Spatial Distribution of Meso- and Microplastics in Floodplain Soilscapes: Novel Insights from Rural to Urban Floodplains in Central Germany

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Fluorescent microplastic pellet
(photograph by Collin J. Weber, 2021)

Preface

> *"We know so little of the worlds beneath our feet. Look up on a cloudless night and you might see the light from a star thousands of trillions of miles away, or pick out craters left by asteroid strikes on the moon's face. Lock down and your sight stops at topsoil, tarmac, toe. I have rarely felt as far from human realm as when only ten yards below it, […] The underland keeps its secrets well."*
>
> *Robert MacFarlane, Underland – A deep time journey (2019, p. 11)*

At the end of my personal "deep time journey" trying to learn some secrets from our soils, I would like to thank those people who supported and accompanied me on my way.

First of all, I would like to sincerely thank Christian Opp for his early and continuous support, the opportunity to write work on this thesis and for the constant liberties in my scientific work. Furthermore, I would like to express my gratitude to Peter Chifflard for his steady support and enabling the development and implementation of many additional ideas.

As the first steps and maybe also some further ones, are always the hardest, I am especially thankful to Christoph Weihrauch, for his support in all scientific questions, the best discussions and for everything he taught me. Further, thanks to my colleague Alexander Santowski, who was a lifesaver during all field work and for staying at my side whenever I needed help. Furthermore, this thesis would not have been possible without the support and cooperation with Martin Koch and Julia Prume from the Department of Physics at the University of Marburg. I am grateful for three years of fruitful discussion, sharing knowledge and ideas.

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The papers of this thesis were mostly developed in collaboration with several people. I would like to thank all co-authors for their contributions and I am grateful for the collaboration with Jens Hahn and Thorbjørn Joest Andersen which have enabled advanced analytical methods, as well as Simone Lechthaler for sharing our ideas on plastics within the Anthropocene.

However, I would not have been there without the early support of Frank Ullrich, who was responsible that my view does not stop at the topsoil and who has shared with me some of the first secrets of our soils.

Independently from all mentioned support, this thesis could not have been developed without the support and backup from my wife, my family and friends. I am very grateful for my wife, who has accompanied me throughout the entire time and has always supported me, as well as for my parents, who have paved this way for me.

Anyway, enough said.

Collin Joel Weber

Marburg, April 2022

Abstract

Plastics and especially microplastics have become an emerging threat to global ecosystems. Despite the manifold benefits and applications of the human-made material plastic, the uncontrolled release of plastics into the environment has led to a “global plastic crisis”. During the last decades it becomes apparent that this crisis leads to the presence of plastics within different environments including marine, aquatic and terrestrial systems under worldwide evidence. Furthermore, environmental plastic research was able to reveal that although plastic often ends up in oceans, the majority of plastics in the environment are transported as part of a “global plastic cycle” from the land to sea via river systems. Those river systems are not isolated in the landscape, but rather a part of an “aquatic-terrestrial interface” which also encompasses floodplains and their soilscapes.

The present thesis focuses on the spatial distribution and spatio-temporal accumulation of meso- and microplastics in floodplain soilscapes following the overall objective to unravel the role of floodplain soilscapes as depositional areas of plastics within the global plastic cycle. In this context, a number of individual contributions have been published, reaching from conceptual spatial research approaches, over case studies conducted within two different floodplain soilscapes, to further opinions on the scientific benefit of plastic residues in floodplain soils. The individual contributions are linked by the major hypothesis that floodplain soilscapes act as temporal accumulation sites for plastics, driven by flood-related processes and land use over the last 70 years. To proof this major hypothesis and to overcome the lack of spatial reference in microplastics research, a geospatial sampling approach was conducted. Initial spatial data on meso- and microplastics in floodplain soils were obtained by a holistic analysis approach including the analysis of basic soil feature and metal analysis, the quantification of meso- and microplastics as well as sediment dating.

