and Okoffo et al. (2020), for instance, spiked 1 g of quartz sand and biosolids at 0.05–50 g kg⁻¹ of various polymers to evaluate their ASE with THF and DCM, respectively. Irrespective of the spiking level though, our PS recoveries from the clayey RefeSol 06-A were particularly low (<12%). This is in line with Wang et al. (2018) who found comparable recoveries after density separation of nano-sized PS from a silt soil. Luo et al. (2020) and Wu et al. (2020b) reasoned that SOM as well as Fe and Al oxides effectively retain PS particles in soil. The dramatic decrease in PS recovery may be attributed to interactions forming between the delocalized π electrons of the aromatic PS ring and SOM, Fe and Al oxides, or cations bound to the negatively charged surface of clay particles (Newcomb et al., 2017). During the density separation, the aggregated PS may have been preferentially sedimented, and thereby systematically excluded from subsequent solvent extraction. The addition of an anionic surfactant like sodium dodecyl sulfate or nonionic polysorbates during soil aggregate dispersion and density separation could counteract this, but potentially at the expense of introducing another source of PE contamination from the surfactants' n-alkane domains.

Based on the two reference soils tested and on previous work (Chapter 4), we considered our method sufficiently sensitive and quantitative for environmentally-relevant PE and PP levels exceeding the respective method LOQs. The 50% PE and 62% PP we recovered from RefeSol 06-A suggest a rather semiquantitative evaluation of soils with a clay content >47% and a C_{org} content >2.5%. PS is evaluated qualitatively for its low recoveries. These findings once more highlight the importance of specifically testing and evaluating analytical methods for plastic analysis with various soil types (Chapter 5). The extrapolation of specific validity criteria to field samples with a different texture and C_{org} composition thus remains difficult and requires careful interpretation.

6.3.5 PE, PP, AND PS DEBRIS IN SOIL

We detected plastic debris ≤ 2 mm exceeding the average method LOD of 1.5–2.0 mg kg⁻¹ in 15 out of 240 samples from six sites (Figure 6.4). This is equivalent to 6% positive detections. Soil from sites 1, 7, and 8 contained the most PE (10 findings) with single detections peaking at 19 and 35 mg kg⁻¹. Mean PE contents were the highest at the field margin of site 1 (10 \pm 10 mg kg⁻¹) and decreased below the method LOD in the field edge and the field periphery. Furthermore, PE contents were slightly higher in the track rows (furrows) than in the plant rows (ridges) of the field centers and edges of site 1. With 4–7 mg kg⁻¹, sites 7 and 8 showed maximum PE contents in the field periphery. Field centers, edges, and margins contained less than 2 mg kg⁻¹ PE. On these sites, differences in the PE contents between field track and plant rows were mostly indistinct. Sites 2–6 did not contain any PE above the method LOD. The PP findings were driven by single observations of 5–10 mg kg⁻¹ in the field centers of sites 2, 4, and 7. PS was identified twice, namely in the periphery of sites 4 and 5. Due to the poor PS recoveries, these findings are most likely underestimated.

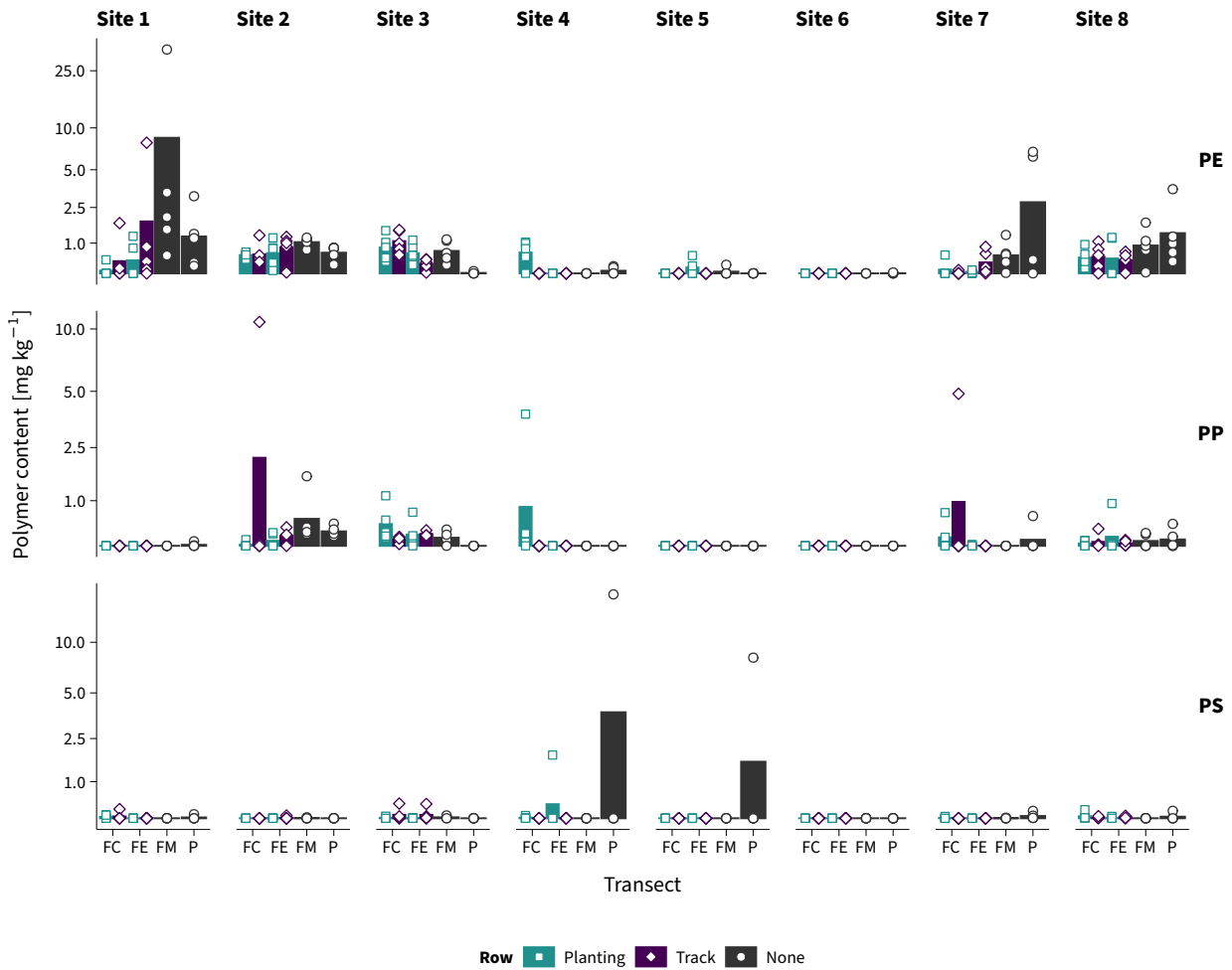


Figure 6.4: Log-scaled PE, PP, and PS contents (≤ 2 mm) at the field center (FC), field edge (FE), field margin (FM), and the periphery (P) of sites 1–8; dots represent single measurements, the underlying bar plot shows the transect average.

Interestingly, elevated PE contents occurred mostly at sites 1, 7, and 8 which were covered with $40 \mu\text{m}$ thick perforated foils. Sites 4–6 covered with thicker mulch films or perforated foils ($50 \mu\text{m}$) did not show any significant PE contamination. On the one hand, this is remarkable because the agricultural films were on site for four months only. On the other hand, the elevated plastic contents may have originated from another, potentially diffuse input source prior to plastic coverage.

Our results are yet in line with Zhang et al. (2016) who attributed elevated plastic emissions to the use of particularly thin agricultural films. In China, for instance, common film thicknesses are $6\text{--}10 \mu\text{m}$, while EU regulations stipulate agricultural covers thicker than $20 \mu\text{m}$ (EN 13655, 2018). This may also explain why studies conducted in non-EU countries often report extraordinarily high plastic levels in soil (Liu et al., 2014), particularly after long-term use of agricultural plastics (Huang et al., 2020; Zhang and Liu, 2018).

Regardless of the film thickness, the increased PE contents at the field margin of site 1 suggested that the mechanical stress of weighing the plastic covers down with soil or digging them in favored the local formation of plastic debris. The close contact with soil and exposure to sunlight may have accelerated polymer aging and embrittlement as indicated by our complementary DSC and FTIR–ATR

measurements. Due to the limited number of PE detections above the method LOD, we did not find a clear indication for the further translocation of plastic debris from the ridged plant rows to lower ground furrows. Tracing experiments by Laermanns et al. (2021), however, recently confirmed that the micro- and macrorelief of the soil surface may indeed favor the water erosion of plastic debris on a meter scale. Even at larger scales though, it remained unresolved to what extent the PE debris in the field periphery (mainly sites 7 and 8) originated from the covered field centers or whether it came from an external source via wind drift. Due to the ubiquity of products made from PE, such an external source cannot be excluded.

Although sites 1 and 2 were both fleeced with PP, only site 2 showed elevated PP contents. At the same time, PP was found at sites covered exclusively with PE for the last four months. Therefore, no clear association between PP detections and the seasonal use of plastic covers was established. This is striking because the fibrous structure of the PP fleece, together with the initial signs of aging detected via DSC and FTIR-ATR, made emissions of plastic debris particularly likely. Unexpectedly, these two study sites were thus most likely dominated by external sources like littering or previous land use rather than receiving plastic debris from the in situ fragmentation of fleeces.

This similarly applied to PS, which is not used for agricultural plastic covers (Bertling et al., 2021), and may thus serve as an indicator for external sources of plastic debris in soil. Another possible explanation for the PS findings at the two neighboring sites 4 and 5 may be a legacy contamination with PS. In the past, beads made from expanded PS were used for the conditioning and stabilization of horticultural soils (Maghchiche et al., 2010). However, it remained unresolved whether this was the case in the agricultural area investigated in this study.

Given that our investigated soils had a clay content of 15–36%, the obtained PE, PP, and PS contents were potentially underestimated by a factor of 1.5–2. Even though taking this uncertainty into account, the plastic contents detected in our study were still up to 100 times lower than the 820 mg kg⁻¹ PE, 40 mg kg⁻¹ PP, and 56 mg kg⁻¹ PS that Dierkes et al. (2019) obtained from a non-characterized roadside soil using a comparable solvent-based Py-GC/MS method. A recent modeling study by Brandes et al. (2021) estimated that plastic debris emitted from agricultural plastic covers may increase the plastic contents in agricultural soil by 5–9 mg kg⁻¹ per year. By contrast, conversions from particle counts and shapes to plastic masses resulted in contents of 0.1–1.2 mg kg⁻¹ in agricultural soil covered with plastics (Büks and Kaupenjohann, 2020). However, such conversions are increasingly discouraged for their high estimate errors (Chapter 5; Primpke et al., 2020). All this challenges comparisons since studies investigating plastic debris in agricultural soil have so far exclusively used particle-based microspectroscopic techniques. Nonetheless, our results are approximately in the same order of magnitude as previous findings but should be further corroborated.

6.4 CONCLUSIONS

The combination of soil aggregate dispersion and density separation with solvent-based Py-GC/MS enabled the simple, yet selective quantification of PE and PP debris in agricultural soil. Analyzing a sample amount of 50 g better accounted for the heterogeneous distribution of discrete plastic particles in the soil matrix. The

additional dispersion step further made plastic debris occluded in soil aggregates amenable to quantification. By contrast, poor PS recoveries potentially induced by that additional separation step challenged a reliable PS quantification.

We applied the new method to soil randomly sampled from four predefined transects located in and around eight agricultural fields covered with plastic films. This screening approach revealed first insights into the potential contribution of agricultural plastic covers to plastic pollution in soil: While PP fleeces and 50 μm thick PE films were not shown to emit plastic debris into their surrounding during their use, four months of covering with thinner perforated PE foils (40 μm thickness) was associated with elevated PE contents in and around the covered fields. Due to the ubiquitous use of plastic covers and potentially interfering external plastic sources, a causal relationship between the use of plastic covers and elevated plastic levels in soil needs yet to be shown, for instance, by conducting more controlled and systematic experiments.

The maximum plastic levels were 35 mg kg^{-1} and with that about 30 times higher than those previously reported for covered agricultural soil (Büks and Kaupenjohann, 2020) but several orders of magnitude lower than in a roadside soil (Dierkes et al., 2019). This could mean that current EU regulations (EN 13655, 2018) and recycling efforts for agricultural plastics are starting to take effect but should be further intensified. The long-term use of thin perforated foils, in particular, is likely to contribute to the accumulation and further distribution of plastics in the environment. The use of thicker and more durable plastic covers may be preferred to prevent this.

To scrutinize this, future research should aim for the continuous monitoring of plastic contents in soil. This may also include samplings of deeper soil and more sensitive screenings of polymer-associated compounds including additives and agrochemicals sorbed to the plastic covers. Advancing the field of mass spectrometric methods for the quantification of plastic debris in heterogeneous matrices will help to bridge the gap between modeling and monitoring, further the science-based regulation of agricultural plastic products, and contribute to their sustainable use.

7

FINAL DISCUSSION AND OUTLOOK

7.1 THERMOANALYTICAL APPROACHES FOR THE QUANTIFICATION OF PLASTICS IN SOIL

Mass-based information on the level of plastic pollution in soil is essential to link exposure data with modeling and effect data. Up to now, such data has remained largely missing for the lack of appropriate analytical methods. This has emphasized the need for further advances in analytical techniques for the mass-based quantification of plastic debris, particularly in heterogeneous samples like soil (Chapters 2 and 5).

A first proof-of-principle study using PET as a model (Chapter 3) demonstrated the potential of thermoanalytics for the mass-based plastic quantification in soil. The taken TGA/MS approach permitted the direct analysis of ground soil. This reduced sample preparation to a minimum and thus considerably sped up analysis times with regard to microspectroscopic methods. Microspectroscopic methods normally require an extensive sample preparation including multiple separation, cleanup, and filtration steps (for instance, Löder et al., 2017; Chapter 5). But TGA/MS also involved certain limitations: (1) Sample amounts of about 50 mg hindered the preparation of a representative sample prior to analysis, (2) the MS only detected PET contents $>0.7 \text{ g kg}^{-1}$, and (3) the absence of chromatographic separation potentially limited the simultaneous analysis of different polymers or polymer mixtures with overlapping degradation temperatures (Table 1.1). In the further course of the project, the participation in a round robin test revealed that the developed TGA/MS method was particularly suitable for distinguishing aromatic polymers like PS and PET from aliphatic ones such as PE and PP (Becker et al., 2020). The sum of aliphatic and aromatic polymers was each quantified accurately. Such a rough classification may suffice for simple prescreenings that aim at the identification of distinct plastic hotspots. Chemometric analyses of TGA/MS data, for instance, using principal component analysis and principal component regression may help to pursue a rapid identification and quantification of polymer mixtures by linking TGA and MS data better or by deconvolving interfering signals from other polymers and soil matrix (David et al., 2019). But this certainly requires further research, which is in line with Mansa and Zou (2021) who reasoned that TGA-based methods are still underutilized for the complexity of the generated

data but may provide a robust screening tool for future plastic analyses. However, advances in TGA/MS data analysis will most likely help measurement selectivity more than measurement sensitivity since the latter is physically restricted by the used MS.

Using Py-GC/MS instead allowed for the chromatographic separation of polymer analytes after pyrolysis and their selective quantification, as recently acknowledged by Jiménez-Skrzypek et al. (2021). The key to the method developed in Chapter 4 was the use of TCB to selectively dissolve the target analytes PE, PP, and PS prior to quantification. Solvent-based Py-GC/MS not only facilitated the preparation of dilution series and sample aliquots but also the extraction of the polymer analytes from the soil matrix. Thereby, up to 4 g of soil sample were analyzed while decreasing method LODs to 1–86 mg kg⁻¹. At such low plastic contents though, the method became sensitive to interferences from the soil matrix (Chapter 1). The interferences most likely originated from polymeric SOM fractions that were co-dissolved with the polymer analytes. These polymeric SOM fractions particularly interfered with the quantification of PE at levels <50 mg kg⁻¹. Dierkes et al. (2019) observed similar interferences using an ASE-based Py-GC/MS approach.

Since this problem could not be tackled from a mere instrumental perspective, the outcome of Chapter 4 involved a critical (re-)evaluation of existing sample preparation and analytical techniques for soil samples (Chapter 5). The current literature highlighted the importance of removing soil matrix by density separation and/or oxidative SOM digestion prior to Py-GC/MS analyses to reduce matrix interferences. However, such sample preparation methods usually require a final filtration step and thereby come at the expense of systematically excluding particles not retained by the filter. These lower size limits are typically 1–10 μm and thus result in a complete loss of the nanoplastics fraction. But the major finding of the literature research was that analytical methods should aim for sample amounts larger than several grams to account for the particulate nature of discrete plastic debris embedded in a highly heterogeneous soil. The review called for sample preparation techniques specifically tailored to soil, for instance, by including preparative measures for dispersing soil aggregates that potentially occlude plastic debris (Chapter 1; Zhang and Liu, 2018). Numerical simulations by Yu and Flury (2021) recently underpinned this. The authors recommended the sampling of at least five 1 × 1 m² grid squares to enable the representative quantification^[1] of ≤2 homogeneously distributed plastic particles kg⁻¹ agricultural topsoil (0–5 cm). Although particle-to-mass conversions are increasingly discouraged (Chapter 5), this approximates the minimum amount of plastic debris typically found in agricultural soil (Büks and Kaupenjohann, 2020). An expectably non-homogeneous plastic distribution would already require the sampling of more than 750 m² (Yu and Flury, 2021). As discussed in Chapter 5, the removal of such large quantities of fertile agricultural soil for trace plastic analysis may contradict sustainability efforts and economic interests of farmers and land owners. Hence, practicability and the desired measurement sensitivity need to be carefully balanced.

In the light of these findings, I further refined the solvent-based Py-GC/MS approach presented in Chapter 4. This mainly involved the combination of the previously developed method with an efficient yet simple sample preparation scheme (Chapter 6). The overall sample throughput of the complete procedure was 25 samples per week. In brief, 50 g of soil were aggregate-dispersed with aqueous sodium hexametaphosphate solution and density-separated with saturated NaCl solution.

^[1] Accepting 15% variation.

Moreover, *p*-xylene was added to the extraction mixture to increase polymer solubility (see Table C.1 for solubility tests of a difficultly soluble ultra high-density PE). Both measures helped to further decrease method LODs to 0.7–3.3 mg kg⁻¹ and reduce matrix interferences. At a soil C_{org} content of less than 2.5%, matrix interferences were exclusively below the LOD. The recovery of 20 mg kg⁻¹ PE, PP, and PS from a reference loamy sand was 86–105%. However, recoveries dropped below 70% in the reference silty clay or at a spiking level of 2 mg kg⁻¹. This was particularly pronounced for PS which was hardly detectable in the silty clay suggesting a rather qualitative evaluation of PS. While this clearly defined the quantitative limits of the developed method, it also demonstrated its applicability as a rapid screening tool for the selective quantification of PE and PP. This is remarkable because the majority of published solvent-based Py-GC/MS methods have hardly left the stage of method development and validation (Dierkes et al., 2019; Okoffo et al., 2020). As outlined in Chapter 5, solvent-based approaches are a constantly evolving field that not only couples batch extractions with Py-GC/MS (Chapters 4 and 6) but keeps exploring combinations of ASE and MWE with Py-GC/MS or ¹H NMR (Okoffo et al., 2020; Hermabessiere and Rochman, 2021; Nelson et al., 2019; Peez and Imhof, 2020). Yet, all these mass-based methods remain limited in their application range in terms of the analyzable target polymers and matrices. In this respect, future method refinements will need to increase method robustness and widen the analytical window, for instance, towards biodegradable plastics, particularly clayey soil, and organic-rich environmental matrices like forest soil and compost. This should include the testing of organic solvents or solvent mixtures for the dissolution of polymers other than PE, PP, and PS as well as adapting and optimizing sample preparation and purification techniques for challenging matrices. In addition, sample preparation techniques for nanoplastics in soil are still to be developed. As for TGA/MS, emerging machine learning-based peak identification and deconvolution algorithms could further support the analysis of Py-GC/MS data with extraordinarily high interferences or background noise (Cowger et al., 2020; Matsui et al., 2020). The typically more time consuming microspectroscopic methods could be applied complementarily, particularly to previously identified plastic hotspots, and provide additional information on particle shapes and sizes (Chapter 5).

7.2 PLASTIC DEBRIS IN PLASTIC-COVERED SOIL

The scientific literature reviewed in Chapter 2 suggested a successive enrichment of plastic debris originating from agricultural plastic covers. However, empirical evidence was scarce when the review was published in 2016 because the required analytical methods were still at an early stage of development. Meanwhile, particle-based plastic screenings have corroborated that initial assumption (Huang et al., 2020; Zhou et al., 2020). Huang et al. (2020), for example, found 5–24 years of continuous plastic mulching correlated with plastic counts of 60–1000 particles kg⁻¹ agricultural soil. The identified particles bore a resemblance to the applied plastic mulches. Still, mass-based information on the level of plastic pollution in agricultural soil remained missing.

Complemented by qualitative FTIR analyses of debris >2 mm (Cowger et al., 2021), my refined Py-GC/MS method enabled a first mass-based assessment of soil-associated PE and PP plastic debris ≤2 mm in topsoil previously covered with

plastic films (Chapter 6). As stated above, PS was only evaluated qualitatively for its low recovery. The screening revealed that the seasonal application of 40 μm thin, perforated films may already lead to a 30-fold increase in soil plastic contents (up to 35 mg kg^{-1}) compared to soil covered with thicker films (50 μm) and fleeces which hardly emitted any plastics above LOD. DSC and FTIR analyses of the applied plastic covers further showed first signs of polymer aging that may have triggered the formation of plastic debris.