Within both studied river floodplains geospatial sampling enables a detection of meso- and microplastics over the entire floodplain area and within the entire soil column reaching depths of two meters. Additionally, a frequent accumulation of plastics was found within the upper 50 cm of floodplain soils. In combination with dating of near-channel floodplain sites, it could be demonstrated that those plastic accumulations are related to recent sedimentary deposits since the 1960s. However, evidence of plastic from deeper soil layers suggests that vertical displacements in floodplain soils occur and that plastics become mobilized. Furthermore, the presence of plastics in upstream areas suggests that plastics are released to river systems and deposited via flood dynamics already in rural areas. Additionally it appears that anthropogenic impacts, such as tillage or floodplain restoration influence plastic distributions.

The findings of this thesis clarify that floodplain soilscapes are part of the global plastic cycle as temporally depositional areas of plastics, but raising further questions on the mobility of plastics in soils and about the exact contribution of different environmental drivers towards plastic deposition. Finally, the present thesis indicates that the spatial reference of environmental plastic research should be rethought, in order to understand the spatial dynamics of plastics within the aquatic-terrestrial interface.

Zusammenfassung

Plastik und insbesondere Mikroplastik sind zu einer neuen Bedrohung für globale Ökosysteme geworden. Trotz der vielfältigen Vorzüge und Anwendungsmöglichkeiten des durch den Menschen entwickelten Kunststoffen, hat die unkontrollierte Freisetzung von Plastik in die Umwelt zu einer „globalen Plastik-Krise“ geführt. Innerhalb der letzten Dekaden wurde offensichtlich, dass diese Krise zu einer weltweiten Präsenz von Plastik in unterschiedlichsten Umweltsystemen wie marinen, aquatischen und terrestrischen Systemen geführt hat. Darüber hinaus, konnte die Forschung zu Plastik in der Umwelt aufdecken, dass selbst wenn Plastik oftmals in den Weltmeeren endet, ein Großteil des Plastiks in der Umwelt als Teil eines „globalen Plastikkeislaufs“ vom Land zum Meer durch Flusssysteme transportiert wird. Solche Flusssysteme sind dabei nicht innerhalb der Landschaft isoliert, sondern vielmehr Teil einer „aquatisch-terrestrischen Schnittstelle“ welche auch Auen und ihre Bodenlandschaften umfasst.

Die vorliegende Arbeit beschäftigt sich mit der räumlichen Verteilung und der raum-zeitlichen Akkumulation von Meso- und Mikroplastik in Auen-Bodenlandschaften und folgt dabei dem übergeordneten Ziel, die Rolle von Auen-Bodenlandschaften als Depositionsräume für Plastik innerhalb des globalen Plastikkeislaufs zu verstehen. Innerhalb dieses Kontextes wurden eine Reihe von individuellen Beiträgen veröffentlicht welche von konzeptionellen, räumlichen Forschungsansätzen, über Fall-Studien innerhalb von zwei unterschiedlichen Auen-Bodenlandschaften, bis hin zu weiterführenden Überlegungen zum wissenschaftlichen Nutzen von Plastikrückständen in Auenböden, reichen. Die einzelnen Beiträge sind dabei durch die übergeordnete Hypothese verbunden, dass Auen-Bodenlandschaften als temporäre Akkumulationsgebiete für Plastik fungieren, welche maßgeblich durch Hochwasserprozesse und Landnutzung, in den vergangenen 70 Jahren, beeinflusst wurden. Um diese Hypothese zu prüfen und das Fehlen von Raumbezug in der Mikroplastikforschung zu überwinden, wurde ein „geo-räumlicher“ Untersuchungsansatz durchgeführt. Erste räumliche Daten zu Meso- und Mikroplastik in Auenböden wurden durch einen ganzheitlichen Analyseansatz mit der Analyse von grundlegenden Bodeneigenschaften und Metallgehalten, der Quantifizierung von Meso- und Mikroplastikgehalten und Sedimentdatierungen erlangt.