In general, the plastic levels identified in Chapter 6 were about 30 times higher than those previously estimated for plastic-covered agricultural soil based on particle counts (Büks and Kaupenjohann, 2020) but several orders of magnitude lower than those measured in an exemplary roadside soil (Dierkes et al., 2019). Projections by Brandes et al. (2021) indicated that plastic debris emitted from agricultural plastic covers may increase the plastic contents in agricultural soil by 5–9 mg kg^{-1} per year. Although this mostly corresponds to the plastic levels $\leq 35 \text{ mg kg}^{-1}$ I found, the use of different methods and units impedes exact comparisons. Moreover, the equivocal distribution of plastic debris in and around the agricultural fields investigated in Chapter 6 did not allow for a reliable identification of plastic sources. This is in line with Zhou et al. (2020) who used FTIR microspectroscopy to screen Chinese farmlands for plastic debris. While the authors found twice as much plastic debris in plastic-covered soil than in noncovered soil, they also identified a large variety of plastics from other sources like irrigation and littering. Corradini et al. (2021) screened various land use types for plastic debris at a regional level. They found the highest numbers of plastic particles on cropland and grassland but were not able to track down the source of plastic pollution. This is most likely due to the ubiquitous use of various kinds of plastic products and their as of yet incompletely understood fate. In addition, most of the studies, including the one presented in Chapter 6, have so far restricted their samplings to the uppermost 5–10 cm of agricultural or industrial soils, quantified only selected polymers, and excluded nanoplastics. An unequivocal source identification will most likely require a more comprehensive monitoring. This requires extensive knowledge of the land use history on site, a more representative sampling scheme with a higher number of replicates per transect, and larger sample amounts (Section 7.1; Yu and Flury, 2021). Additional analytical techniques such as stable isotope analysis or inductively coupled plasma/mass spectrometry may help trace ^{13}C -labeled or metal-doped polymers (Mitrano et al., 2019).

Yet, the insights gained in Chapter 6 suggest that the short-term use of thicker and more durable plastic covers should be preferred over thin or perforated foils to limit future plastic emissions and accumulation in soil. Future research will not only need to systematically trace the major sources of plastic inputs back to different land use systems but also aim for a better understanding of the mass fluxes of plastic debris in and on soil as well as on landscape level.

7.3 FATE OF PLASTIC DEBRIS IN SOIL AND BEYOND

Soil and plastic debris share common characteristics like their particulate and polymeric structure (Chapter 1). These structural similarities feed back to their fate. Low-density SOM, for instance, is well-known to preferentially erode from agricultural fields (Lal, 2005; Rumpel et al., 2006). In the same way, fragments of low-density PE or PP covers ($\rho = 0.9\text{--}1.0 \text{ g cm}^{-3}$) are transported by wind (Rezaei

et al., 2019; Bullard et al., 2021; Ren and Ni, 2021) and water (Laermanns et al., 2021; Rehm et al., 2021) and are thus capable of traveling distances comparable to other non-volatile and water-soluble contaminants (Stubbins et al., 2021). Zhang et al. (2020) estimated that 96% of low-density PE debris resting on the soil surface (5° hillslope) readily runs off during heavy rainfall events (>300 mm) while the remaining 4% is retained in the soil. By contrast, Schell et al. (2022) only attributed 0.2–0.4% of plastic debris from a previous sewage sludge application to surface runoff in a semi-arid region. On the one hand, these contrasting findings may be explained by the different climatic conditions prevailing at the experimental sites of both studies. On the other hand, polymers with higher densities like PET ($\rho = 1.4 \text{ g cm}^{-3}$), which are frequently found in sewage sludge, may be retained better in soil than low-density PE ($\rho = 0.9 \text{ g cm}^{-3}$) due to gravitational sedimentation (Dong et al., 2021; O'Connor et al., 2019).

Once deposited, the plastic debris is likely to age and fragment further (Chapter 6), partially mix with soil, and become entrapped in soil pores or incorporated into soil aggregates (Rillig et al., 2017a). Zhang and Liu (2018) found 72% of plastic debris (0.05–1 mm) associated with soil aggregates of an arable soil. The polymeric nature of both plastics and SOM probably facilitates their mutual intermolecular stabilization and heteroaggregation (Schaumann, 2006; Luo et al., 2020). Dependent on the polarity of the respective polymer, electrostatic or van der Waals interactions may dominate (Luo et al., 2020). Due to an increased surface-to-volume ratio, small particles are most likely better stabilized than larger particles. In line with this, field-scale rainfall simulations showed that 250–300 μm high-density PE particles eroded faster than those of 50–100 μm size (Rehm et al., 2021). Column experiments by Wu et al. (2020b) indicated that PS nanoplastics (100 nm spheres) are effectively immobilized by Ca^{2+} and Fe or Al oxides but may be remobilized at a soil pH >9.

Advective transport of plastic particles through the soil column was not observed in Chapter 6 since the soil sampling was restricted to the uppermost 5 cm. However, vertical plastic transport is often <50% lower than conservative tracers and thus mostly limited to the uppermost 10–25 cm of the soil anyway (Keller et al., 2020; Wu et al., 2020b). Instead, plastic debris is rather transported to deeper soil via tillage, bioturbation, and preferential flow through soil cracks and earthworm burrows (Rillig et al., 2017b; Yu et al., 2019; Li et al., 2021a; Heinze et al., 2021). Preferential flow may eventually make plastic particles reach agricultural drainage systems (Bigalke et al., 2022) or groundwater where saturated conditions could promote their mobility^[2]. Under such saturated conditions, spherical particles were shown to be more mobile than fragmented or fibrous ones, particularly if the size of the plastic particles is lower than that of the medium (Waldschläger and Schüttrumpf, 2020). Worst case projections by Waldschläger and Schüttrumpf (2020) indicated a maximum infiltration depth of spheres in medium gravel of about 2 m when applying an immense water flow of $150 \text{ L min}^{-1} \text{ m}^{-2}$ for 1 h. Plastic fragments and fibers infiltrated less than 10 cm into matrices with smaller particles sizes like fine gravel, medium sand, or coarse silt. This may also explain why elevated microplastic levels of up to 80 particles L^{-1} groundwater have so far only been detected in the immediate vicinity of heavily contaminated sites such as landfills (Manikanda Bharath et al., 2021). Groundwater wells were virtually free of plastics (Mintenig et al., 2019). Yet, agricultural drainage systems may bypass the natural particle retention of the soil and favor the transfer of plastic

^[2] See Ren et al. (2021) for a review on plastic fate at the soil–groundwater interface.

debris to adjacent water bodies (Bigalke et al., 2022).

Hence, current research suggests that:

- Plastic particles larger than soil particles and less dense than the soil bulk density are preferentially eroded, particularly at extreme weather events.
- If not entrained by preferential flow, smaller plastic debris with a density close to the soil bulk density may be retained more easily and accumulate in soil.
- Nanoplastic mobility probably depends on the prevailing soil physicochemical properties such as ionic strength, pH, and the presence of Fe and Al oxides; but this requires further research.

This indicates that the low-density plastics >2 mm identified in Chapter 6 were probably rather mobile when released from the plastic covers. Upon fragmentation into debris ≤ 2 mm, they may become increasingly incorporated into the bulk soil and accumulate there. The continuous use of agricultural plastic covers as well as sewage sludge applications were in fact already shown to accumulate plastic debris in agricultural topsoil (Huang et al., 2020; Corradini et al., 2019b)^[3]. Weber et al. (2021) even found plastic debris at 2 m depth of a floodplain soil that was dated back to the 1960s. In this sense, plastic debris may become an artificial SOM fraction in the long term. Stubbins et al. (2021), for example, recently numbered plastic debris among soil C_{org} stocks. This concerns aged plastics in particular that will become more similar to the surrounding soil with time (Table 7.1). On the contrary, Rillig (2018) argued that plastic debris is too different in its physicochemical properties and function to be considered a part of SOM. Due to the recalcitrance of conventional plastics towards degradation, they will, if at all, only participate in the soil's long-term carbon cycle, probably comparable to the pyrogenic biochar components of *Terra preta* (Rillig et al., 2021). The contemporary contribution of plastic debris to soil functions and quality may, however, be limited if not detrimental. Moreover, changing environmental conditions and agricultural practices like tillage have the potential of remobilizing deposited plastics. This may particularly apply to nanoplastics which are still largely understudied. Apart from the plastics themselves, their capability of releasing additives and other polymer-associated compounds into the environment potentially contributes to the adverse effects on soil quality.

^[3] See Büks and Kaupenjohann (2020) for a comprehensive review on plastic debris in soil.

Table 7.1: Changes in polymer properties while aging (Ren et al., 2021; Zha et al., 2021).

Surface roughness	+
Microcracks	+
Tensile strength	–
Crystallinity	+
Polarity	+
Molecular weight	–
Functional groups (COOH, C=O, C–OH, =CH)	+
Leaching of additives	+
Sorption capacity	+

7.4 EFFECTS OF PLASTIC DEBRIS ON SOIL QUALITY

While the effects of agricultural plastic covers on soil quality are extensively discussed in Chapter 2, the potential effects of plastic debris accumulating in soil were virtually unknown at the time of writing. Current reviews point out that plastic debris may affect soil quality either directly or indirectly, namely mediated by changes in the soil's physicochemical properties and microstructural environment (Zhang et al., 2021c; Rillig et al., 2021; Wang et al., 2022). Changes in the soil's microstructural environment could then trigger adverse effects on the soil microbial community, plant growth, net primary production, and litter decomposition (Rillig et al., 2021; Mbachu et al., 2021; Qi et al., 2020).

De Souza Machado et al. (2019), for instance, spiked a loamy sand at 2 and 20 g kg⁻¹ PET fibers, PA beads, and PE, PP, PS, and PET fragments (8–5000 μ m

size) and assessed various soil quality criteria after 12 weeks of incubation. Fragments and fibers decreased the soil bulk density by up to 20% and thereby significantly altered the soil structure. The water holding capacity increased by 10–40%; the effect was most pronounced for PET fibers. Evapotranspiration and the fraction of water stable aggregates were reduced by up to 60 and 25%, respectively, in the presence of PET fibers and PA beads. These changes in the soil water dynamics are probably SOM-dependent (Zhang and Zhang, 2020; Liang et al., 2021) and propagated to an increase in soil microbial activity^[4] and root and bulb growth of *Allium fistulosum*, the spring onion (de Souza Machado et al., 2019). In general, the effects observed by de Souza Machado et al. (2019) were more pronounced for fibers and beads whose shape considerably differs from natural soil particles^[5]. Film debris was not assessed. But a meta analysis by Gao et al. (2019) found adverse effects of residual plastic films on crop yield at levels $>24 \text{ g m}^{-2}$ agricultural soil. Although inconsistent units impede detailed comparisons, this may approximate $0.4\text{--}1.0 \text{ g kg}^{-1}$ when assuming a homogeneous plastic distribution in the uppermost 5 cm soil layer with a bulk density range of $0.9\text{--}2.0 \text{ g cm}^{-3}$ (Horn, 2016). The effect levels reported by de Souza Machado et al. (2019) and Gao et al. (2019) are thus about 1–3 orders of magnitude higher than the plastic contents I measured in previously plastic-covered soil ($\leq 35 \text{ mg kg}^{-1}$, Chapter 6). This indicates a limited impact of the found plastic debris on soil quality and productivity. However, it is worth noticing that my solvent-based Py-GC/MS approach only covered PE, PP, and PS, which are the most abundant polymers (Chapter 1), but may have underestimated total polymer contents.