In beiden untersuchten Flussauen ermöglichte der räumliche Untersuchungsansatz den Nachweis von Meso- und Mikroplastik in der gesamten Auenfläche und über die gesamte Bodensäule bis in Tiefen von zwei Metern. Zusätzlich, konnte eine regelmäßige Akkumulation in den oberen 50 cm der Auenböden gefunden werden. Mit der Kombination von Datierungen von Auenstandorten in Flussnähe, konnte ebenfalls demonstriert werden, dass diese Plastik-Akkumulationen mit rezenten Sedimentdepositionen in Verbindung stehen. Jedoch, deutet der Nachweis von Plastik in tieferen Bodenschichten auch eine vertikale Verlagerung von Plastik und damit eine generelle Mobilität des Plastiks in Böden an. Der Nachweis von Plastik in stromaufwärts gelegenen Gebieten zeigt, dass Plastik bereits in ruralen Gebieten in Flusssysteme gelangt und durch Flutdynamiken in Auen abgelagert wird. Auch direkte anthropogene Einflüsse, wie Bodenbearbeitung oder Auenrenaturierungen beeinflussen die räumliche Verteilung des Plastiks.

Die Ergebnisse dieser Arbeit verdeutlichen, dass Auenböden als zeitlich begrenzte Ablagerungsgebiete von Plastik ein Teil des globalen Plastikkreislaufs sind, wobei jedoch weitere Fragen zur Mobilität von Plastik in Böden und zum genauen Beitrag der verschiedenen Umweltfaktoren zur Plastikablagerung aufgeworfen werden. Schließlich zeigt die vorliegende Arbeit, dass der räumliche Bezug innerhalb der Plastikforschung überdacht werden sollte, um die räumliche Dynamik von Plastik an der aquatisch-terrestrischen Schnittstelle in Zukunft besser zu verstehen.

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List of Acronyms

ABS	Acrylonitrile butadiene styrene
AD	Anno domini
BC	Before Christ
CMP	Coarse microplastics (5-2 mm)
MAP	Macroplastics (>25 or >5 mm)
MEP	Mesoplastics (25-5 mm)
MP	Microplastics (5-0.01 mm)
(micro-)plastics	Environmental plastics within micro- to macroplastic size range
Mt	Megaton (1 million tons)
NGO	Non-Governmental Organisation
PA6	Polyamide
PC	Polycarbonates
PE	Polyethylene
PE-HD	High density Polyethylene
PE-LD	Low density Polyethylene
PES	Polyethersulfones
PET	Polyethylene terephthalate
PMMA	Polymethyl methacrylate
POM	Polymethylene
PP	Polypropylene
PS	Polystyrene
PUR	Polyurethane
PVC	Polyvinyl chloride
SAN	Styrene acrylonitrile resin
SBR	Styrene-butadiene
SOM	Soil organic matter
SUP	Single-use plastic
WRB	World reference base for soil resources

1. Introduction

1.1 Living in the plastic age

Plastics have become the most common material that people hold in their hands every day. Thus, plastics have revolutionized daily lives in all sectors, from private households to industry and transport, to technology and science. Plastic material are polymers, which are composed of unique molecular structures of long, chain-like molecules (*monomers*) with C-C bonds (Andrady 2017; Chen et al. 2021b). If those structures of monomers are repeated with thousands of repeats, the chemical structure is called a *polymer*, showing common plastic characteristics. For example, one of the most common polymers, *Polyethylene* (PE), has the structure of $(\text{-CH}_2\text{-CH}_2\text{-})_n$, and with thousands of repeats (n) the material becomes a solid plastic (Andrady 2017).

Polymers are generally divided into three groups: (1) thermoplastic polymers, which showing a chain-structure and can be melt processed; (2) thermoset polymers, which showing a network structure and cannot be melt processed (e.g., polyurethane foams, rubber tires); and (3) natural-polymers like cellulose or rubber (Andrady 2017; PlasticsEurope 2018). Each non-natural polymer can be designated as a *synthetic organic polymer* and is made from non-renewable petrochemicals obtained from fossil fuel, oil, natural gas, or coal (Chamas et al. 2020). After the utilization of natural polymers within the mid-19th century and the first synthesis of polyvinyl chloride (PVC) in 1872, the first synthetic-plastic *Bakelite*, a thermosetting phenol-formaldehyde resin, was developed in 1907 (Figure 1) (Frias und Nash 2019; British Plastic Federation 2020). Further development of plastics took place mainly in the 1920s and ’30s, although these were only used to a limited extent or for military purposes (Andrady 2017; Zalasiewicz et al. 2016).