Büks et al. (2020) comprehensively reviewed the current state of research on the effects of plastic debris towards the multicellular soil fauna. The authors inferred that nematodes, gastropods, and rotifers responded the most sensitively to plastic levels $\leq 100 \text{ mg kg}^{-1}$ (for instance, Kim et al., 2020; Song et al., 2019). By contrast, springtails and earthworms were more robust and required barely realistic plastic contents of $>1 \text{ g kg}^{-1}$ to induce adverse effects (Ju et al., 2019; Ding et al., 2021; Lahive et al., 2019). Beetles, termites, ants, and mites remained largely unaffected by plastic debris (for instance, Peng et al., 2019; Zhu et al., 2018). The observed effects were mostly sublethal and included changes in the gut microbiome, oxidative stress, metabolic malfunctioning (Ju et al., 2019; Chen et al., 2020b; Rodríguez-Sejjo et al., 2018), avoidance (Ding et al., 2021), or a reduced motility, growth, or reproduction (Boots et al., 2019; Lahive et al., 2019). In line with the findings by de Souza Machado et al. (2019) discussed above, smaller and more irregularly shaped particles like fragments and fibers tended to be more ecotoxicologically active than larger and spherical particles; yet, PS microbeads still dominate effect studies (Büks et al., 2020). The polymer type appears to be less influential (Rillig and Lehmann, 2020), which may be different for nanosized particles, though (Rillig et al., 2019). However, particle shapes and sizes were not assessed in Chapter 6 and would have required a complementary particle-based analysis.

Baho et al. (2021) criticized that the vast majority of effect studies have focused on single species so far and were rather short-term (30 d). The authors advocated for longer-term multispecies and ecosystem level studies to prevent an “ecological surprise”; this is when ecosystems behave fundamentally differently than previously anticipated from smaller-scale laboratory or mesocosm experiments. Despite the desire for more realistic testing, the majority of studies applied plastic contents far beyond realistic exposure levels (Büks et al., 2020). The actual contribution of

^[4] See also de Souza Machado et al. (2018).

^[5] See also Rillig et al. (2019) and Lehmann et al. (2021).

plastic debris to the degradation of soil ecosystem functioning therefore remains incompletely understood. This uncertainty is also because effect studies typically refer to plastic contents on a mass basis while the greater part of exposure studies reports particle counts (Leusch and Ziajahromi, 2021). Here, the mass-based Py-GC/MS method developed in Chapters 4 and 6 might be particularly useful for the harmonization of effect and exposure data.

A first risk assessment recently conducted by Jacques and Prosser (2021) estimated environmental exposure distributions ($n = 48$) and species sensitivity distributions ($n = 37$) by converting published no observed and lowest observed effect particle masses to counts. Contrary to the reasoning by Büks et al. (2020), particle sizes or shapes were not considered. The hazardous plastic levels at which 5% of species would be affected were 230 and 160 particles kg^{-1} based on no observed and lowest observed effect levels, respectively. These species were *Caenorhabditis elegans*, a model nematode, garden cress (*Lepidium sativum*), and *Aspergillus flavus*, a pathogenic fungus. The hazardous levels were exceeded in about 60% of the investigated exposure studies. At 8100 particles kg^{-1} , this is the 95th percentile of the environmental exposure distribution, 22–28% of species would be affected. The three sites exceeding that level were industrial, urban, and agricultural. While this is certainly alarming, the results contrast previous mass-based studies that scarcely identified adverse effects on soil organisms at realistic exposure levels (Büks et al., 2020). The distributions calculated by Jacques and Prosser (2021) highly depend on the quality of the input data and are subject to great uncertainties due to the underlying mass-to-particle conversions as emphasized in Chapters 5 and 6. For example, some of the included studies conducted their ecotoxicity tests in aqueous soil solution, did not state the polymer used, or reported plastic levels per unit area. Therefore, more systematic and unit-harmonized research is indispensable for a comprehensive eco(toxico)logical risk assessment. This should then also acknowledge plastic shapes, sizes, and aging and include interactive effects with other stressors like polymer-associated compounds.

7.5 INTERACTION OF PLASTIC DEBRIS WITH ADDITIVES, AGROCHEMICALS, AND OTHER PLASTIC-ASSOCIATED COMPOUNDS

The interaction of plastic debris with organic substances, be it additives or (agro)-chemicals from external sources, is still understudied and to some extent contradictory^[6]. In fact, the majority of polymers including agricultural plastic covers contain additives like color pigments, antioxidants and light stabilizers, plasticizers, lubricants, or flame retardants (Chapters 2). But contrary to the assumptions made in Chapter 2, the qualitative additive screening of the plastic covers via TED-GC/MS (Chapter 6) did not show any PAEs but UV stabilizers and lubricants only. This is not surprising as PAEs are plasticizers mostly added to PVC rather than PE or PP (Walters et al., 2020). Lubricants may facilitate spreading the covers out on site and UV stabilizers prolong their lifetime when exposed to sunlight (Chapters 2 and 6). However, leaching of additives from the polymer backbone and their release into the surrounding soil are often hypothesized (Chapter 2; Pathan et al., 2020; Zhang and Xu, 2020) and modeled (Zhang et al., 2021a) yet hardly observed in field studies (Qi et al., 2020). Li et al. (2021b), for instance,

^[6] See Xiang et al. (2022) for a detailed overview.

found up to five times higher PAE contents in greenhouse soil than in noncovered soil. But no clear correlation was established with the amount or type of plastic debris found, suggesting another input source or factor driving their distribution^[7]. This could be seed coatings, impure agrochemicals, or changing environmental conditions remobilizing legacy contaminations. Other additives than PAEs are typically added to polymers in much smaller quantities (Hahladakis et al., 2018) so that their detection after desorbing and dispersing into the surrounding is even more challenging (Chapter 6).

In contrast to polymer additives desorbing from the polymer backbone, sorption of organic compounds to plastic particles has been more systematically investigated. Hüffer and Hofmann (2016), for example, studied the sorption behavior of numerous apolar, monopolar, and bipolar organic pollutants to PE, PVC, PA, and PS particles in aqueous solution. Aromatic compounds were shown to preferentially interact with PS via π - π stacking. Interactions with PE were mostly driven by migration of the organic compounds into the polymer bulk phase, while surface interactions dominated with PA and PVC. Similarly, a PE mulch sorbed about 23% of various agrochemicals in aqueous solution, which additionally slowed down their degradation by 30% (Beriot et al., 2020). The sorption potential correlated well with the K_{ow} of the agrochemicals (Beriot et al., 2020; Wang et al., 2020; Šunta et al., 2020; Lan et al., 2021). The molecular mechanisms controlling the sorption process were hydrophobic partitioning and electrostatic forces (Tourinho et al., 2019; Lan et al., 2021). However, Ramos et al. (2015) already showed that migration of pesticides to/from PE covers may be bidirectional. The state of the dynamic equilibrium depends on the organic substance of interest and its polarity (K_{ow}) as well as the polymer type, the degree of polymer aging, interactions with other environmental compartments, and prevailing environmental conditions. Diffusion models by Castan et al. (2021), for instance, indicated that the sorption of organic contaminants to plastics is only stable for sorbates with a $\log K_{ow} > 5$. An increase in the soil water content, however, mobilized the disinfectant triclosan ($\log K_{ow} = 4.8$) previously sorbed to PE (Chen et al., 2021).

In aqueous solution, UV-aged PS particles sorbed up to 10 times less organic pollutants than virgin particles (Hüffer et al., 2018a; Hüffer et al., 2018b). This was attributed to the oxidation of the polymer surface as indicated by an increased number of carbonyl moieties. By contrast, the broad-spectrum insecticide fibronil sorbed best to polymers containing carbonyl groups (Gong et al., 2019).

An agricultural sandy loam spiked at 100 g kg^{-1} PE reduced the soil's overall sorption capacity towards the herbicides atrazine and 2,4-D by half compared to blank soil (Hüffer et al., 2019). However, this effect was most pronounced at pH 3–5, and PE contents were particularly high. In line with this, 100 g kg^{-1} PE, PP, and PS decreased the sorption of diazepam, a sewage sludge-borne anxiolytic, to sandy loam and silty clay (Xu et al., 2021). At 10 g kg^{-1} PE, PP, and PS, however, the sorption potential of phenanthrene increased. Phenanthrene sorbed best to PE, followed by SOM, PP, and PS. Polymers pretreated with SOM were decreased in their sorption capacity (Xu et al., 2021). By contrast, Ateia et al. (2020) assessed the interaction of atrazine, acetamidophenol, and two perfluoroalkyl compounds with eight different polymers and kaolin in the presence of dissolved organic matter. The sorption to kaolin was generally about one order of magnitude lower than the sorption to polymers. Recycled plastics and polymers inoculated for two weeks with organic matter sorbed a higher amount of organic substances than virgin

^[7] See also Billings et al. (2021) for a comprehensive review on plasticizers in the terrestrial environment.

polymers. In line with this, sorption to PE debris reduced the adverse effects of phenanthrene and anthracene towards bacteria (Kleinteich et al., 2018). On the contrary, the bioconcentration of perfluoroalkyl compounds in earthworms doubled in the presence of PVC particles (Sobhani et al., 2021).

Current literature indicates that the desorption and release of polymer additives into the surrounding soil requires more basic research. The sorption of other, non-additive organic compounds like agrochemicals or pharmaceuticals to plastic particles is understood better but their competitive sorption potential in the presence of different soil constituents and polymer types should be assessed more systematically. All in all, the sorption behavior of organic substances to plastic particles seem to depend mainly on the polarity of the sorbing organic substance (K_{ow}), the quantity and type of the polymer present, and the soil characteristics including its texture, water content and cation exchange capacity. For more comprehensive quantitative structure–activity relationships, other important physicochemical parameters like the surface tension or the specific surface area of the soil, sorbent polymers, and potential sorbates should be investigated further. In comparison to the plastic contents reported in Chapter 6 ($\leq 35 \text{ mg kg}^{-1}$), sorption studies have so far used >20 times higher plastic contents. As opposed to the assumptions made in Chapter 2, such low plastic contents are suggested to have only a limited influence on the soil's overall (de)sorption potential. Nanoplastics with particularly high surface areas may need to be separately assessed though. Moreover, it is still unknown how plastic aging may affect the fate of polymer-associated compounds in the long term (Zha et al., 2021).

7.6 TOWARDS A SUSTAINABLE USE OF AGRICULTURAL PLASTIC COVERS?

Given the current uncertainties about the long-term fate and effects of plastic debris in the terrestrial ecosystem, a sustainable agriculture may be advised to act according to the precautionary principle (Rhodes, 2018; Backhaus and Wagner, 2020; Möller et al., 2020). This is not only to protect the environment but also agronomic revenues. Bertling et al. (2021) stated that German agricultural fields with plastic levels $>1 \text{ g kg}^{-1}$ become unattractive to farmers and thus practically lose their economic value. This coincides with the effect levels discussed in Section 7.4. However, subtle or long-term effects on the soil ecosystem may already occur at plastic levels $<1 \text{ g kg}^{-1}$. Overstepping certain, yet unknown “microplastic tipping points” is to be avoided (Qi et al., 2020).