In the meantime, thermoplastics such as *polyethylene* (PE), *polypropylene* (PP), *polystyrene* (PS), *polyvinyl chloride* (PVC), *polyamide* (PA6), *polyethylene terephthalate* (PET), or *polycarbonates* (PC) build the majority (>90%) of total plastic produced and used (Porta 2021; PlasticsEurope 2020). The characteristics of these thermoplastic polymers such as inexpensive raw materials and production—recalcitrance toward mechanical forces and chemicals, non-permeability toward water or air, low density, long durability, and easy item production by melting—have turned plastic to the most used material in the world (Andrady 2017; Geyer et al. 2017; Shen et al. 2020).

Against the background of the manifold applicability and usefulness of plastics, this material becomes crucial for the technological revolution from the start of the post–World War II “Great Acceleration” (Figure 1). The widespread use of plastics within every part of human life after World War II has led to a rapid and exponential growth of global plastic production from two megatons (Mt) in 1950 up to 367 Mt in 2020 (Geyer et al. 2017; PlasticsEurope 2020, 2021). Within 70 years of global plastic production, the annual production volume was increased by 18,250%.

Currently, the largest plastic producers are China, followed by Europe and North America (Shen et al. 2020). For example, European production accounts for 55 Mt in 2020, of which 40.5% are produced for packaging purpose, 20.4% for construction, 8.8% for automotive, and 3.2% for agricultural usage, among others (PlasticsEurope 2021; 2020). Within European plastic production, the top polymers are PE (high density and low density), PP, PVC, PET, PS, and PA6 (PlasticsEurope 2021). The rapid growth of plastic production and the associated consumption of resources since the 1950s is only comparable to the growth in global steel and concrete production (Geyer et al. 2017).With the ongoing growth of global plastic production, which is expected to double again in the next two decades by the MacArthur Foundation (2017), this revolutionary synthetic material has displaced other materials in multiple applications and has become a social and economic symbol (Porta 2021; Ellen MacArthur Foundation 2017).

Like previous materials that have shaped human history and societies, plastics can be referred to as the symbol of a definitive transition to modernity, according to Porta (2021). No other material like plastic has transformed and characterized human life as an "any-use product" since the Great Acceleration starting in the 1950s. Following the concept of the three-ages division of prehistory and history of humanity, where each age is characterized by the major material used by humans, different scholars suggest that we are now living within a new cultural age (Porta 2021). Following the "Stone Age" (>2.6 M–2200 BC), the "Bronze Age" (2200–800 BC), and the "Iron Age" (800 BC–AD >1000), humankind now may live within the "Plastic Age".

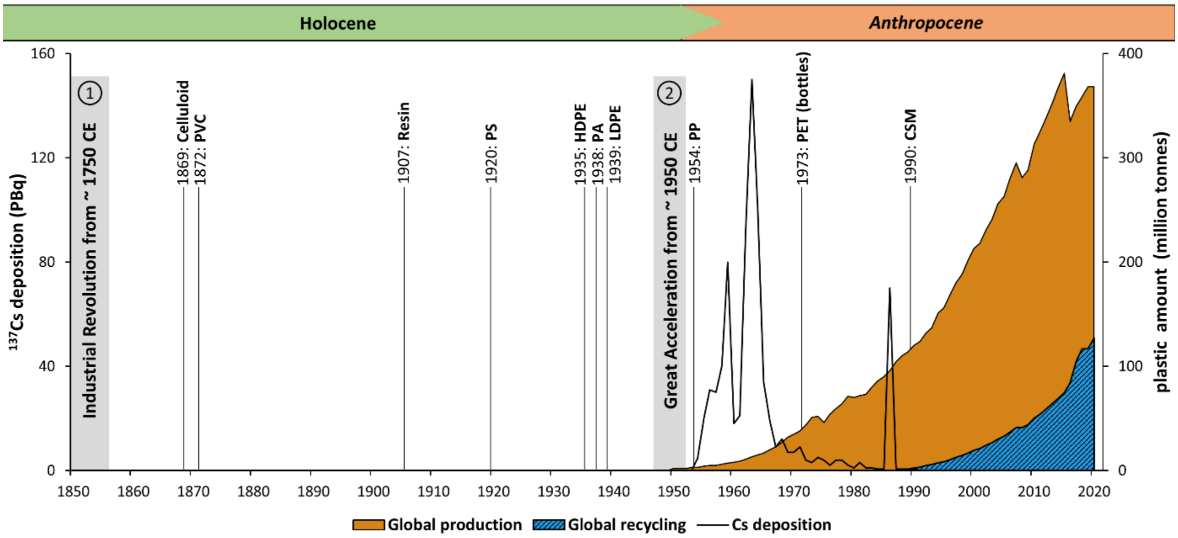

Figure 1: *Plastic age within the Anthropocene.* Global plastic production and recycling rates with common polymers development dates compared with global 137Cs deposition and possible start dates (circles 1 and 2) of the proposed "Anthropocene" epoch. Data basis: Agudo 1998; Geyer et al. 2017; PlasticsEurope 2021.

The term *Plastic Age* expresses more than a human epoch of material use. The development of this revolutionary material and the rapid growth of its global production also initiated a global environmental crisis. The so-called *global plastic crisis* is a modern and complex phenomenon caused by the increasing presence of plastic residues in the global environments (Shen et al. 2020). Although the reasons for the emergence of this crisis are essentially very complex, they are most easily explained by the loss of plastics from the value chain and certain properties of polymers (Syberg et al. 2022).

In general, none of the commercially used plastics is biodegradable. Because of the chemical and physical properties of polymers, which make the material so versatile and ensure a long product lifetime, the loss of plastic in the environment becomes a problem. According to Syberg et al. (2021), plastics can become lost during their life-cycle at any stage of the value chain and can accumulate in the environment because plastics are not soluble and have a long environmental persistency. Reasons for the environmental loss of plastics could be found within the mismanagement of plastics during their life-cycles and afterwards. Regarding the generated plastic waste in high- and medium-income countries, plastic recycling and incineration were negligible before the 1980s (Geyer et al. 2017). Global plastic recycling rates have therefore been rising slowly only since the 1980s and reached a mass of approximately 127.33 Mt in 2020 (Figure 1). Thus, in 2020, only 34.7% of the annual global plastic production were recycled (Chen et al. 2021b; Shen et al. 2020). For Europe, the total plastic waste collected increased from 24.5 Mt in 2016 up to 29.5 Mt in 2020. Waste processing includes 34.6% recycling, 42.0% energy recovery, and 23.4% landfill deposition of post-consumer products (PlasticsEurope 2021). However, only a few countries have a well-functioning waste management system, creating major waste management gaps at the global level with global recycling rates below 25% of consumed plastics (Geyer et al. 2017).

In addition to mismanagement and insufficient recycling rates, modern plastic production has shifted from manufacturing durable plastics to so-called *single-use plastics* (SUPs) (Chen et al. 2021b). For example, the European plastic industry produced 39.9% of plastics for packaging, and the plastic film sector focuses on SUP bags and agricultural SUPs (e.g., mulching films, greenhouse materials) (Chen et al. 2021b). Another development contributing to the global plastic crisis has been the development and use of small plastic particles in various consumer products (Andrady 2017). For example, personal care products or cleaners contain small plastic particles that simply enter the environment via wastewater (Andrady 2017; Syberg et al. 2022). The use of synthetic fibers for clothing production, which has replaced cotton in many cases, also contributes to the crisis as synthetic fibers are released into the environment during clothing use and washing (Syberg et al. 2022).

Awareness about plastics in the environment started with scientists' descriptions of plastics in coastal waters in the 1970s (Carpenter und Smith 1972; Carpenter et al. 1972). Since then, research on plastic residues in the marine environment and their risks to marine ecosystems has increased (Cole et al. 2011) and has subsequently expanded to research in other aqueous environmental systems (inland waters) (Emmerik und Schwarz 2020), such as glaciers and sea ice (Bergmann et al. 2017), and most recently to terrestrial systems and the atmosphere (Souza Machado et al. 2018a). It became obvious early in the research process that plastics in the environment are clearly distinguishable from other anthropogenic contaminants (Cole et al. 2011).