In order to limit future plastic emissions into the environment, Thompson et al. (2009), Scalenghe (2018), and Rhodes (2018) proposed a holistic systems thinking approach that integrates plastic production, consumption, and disposal into a sustainable circular economy. As discussed in Chapter 2, this means:

- (1) Reducing plastic products and, if possible, replacing them with viable alternatives.
- (2) (Re)using plastic materials as long as possible.
- (3) Recycling the plastics at their end of life.

The FAO (2021) recently amended these three R's of waste management with the recommendation to refuse, redesign, and recover agricultural plastics. Refusing

means completely avoiding the use of a specific product if possible. A product redesign implies modifying plastics to facilitate their retrieval and waste management. In terms of redesigning plastics, Simon et al. (2021) additionally advocated for a greater durability of newly produced plastics that would virtually eliminate single use, an increased product safety, as well as a transparent labeling of biodegradable and bio-based plastics. The FAO's recommendation for energy recovery, by combustion of hardly recyclable plastics, is considered as a last resort to avoid landfilling (FAO, 2021).

Drastically reducing the application range of agricultural covers made from conventional plastics would probably decrease the global agricultural production (Chapter 2; FAO, 2021). Therefore, replacing conventional plastics with biodegradable alternatives or other, natural materials seems more practicable (Brandes et al., 2020) and is, in fact, increasingly implemented. Agricultural covers made of biodegradable polymers like PLA or starch blends already capture a market share of 7% in Germany (Bertling et al., 2021). However, the main challenge in the development of biodegradable agricultural covers remains: This is making them resistant to degradation while in use but ensuring their complete degradation under realistic environmental conditions at the end of life (Chapter 2; Bertling et al., 2021). The use of biodegradable plastic covers thus continues to bear the risk of leaving incompletely degraded plastic debris in the soil after the growing season (Sander, 2019; Viera et al., 2021).

At the same time, conventional PE mulches covering asparagus or strawberry cultivations ($\geq 50 \mu\text{m}$ film thickness) are already reused for up to 10 years. Thinner perforated foils or fleeces have shorter life times and are often replaced after one growing season (Chapter 6; Bertling et al., 2021). If not replaced, their low durability will make plastic emissions more likely over time. Zhang et al. (2022), for instance, recently showed that a reused $8 \mu\text{m}$ PE film emitted 16–27% more plastic than a new film. For their higher durability, thicker covers also have a greater chance of being removed intact after their use (Chapter 2), particularly if the soil is moist or has been wetted before retrieval. Therefore, the use of thicker covers may not only reduce the formation of plastic debris but also their potential for reuse.

The recycling of used plastic covers was challenging in the past for their contamination with soil and agrochemicals (Chapter 2). However, advances by the German recycling system “ERDE” recently enabled the retrieval, collection, and mechanical recycling of 50% of all agricultural plastic covers used across the country (Bertling et al., 2021; ERDE Recycling, 2021). Ideally, such initiatives should be extended to other countries in the future. China, for instance, still consumes the vast majority of agricultural plastics (Chapter 2; Mormile et al., 2017) while less than 10% are currently recycled (FAO, 2021).

Life cycle assessments show that conventional, petrochemically produced PE mulches emit 2.7 and 3.6 kg CO₂ kg⁻¹ mulch when landfilled or incinerated, respectively. Mechanical recycling has a carbon footprint of 1.2 kg CO₂ kg⁻¹ PE mulch (Bos et al., 2008). In contrast, biodegradable and bio-based alternatives like PLA have the potential to close material cycles and thus reduce their carbon footprint to up to 1.7 kg CO₂ kg⁻¹ (Koller, 2019; Rezvani Ghomi et al., 2021). At least for PLA, such a low carbon footprint is achieved only if the PLA is mechanically recycled instead of being left for degradation. This is because polymer production is still energy intensive and may cause greenhouse gas emissions of up to 2.8 kg CO₂ kg⁻¹ PLA (Rezvani Ghomi et al., 2021; Altman, 2021). Further

research and development is thus needed to make the production of biodegradable and bio-based polymers more energy efficient (Viera et al., 2021). This may also include the intelligent (re)design of novel polymers that are optimized towards low energy production and recycling (Viera et al., 2021; Korley et al., 2021; Kakadellis and Rosetto, 2021) while avoiding competition with food supplies (Rhodes, 2018). The latter could be tackled with novel biotechnological processes that, for example, convert waste or sewage sludge to polyhydroxybutyrate using genetically modified bacterial strains (Leong et al., 2021). However, it is still largely unknown how and to what extent biodegradable agricultural covers and plastic debris at various stages of decomposition may affect the soil ecosystem (Sander, 2019; Qin et al., 2021; Altman, 2021). Adding fresh and easily available carbon sources to soil is well known to stimulate the decomposition of older and more recalcitrant SOM; an effect called “priming” (Chen et al., 2020a).

For agricultural plastics escaping the material cycle and entering the environment, Bertling et al. (2021) suggested the implementation of some sort of “emergency degradation” that ensures the decomposition of plastics lost in the field for at least 50 years. This, as well, would imply the development of new polymers or the modification of biodegradable polymers to resist degradation for a longer period of time. On the contrary, Scalenghe (2018) raised the question whether it may be generally acceptable to leave certain amounts of chemically inert plastics in the environment. This idea may have been motivated by the fact that the remediation and removal of plastic debris from soil is still at an early stage of development (Padervand et al., 2020) and will most likely come with unwanted side effects on soil quality and functioning.

For the lack of ready-to-use alternatives, a sustainable use of agricultural plastic covers should first and foremost aim to reduce plastic emissions by using fewer or more durable plastic covers that prevent the emission of plastic debris and thus long-term plastic accumulation in the environment (Chapter 2). The FAO (2021), for instance, recently recommended developing a voluntary code of conduct to make agricultural plastics more sustainable. In addition, the transition to a more plastic-aware agriculture could be guided by targeted policy and regulatory measures. While the EU has already banned agricultural plastic covers thinner than 20 μm (Chapter 6; EN 13655, 2018), Stubenrauch and Ekaradt (2020) elaborated that the current “command-and-control legislation” by the EU and Germany still insufficiently protects agricultural soil from plastic emissions. The authors came to the conclusion that the current legislation particularly neglects the monitoring and regulation of plastic debris ≤ 2 mm, which has so far been justified with restricted analytical capabilities. The analytical advances outlined in this dissertation (Chapters 3–6) may thus eventually contribute to a better regulation of plastic debris in soil.

7.7 CONCLUDING THOUGHTS

The aim of this dissertation was to scrutinize the extent to which agricultural plastic covers emit plastic debris into the surrounding soil. To this end, thermoanalytical techniques were assessed, developed, and validated. The final solvent-based Py-GC/MS method enabled the simultaneous and selective routine analysis of PE and PP debris in soil. PS was only assessed qualitatively for its low recovery. For PE and PP, the method had the clear advantage of delivering highly sensitive

mass-based information that could be readily compared with modeling or effect data. Applying the method in a first screening study indicated indeed that plastic covers were associated with elevated PE levels in agricultural topsoil, particularly if thinner and less durable films were applied. However, the ubiquitous use of plastic products made it difficult to pinpoint plastic covers as *the* source of plastic debris. Moreover, the solvent-based Py-GC/MS approach systematically excluded other polymers than PE, PP, and PS as well as nanoplastics so that total plastic levels may be higher. Yet, the found plastic levels were in agreement with previous reports but still several orders of magnitude lower than the reviewed effect levels. At the current state of research, the risk of plastic debris to soil organisms thus appears limited but may increase with more and nanosized plastics accumulating in the environment. This calls for precaution particularly because current literature suggests that adverse effects of plastic debris on soil life and quality largely depend on the size and shape of the plastics. Particle shapes and sizes cannot be assessed with the mass-based approach taken in this thesis and require complementary microspectroscopy of potential hotspots. Furthermore, the distribution processes and material fluxes of plastic debris in the terrestrial environment are still incompletely understood and need to be assessed in future, more systematic research. This should extend to other polymers including biodegradable plastics and nanoplastics which still lack appropriate analytical techniques.

8

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Appendices

A

EVALUATION OF THE TGA/MS SETUP

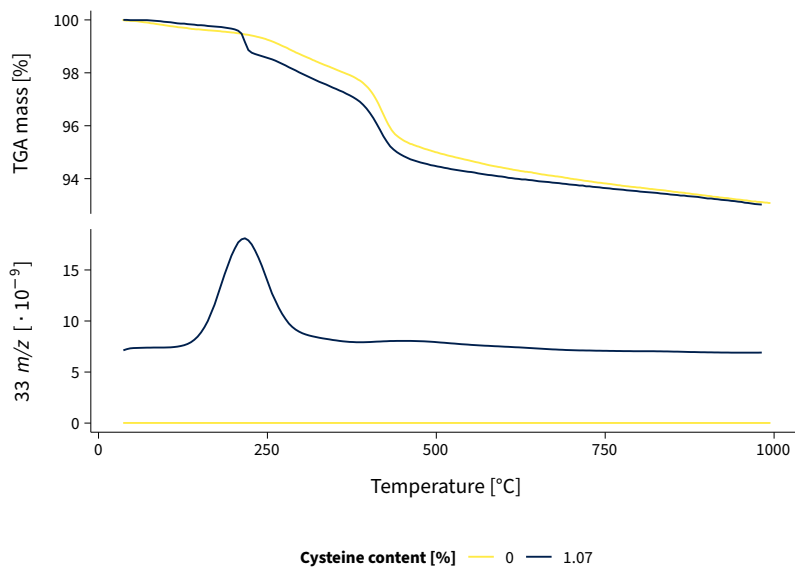


Figure A.1: Exemplary TGA curves and 33 m/z signals of PET in soil with and without addition of DL-cysteine (1.07%) as internal standard.

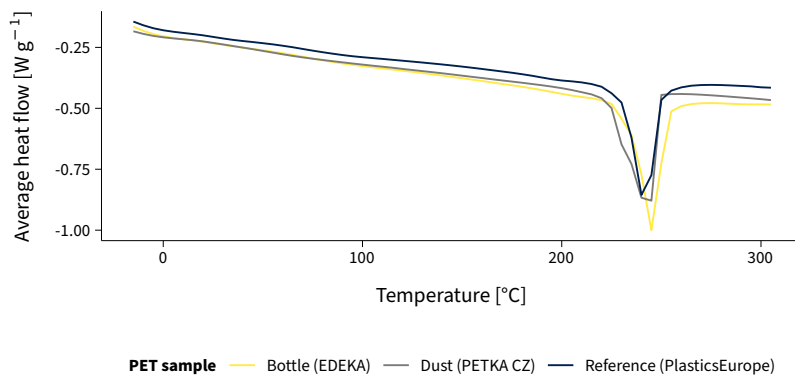


Figure A.2: Comparison of characteristic melting points (averages of triplicate DSC measurements) of bulk PET from a water bottle, ground PET recycle, and a PET reference.

Figure A.3: (a) Linear response of SH^- ($33\ m/z$) evolving from DL-cysteine pyrolysis in soil (adj. $R^2 = 0.969$, RSE = 8.96%) with corresponding (b) TGA curves.

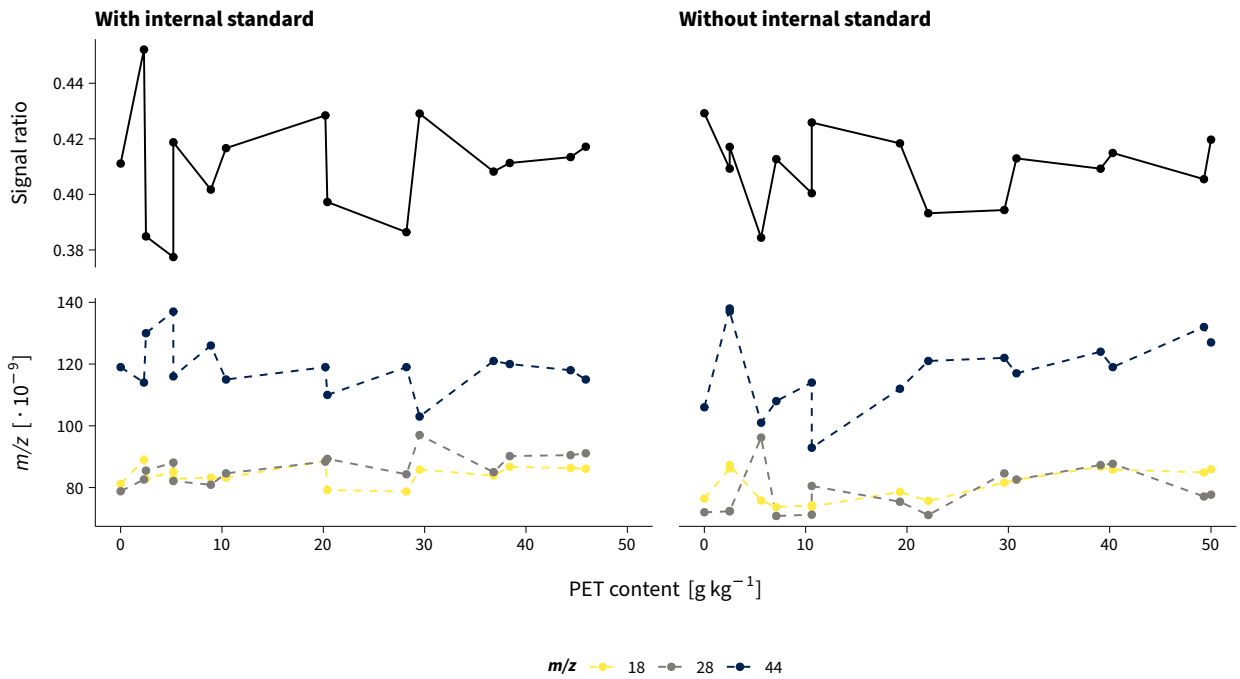
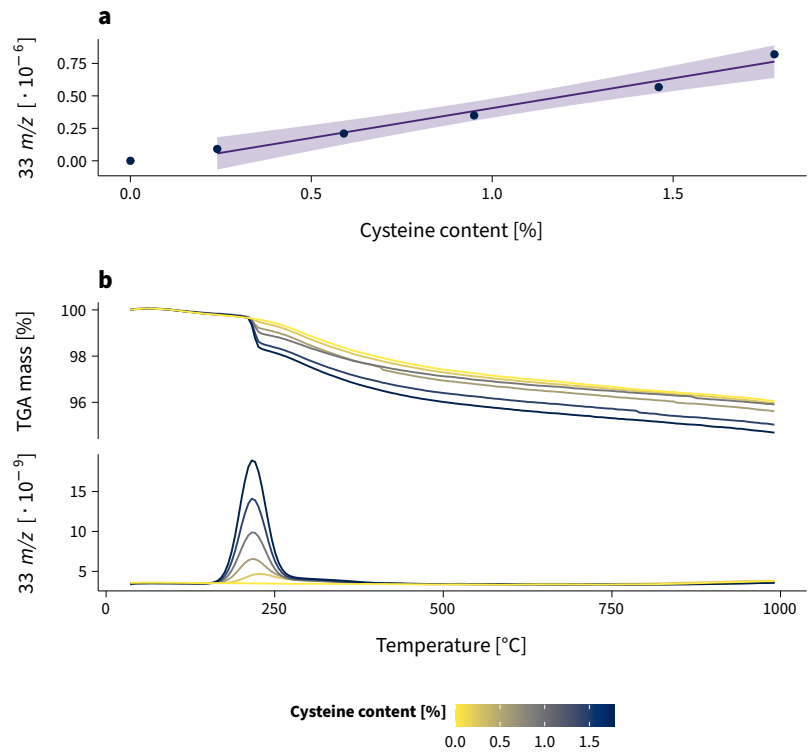


Figure A.4: Integrals of H_2O ($18\ m/z$), CO ($28\ m/z$), and CO_2 ($44\ m/z$) from control calcium oxalate hydrate pyrolyses after analyzing PET-spiked soil; signal ratio = $18\ m/z / (28\ m/z + 44\ m/z)$.

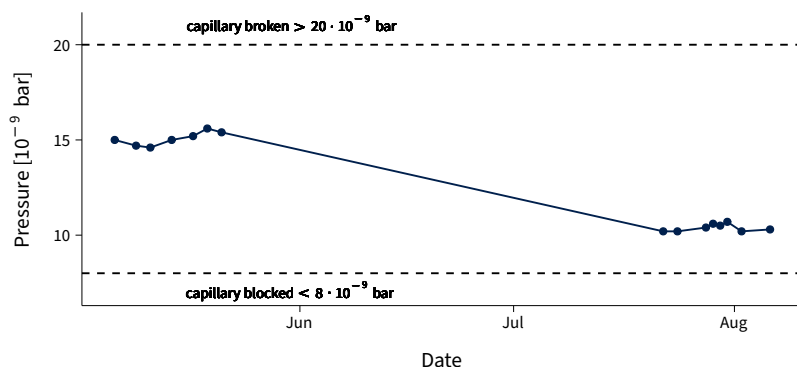


Figure A.5: Pressure measurements in the TGA capillary during analyses.

B

SUPPORTING INFORMATION ON THE SCREENING STUDY

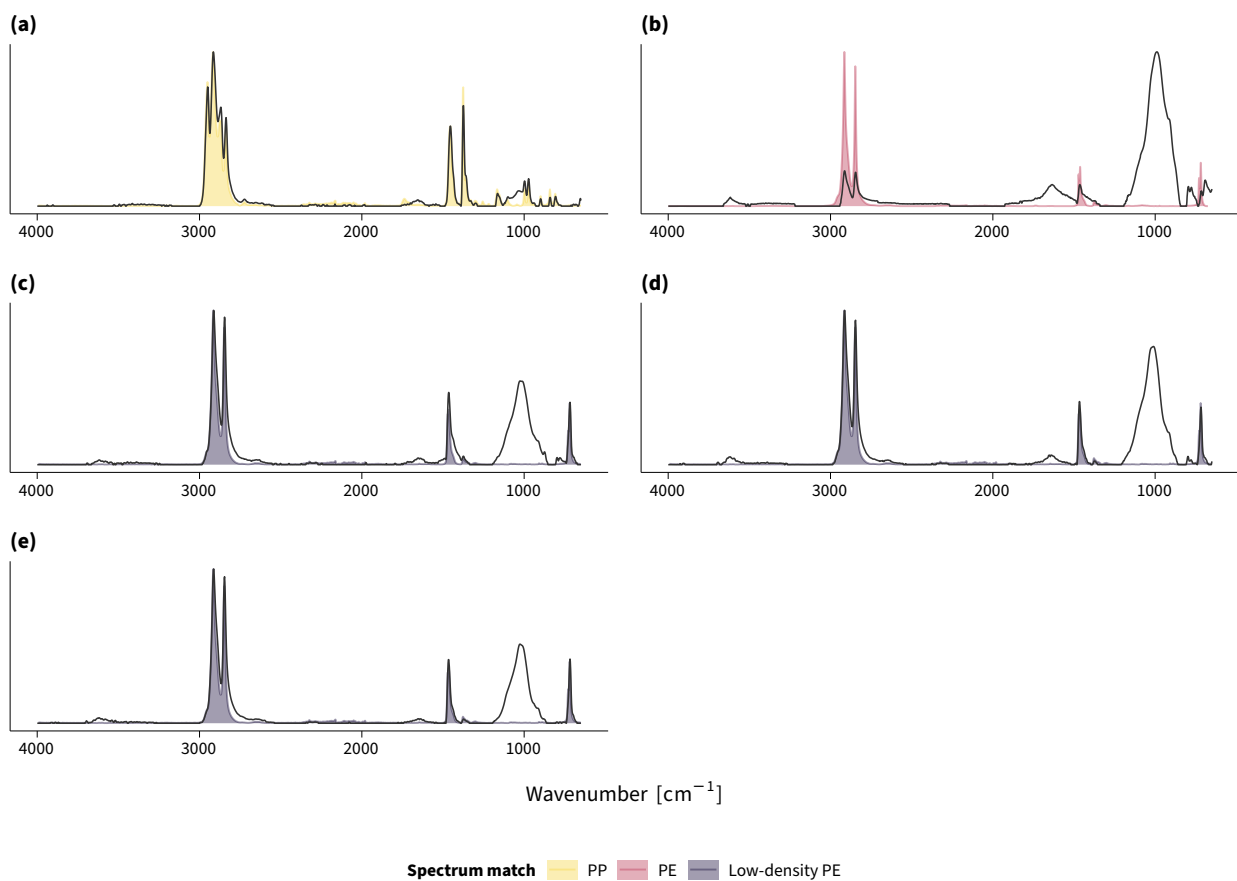


Figure B.1: Exemplary FTIR spectra of (a) the PP fleece from site 1, (b) the PE mulch from sites 2 and 3, (c) the PE fleece and (d) PE perforated foil from sites 4 and 5, and (e) the PE perforated foil from site 8. The measured FTIR spectra are in gray; the colored shades depict the respective Open Specy library match.