Plastics in the environment appear as particles that can be defined as human-made, polymeric or co-polymeric, solid and insoluble materials; they are mainly described by their particle size (Andrady 2017; Barnes et al. 2009; Frias und Nash 2019). Within the scientific community, the particle size definitions are still discussed but can be stated as follows: macroplastics with a particle size >25 mm, mesoplastics (25 to 5 mm), microplastics (5000 to 1 µm) or separated into large-microplastics (5000–1000 µm), microplastics (1000–1 µm), and nanoplastics (<1 µm) (ISO/TR 21960:2020; Kooi und Koelmans 2019; Hartmann et al. 2019). Despite the easily graspable large plastic debris in the environment—such as complete consumer-products (e.g., PET bottles) or larger fragments of them, often part of the macro- or mesoplastic size classes—recent research has focused more and more on the often non-visible microplastic contaminations.

Microplastics can occur as primary microplastics that are industrially manufactured as microbeads (e.g., within personal care products or clothing fibers), which enter the environment via leakage during production or the later life-cycle (Andrady 2017). In contrast, secondary microplastics arise through the fragmentation of larger plastic debris (e.g., PET bottles) during their life cycle or later within the environment. Although plastic is not soluble and very resilient against several impacts, plastic in the environment can slowly degrade and fragment through physical, chemical, and biological processes. Even if a wide variety of additives (e.g., antioxidants, stabilizers, plasticizers) is added to polymers to achieve certain properties and long durability of plastic materials, different degradation processes take place in the environment (Hahladakis et al. 2018; Catrouillet et al. 2021). For example, mechanical cracking, photodegradation by sunlight ultraviolet rays, hydrolysis in aqueous environment, or oxidation if oxygen is present can contribute to the fragmentation of plastic particles (Chamas et al. 2020). These degradation processes include the fact that larger plastic particles in the environment (e.g., macroplastics) turn into microplastics and nanoplastics over time. However, these processes occur slowly, as shown by modeled half-lives of up to >5000 years for buried HDPE particles (Chamas et al. 2020).

The global evidence of microplastic has now reached all environmental systems and continents. Microplastics were found in each environmental medium including water, ice, air, and soil (Bergmann et al. 2017; Peeken et al. 2018; Christensen et al. 2020; Wang et al. 2019).

For example, microplastics were found within deep-sea sediments (van Cauwenberghe et al. 2013), Arctic and Antarctic ice (Kelly et al. 2020; Peeken et al. 2018), remote mountain areas including freshwater and glaciers, and within snow samples on Mt. Everest (Allen et al. 2019; Napper et al. 2020).

Besides these supposedly remote areas, microplastics have become common in marine waters and sediments, freshwater and river sediments, and soils, especially agricultural soils (Cole et al. 2011; Fahrenfeld et al. 2019; Stock et al. 2019; Souza Machado et al. 2018b). The resulting environmental risks are currently the focus of scientific research, but it is already known that micro- and nanoplastics can influence a wide variety of organisms, can enter different food chains including the human food chain, and can be present within human bodies, which may impact health (Ragusa et al. 2021; Hurley und Nizzetto 2018; He et al. 2021b; Rillig et al. 2017a; Rillig et al. 2019). In addition, environmental degradation processes of plastics can release polymer components, especially additives, which can be highly harmful and hazardous for health and the environment (Catrouillet et al. 2021; Hahladakis et al. 2018; Shen et al. 2020).

With the global evidence of plastics and the potential environmental and health risks, people have become increasingly aware and concerned about the global plastic crisis. This awareness had led to different actions on both international and local levels, from legislation to NGOs to the private sector (Shen et al. 2020; Syberg et al. 2022). For example, resolutions on SUPs, microplastics, and marine litter have been developed (Chen et al. 2021b). Today 127 countries regulate SUP bags, and 91 countries have introduced legislation banning different plastic products (Chen et al. 2021b). Bio-based (meaning non-petrochemical) polymers have also been developed to replace conventional polymers. Those "bioplastics" can be durable and non-degradable or biodegradable made from biological sources, allowing circular economy and could be part of a solution to overcome the plastic crisis in the future (Bishop et al. 2021). Despite the numerous policy initiatives and the development of new materials, the amount of plastic entering the environment is still rising (Syberg et al. 2022). In addition, the production of a revolutionary material that has become a global threat spans 70 years with almost unregulated plastic release into the environment, leading to a major human footprint on the Earth.