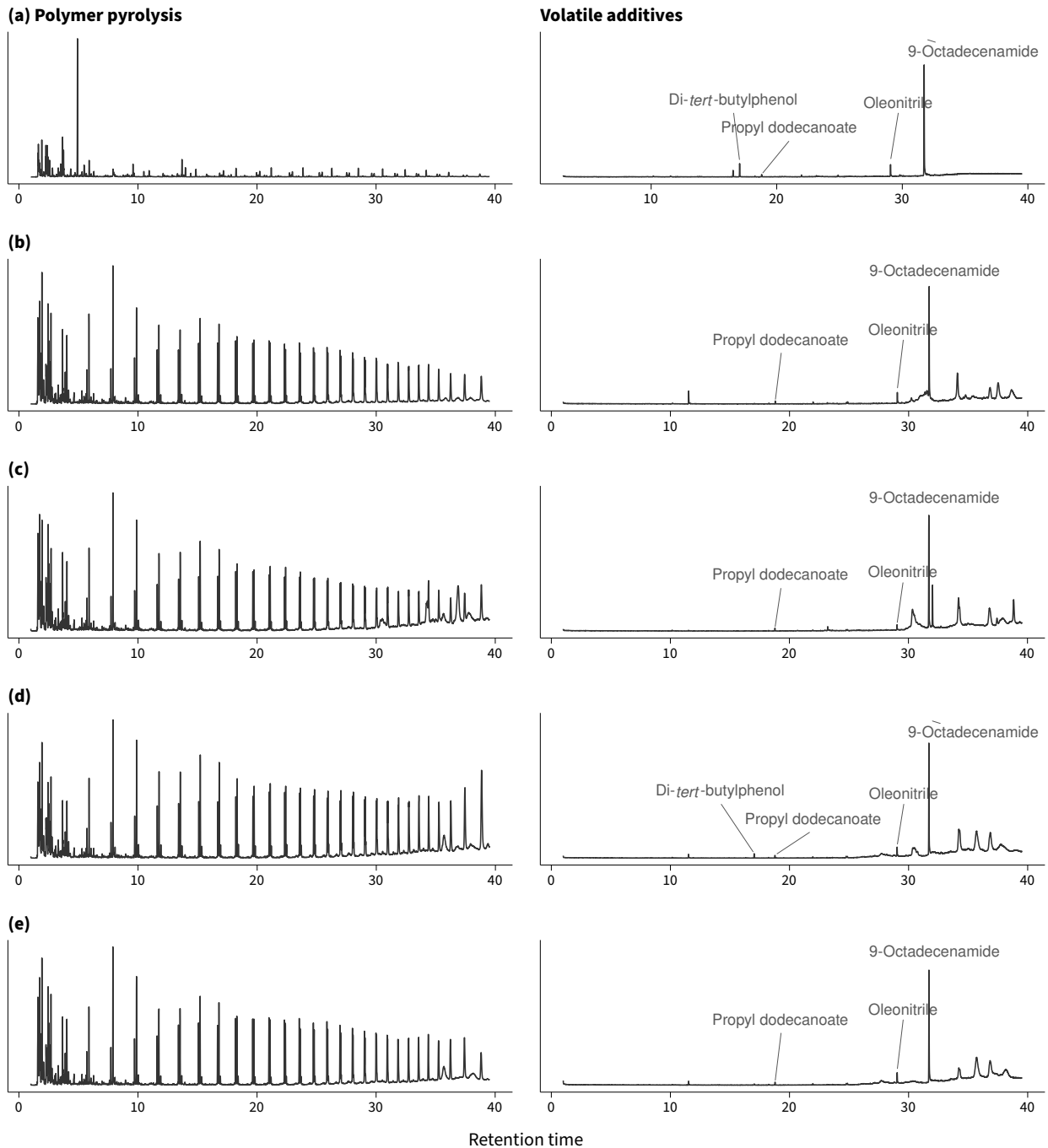


Figure B.2: Exemplary chromatograms of polymer pyrolyses (750 °C, left) and thermal desorptions (300 °C, right) of polymer additives; (a) PP fleece from site 1, (b) PE mulch from sites 2 and 3, (c) PE fleece and (d) PE perforated foil from sites 4 and 5, and (e) PE perforated foil from site 8; see Figure B.3 for mass spectra.

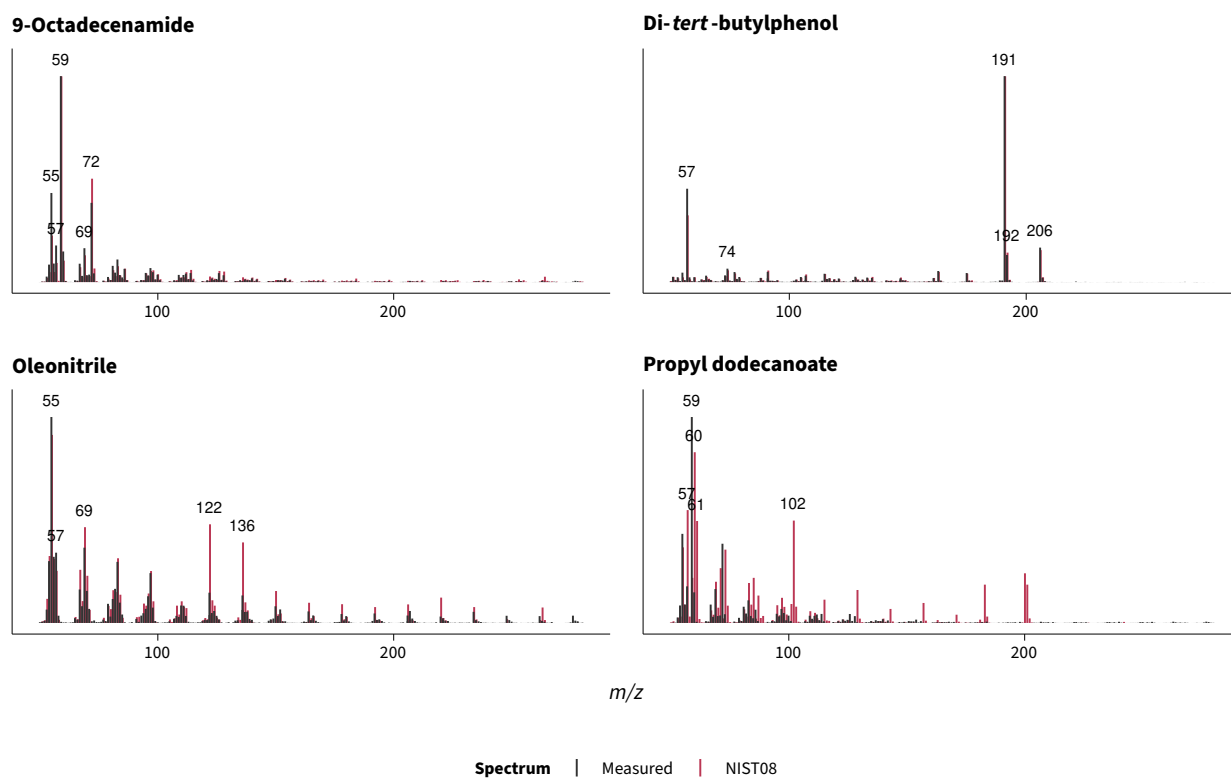


Figure B.3: Mass spectra and NIST08 library matches of the identified polymer additives that thermally desorbed from the agricultural films; see Figure B.2 for chromatograms.

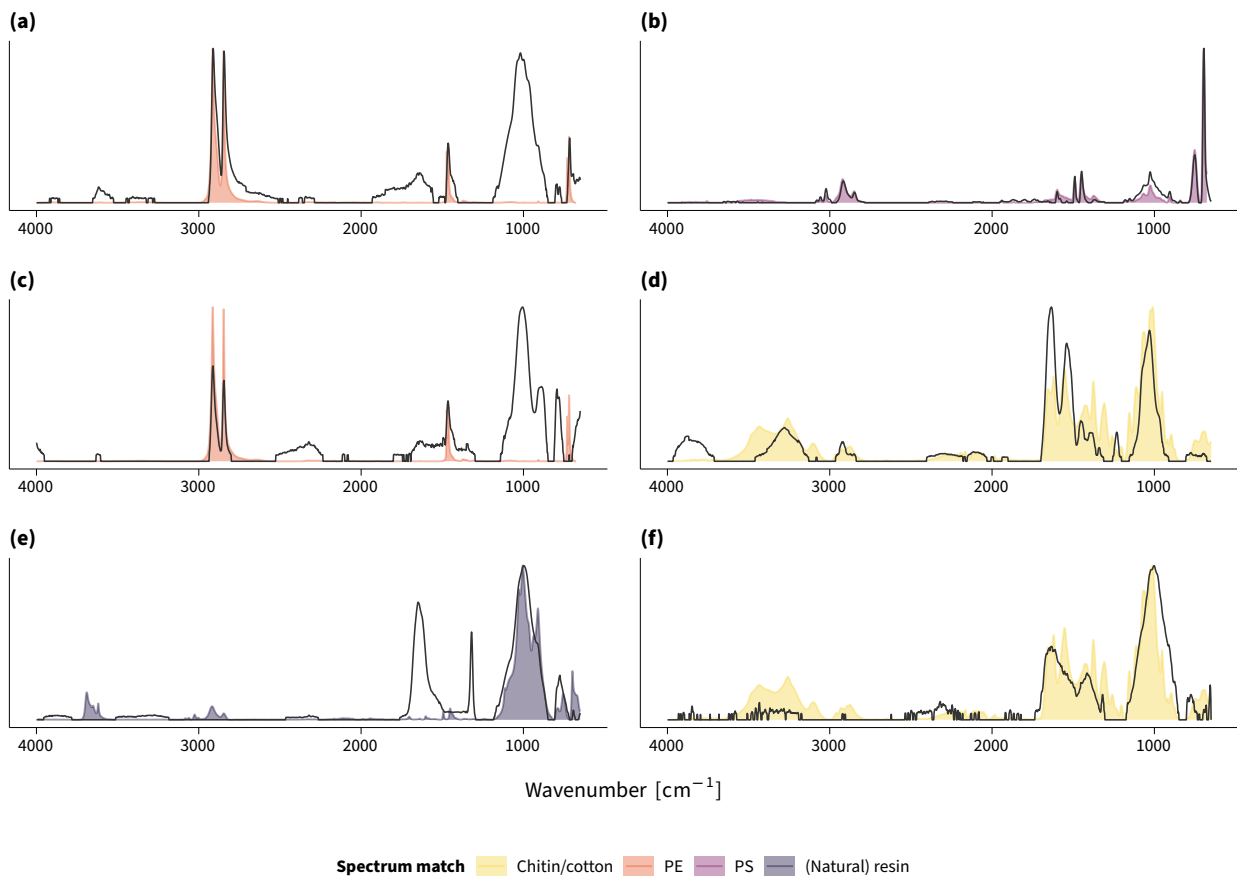


Figure B.4: FTIR spectra of the debris shown in Figure 6.3; (a) PE film and (b) PS fragment from the field center of site 5, (c) PE film and (d) chitin shell from the field center of site 6, and (e) resin or natural fragment and (f) cotton fiber from the field edge of site 7. The measured FTIR spectra are in gray; the colored shades depict the respective Open Specy library match.