The human footprint on the Earth is obviously not determined by plastics alone. Climate change, ozone depletion, ocean acidification, biosphere changes, land-system changes, and impacts on biogeochemical flows were caused by humans and interact in a complex environment (Tulus et al. 2021). The global plastic crisis must therefore be understood as neither a stand-alone crisis nor an independent one. For example, the plastic crisis contributes to global greenhouse gas emissions and climate change through a great carbon footprint during production, life cycle, recycling, or release during environmental plastic degradation (Shen et al. 2020). It should not be overlooked that non-renewable raw materials are used for the production of plastics.

To illustrate the scale, 380 billion SUP plastic bags require 1.6 billion liters of fossil oil (Chen et al. 2021b), leading to the fact that large parts of the natural Earth's carbon storage are only transformed into other materials. Nevertheless, Earth's surface has been considerably changed from the mid-20th century onward, not only but excessively by the production of plastic as a modern, long-lasting, and human-made material (Porta 2021).

This circumstance has led to the fact that, in addition to the socio-economic designation of the *Plastic Age* in the context of human history, plastics are now also considered in the context of Earth's history. With ongoing anthropogenic influences on the environment, the idea of human-dominated environmental processes has emerged (Bensaude-Vincent 2021; Waters et al. 2016). Within this context, Crutzen and Stroermer (2000) and Crutzen (2002) proposed the conceptual framework of a new post-Holocene Cenozoic era, the "Anthropocene", in which humans have come to dominate geological processes (Crutzen 2002). In the past two decades, a wide variety of approaches have been discussed against this background, ranging from the existence of the proposed "Anthropocene" to a possible beginning of the epoch, in other words, the point in time when it replaces the currently ongoing Holocene epoch (Bensaude-Vincent 2021). Each geological epoch as a chronostratigraphic unit, needs one or more "Global Stratotype Section and Point" (GSSP) determined by the International Commission on Stratigraphy (ICS), with principle and auxiliary markers as stratigraphic markers to specify the time period of each epoch (Zalasiewicz et al. 2016; Waters et al. 2016). Those GSSPs were, for example, ice cores (Core-2, NGRIP: Holocene start point) or fossils (Zalasiewicz et al. 2016) for recognized eras.

Regarding the Anthropocene, different GSSPs and markers were discussed by scholars, including major events in the history of humankind such as human settlements and agricultural revolution (Neolithic revolution), the industrial revolution (Figure 1), or the modern technical revolution (Waters et al. 2016; Bensaude-Vincent 2021). In the meantime, there is a growing consensus that a starting time of the proposed Anthropocene around the mid-20th century in connection with the post–World War II Great Acceleration could be most appropriate (Zalasiewicz et al. 2016; Zalasiewicz et al. 2021). With the Great Acceleration, the already existing human influence on the Earth's system was increased, transcending scales. Furthermore, the mid-20th century provides different, near-synchronic stratigraphic markers, such as radionuclides, aluminum metals, fly ash particles, persistent organic pollutants, and a variety of biological indicators, which could be used as principle and auxiliary stratigraphic markers (Zalasiewicz et al. 2016). Within this framework, plastics could act as a further potential indicator. The reason for this can be found in the worldwide occurrence and in the comparatively easy detection and the sudden appearance of plastics with respect to geological time scales. For example, the global ^{137}Cs deposition (radionuclide marker) as a consequence of the atomic bomb tests in the 1950s and '60s and the Chernobyl disaster in 1986 correlates with the exponential increase of global plastic production (Figure 1) (Zalasiewicz et al. 2016; Zalasiewicz et al. 2021; Porta 2021).

So far, the question of the preservation of plastic on geological time scales remains open, but plastic properties such as durability, resistance to degradation, and long half-lives indicate a possible long preservation in the environment and especially in sediment archives (De-la-Torre et al. 2021b; Bancone et al. 2020). According Zalesiewicz et al. (2016), plastics in the environment could be regarded as "technofossils", a trace fossil with extremely rapid evolution and detached from the evolution of trace making organisms (here: humans).