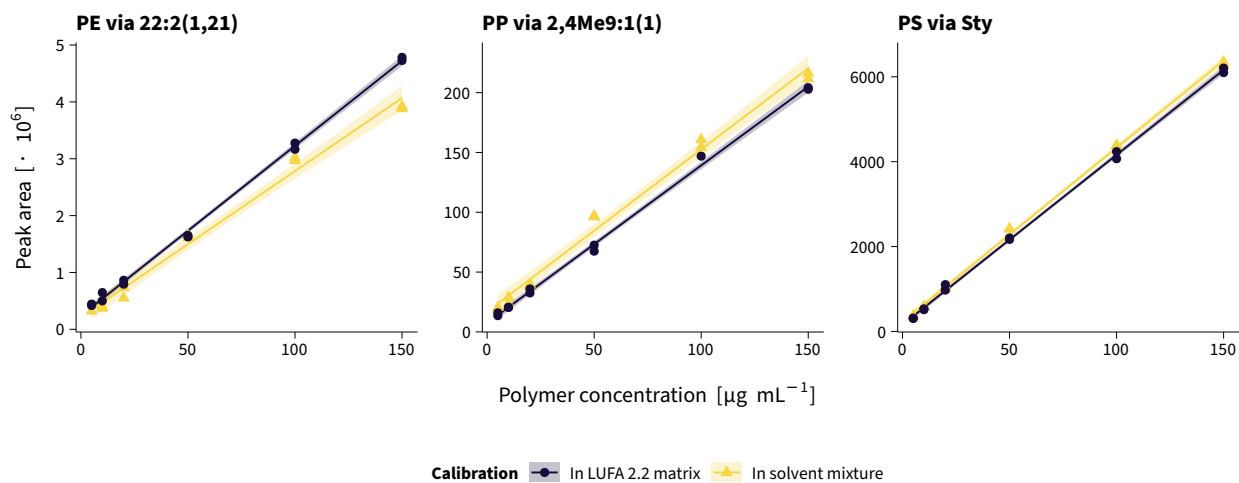


Figure B.5: Py-GC/MS calibration in solvent *p*-xylene/TCB and in LUFA 2.2 matrix compared.

C

SOLUBILITY TESTS

PE [†] concentration [$\mu\text{g mL}^{-1}$]	in TCB	in <i>p</i> -xylene/TCB
500	gel formation	dissolved
1000	gel formation	dissolved
1500	gel formation	dissolved
2000	gel formation	refraction anomaly
2500	gel formation	refraction anomaly
3000	gel formation	gel formation
3500	gel formation	gel formation
4000	gel formation	gel formation

[†] Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany.

Table C.1: Testing the visual solubility of an ultra high-density PE[†] in TCB at 120 °C and in a 1:1-mixture (v+v) of *p*-xylene and TCB at 150 °C after cooling down to room temperature. The used ultra high-density PE was found to be particularly difficult to dissolve in comparison to low-density PE, PP, and PS.

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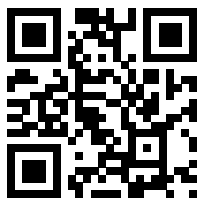
LIST OF ABBREVIATIONS

K_{ow}	octanol–water partitioning coefficient
$^1\text{H NMR}$	^1H nuclear magnetic resonance spectroscopy
ASE	accelerated solvent extraction
ATR	attenuated total reflection
C_{org}	organic carbon
DCM	dichloromethane
DEHP	bis(2-ethylhexyl) phthalate
DSC	differential scanning calorimetry
EC	electrical conductivity
EGA	evolved gas analysis
FTIR	Fourier-transform infrared
GC/MS	gas chromatography/mass spectrometry
GPC	gel permeation chromatography
IR	infrared
LC	liquid chromatography
LC/MS	liquid chromatography/mass spectrometry
LOD	limit of detection
LOQ	limit of quantification
MS	mass spectrometer
MWE	microwave-induced extraction
NIR	near infrared
PA	polyamide
PAE	phthalic acid ester
PBAT	polybutylene adipate terephthalate
PC	polycarbonate

PE	polyethylene
PET	polyethylene terephthalate
PLA	polylactic acid
PMMA	poly(methyl methacrylate)
PP	polypropylene
PS	polystyrene
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride
Py-GC/MS	pyrolysis-gas chromatography/mass spectrometry
RI	retention index
RSD	relative standard deviation
RSE	relative standard error
SD	standard deviation
SEC	size exclusion chromatography
SEM	secondary electron multiplier
SNR	signal-to-noise ratio
SOM	soil organic matter
SPT	sodium polytungstate
SSE	signal suppression/enhancement
TCB	1,2,4-trichlorobenzene
TED-GC/MS	thermal extraction and desorption-gas chromatography/mass spectrometry
TGA	thermogravimetric analysis
TGA/MS	thermogravimetry/mass spectrometry
THF	tetrahydrofuran
TWP	tire wear particles
UV	ultraviolet

ELECTRONIC SUPPLEMENT

All text files, data, and code to reproduce data processing, plotting, and statistical tests are available at the following link/QR code:



<https://git.io/Ja2DV>

THIS INCLUDES THE FOLLOWING FILES AND FOLDERS

<code>README.md</code>	Readme file
<code>thesis.pdf</code>	Dissertation as PDF file
<code>thesis.tex</code>	Dissertation as editable \LaTeX source file including all thesis contents from the following subdirectories: <code>frontback-matter/</code> , <code>chapters/</code> , <code>appendices/</code>
<code>proposal.pdf</code>	Thesis proposal as PDF file
<code>proposal.tex</code>	Thesis proposal as editable \LaTeX source file
<code>references.bib</code>	Complete bibliographical data of the references cited
<code>figures/</code>	Figures
<code>tables/</code>	Tables
<code>supplements/</code>	Supplemental (raw) data and code
<code>cv/</code>	Curriculum vitae
<code>defense/</code>	Slides of the thesis defense

ZACHARIAS STEINMETZ



Horststr. 157
76829 Landau
Germany

✉ info@zsteinmetz.de
id 0000-0001-6675-5033
p AAC-9025-2020

Born September 23, 1989, in Frankfurt am Main (Germany)
Nationality: German

EDUCATION

10/2013–11/2016	M.Sc. Ecotoxicology	University of Koblenz–Landau (Germany)
Thesis title	“Tracking the transformation of phenolic compounds in soil with compound-specific stable carbon isotope analysis.”	
Final grade	1.2	
10/2010–11/2013	B.Sc. Environmental Sciences	University of Koblenz–Landau (Germany)
Thesis title	“Persistence of chemical and biological effects of olive mill wastewater seasonally applied to loessial olive orchard soil.”	
Final grade	1.5	
8/2000–7/2009	Abitur	Christian-Wirth-Gymnasium Usingen (Germany)
Advanced courses	Chemistry and mathematics	

RESEARCH AND WORK EXPERIENCE

12/2016–present	Research Associate	University of Koblenz–Landau (Germany)
	Scrutinizing microplastic fate in agricultural soil using Py-GC/MS.	
8/2019	Guest Researcher	LUT (Finland)
	Exchanging knowledge on microplastic extraction from soil and sediment and Raman spectroscopy.	

4/2015–10/2015	Student Employee	RIFCON GmbH (Germany)
	Conducting individual-based ecological modeling and crop modeling in cooperation with Alterra (Netherlands).	
6/2014–8/2014	Intern	MITOX Consultants/Eurofins (France)
	Assisting in ecotoxicological (semi-)field trials on non-target arthropods.	
6/2013–8/2013	Guest Researcher	Agricultural Research Organization (Israel)

FUNDING

Travel Grants >1000 Euro

8/2019	Finland (Erasmus+)	1895 Euro
1/2018	Chile (Erasmus+)	3020 Euro
	Scholarships	
8/2016–12/2016	“AufLand” publication grant for junior scientists	3000 Euro
3/2015–9/2016	Studienstiftung des deutschen Volkes	7905 Euro

TEACHING EXPERIENCE


10/2021–present	Laborübungen Umweltanalytik	Co-supervisor
10/2017–present	Methoden der Natur- und Umweltwissenschaften	Associate lecturer
12/2016–present	Advanced Environmental Chemistry	Lecturer
10/2015–2/2016	R for Beginners	Teaching assistant

ADMINISTRATIVE EXPERIENCE

12/2016–present	Staff Representative	University of Koblenz–Landau (Germany)
	In various panels including the committee on educational affairs and the PhD committee of the faculty council of Environmental and Natural Sciences.	
1/2014–12/2015	Elected Student Representative	University of Koblenz–Landau (Germany)
	Faculty council of Environmental and Natural Sciences.	

SKILLS

German	native
English	proficient (10 school years, 1 year practice in the Philippines)
French	basic (5 school years)

Analytics	Py-GC/MS, GC/MS, GC/IRMS, GC/FID, HPLC, and FTIR–ATR using OpenChrom, Thermo Xcalibur, LCquan, and Isodat, Agilent ChemStation, and Open Specy for data analysis.
Computer skills	Advanced in R statistics and office applications Competent in GIS (QGIS, GRASS), Python, Linux shell, L ^A T _E X, git Basic knowledge of Docker, SQL, HTML, and PHP.
Software development	Visit  github.com/zsteinmetz for an overview of my open-source software development.

SELECTED SCIENTIFIC CONTRIBUTIONS

Peer-reviewed articles not listed in Parts of
this Thesis and Author Contributions

- Albert, J., More, C. A., Dahlke, N. R. P., Steinmetz, Z., Schaumann, G. E., and Muñoz, K. (2021). “Validation of a Simple and Reliable Method for the Determination of Aflatoxins in Soil and Food Matrices”. *ACS Omega* 6.29, pp. 18684–18693. ISSN: 2470-1343. DOI: [10.1021/acsomega.1c01451](https://doi.org/10.1021/acsomega.1c01451).
- Steinmetz, Z., Kenggott, K. G. J., Azeroual, M., Schäfer, R. B., and Schaumann, G. E. (2017). “Fractionation of Copper and Uranium in Organic and Conventional Vineyard Soils and Adjacent Stream Sediments Studied by Sequential Extraction”. *J Soils Sediments* 17.4, pp. 1092–1100. ISSN: 1439-0108, 1614-7480. DOI: [10.1007/s11368-016-1623-y](https://doi.org/10.1007/s11368-016-1623-y).
- Steinmetz, Z., Kurtz, M. P., Zubrod, J. P., Meyer, A. H., Elsner, M., and Schaumann, G. E. (2019). “Biodegradation and Photooxidation of Phenolic Compounds in Soil—A Compound-Specific Stable Isotope Approach”. *Chemosphere* 230, pp. 210–218. ISSN: 0045-6535. DOI: [10.1016/j.chemosphere.2019.05.030](https://doi.org/10.1016/j.chemosphere.2019.05.030).
- Steinmetz, Z., Kurtz, M. P., Dag, A., Zipori, I., and Schaumann, G. E. (2015). “The Seasonal Influence of Olive Mill Wastewater Applications on an Orchard Soil under Semi-Arid Conditions”. *J. Plant Nutr. Soil Sci.* 178.4, pp. 641–648. ISSN: 1522-2624. DOI: [10.1002/jpln.201400658](https://doi.org/10.1002/jpln.201400658).

See  scholar.google.de/citations?user=klQROs4AAAAJ for a complete publication list.

Referee	<i>Journal of Analytical and Applied Pyrolysis, Science of the Total Environment, Environmental Pollution, Polymers, Frontiers in Environmental Science.</i>
Invited speaker	Steinmetz, Z. (2019). “Back to the Roots. Haben unsere Böden ein Plastikproblem?” Fachschaftstagung Biologie/Chemie des Cusanuswerks (Stuttgart Hohenheim). Steinmetz, Z. (2020). “Are Agricultural Plastic Covers a Source of Microplastics in Soil? First Insights from Pyrolysis-GC/MS Method Development”. Colloquium of the Institute of Soil Science (University of Hohenheim).