The consideration of plastic as a marker of a new geological epoch as a consequence of the global plastic crisis, but also the usefulness of the material and the technical progress within the *Plastic Age*, form the wider context of the present thesis. Research on plastics and microplastics in the environment is imperative in light of the global challenges facing humanity. When formulating research questions, hypotheses, and results from case studies, the larger societal and Earth-historical framework must be considered.

1.2. Plastic residues at the interface of fluvial and terrestrial ecosystems

1.2.1 Plastics in fluvial systems: Global transport corridors

Research on (micro-)plastics in the environment has its starting point within marine environmental systems and has led to the wholesale discovery of plastic in the world's oceans. The research field in marine systems is the oldest in plastics research. Here, the first descriptions of plastic residues, transport, and environmental risks were made, which is why this subject is the most familiar to the public (Cole et al. 2011). However, within this research field, it has become obvious over time that the source of the marine plastic crisis cannot be found in direct inputs into the oceans alone.

Even though around 10% of world's population lives in coastal areas and nearly 40% of world's population live within a 100 km zone from global coasts (United Nations [UN] 2017), a large proportion of the plastic produced and used worldwide is not consumed on or in the immediate vicinity of the oceans. Direct inputs into seawater or beaches from littering on shores, directly discharged urban or industrial effluents, and shipping and fishing do not entirely account for the large amounts of plastic in the oceans (Lebreton et al. 2017). As a global sink for plastic and a natural link between land and sea, rivers and freshwater systems also connect zones of plastic production and consumption and play a crucial role in the accumulation of plastic in the oceans (Emmerik und Schwarz 2020; Hurley et al. 2018; Alimi et al. 2018).

Manifold studies on (micro-)plastics within freshwater systems, including water, sediments, and shorelines have demonstrated that these systems play an important role in the global plastic transport (Xiong et al. 2018; Fahrenfeld et al. 2019; Emmerik und Schwarz 2020; He et al. 2021a; Kiss et al. 2021; Tibbetts et al. 2018; Baldwin et al. 2016; Martin et al. 2017b).

Furthermore, modeling approaches or tracking of larger plastic debris supported the role of rivers as a “highway for microplastics into the oceans” or “global transport corridors”. For example, Lebreton et al. (2017) found within a modelling approach that 1.1 to 2.4 Mt of plastics enter the oceans every year via rivers and that 67% of the total plastics are transported in the 20 most polluting rivers (Lebreton et al. 2017). Therefore, the sources and pathways by which (micro-)plastics can enter rivers are multiple and wide ranging, depending also on rivers located within different regions or countries. Different research data suggests that littering could be the primary source of plastics to freshwater systems and the environment in areas where no or only low waste management is carried out by the public or the state (Cowger et al. 2021b; Lechthaler et al. 2020). For all regions with implemented waste management, however, there remain plenty of plastic-release opportunities into the environment that also exist in areas without waste management (Figure 2a). Taking Europe as an example, a distinction can be made between direct and diffuse plastic inputs into freshwater systems. Runoff from urban areas, streets, and industrial sites, as well as discharge from wastewater treatment (WWT) plants and thus household effluent, can be counted as direct main sources (Fahrenfeld et al. 2019; Horton et al. 2017; Emmerik und Schwarz 2020; Hurley et al. 2018). Furthermore, littering in or near rivers can be counted as direct inputs. Major diffuse sources include atmospheric deposition, wind transport, and inputs from surface or possible subsurface runoff, which can migrate plastic from, for instance, atmospheric deposition, land use (agriculture), or further littering, and discharge it into the aquatic environment (Rehm et al. 2021; Rezaei et al. 2019). Furthermore, diffuse sources can be extended during natural storm and flood events, causing the possibility of construction damages, erosion of buildings, erosion of municipal landfills, and generally increased runoff (Lechthaler et al. 2020).

If plastics enter the river system and therefore an aquatic river network, they can be transported over long distances directly into marine environments and the proposed marine plastic sinks (Siegfried et al. 2017). However, this basic transport process is not fundamentally simple to understand directionally. Recent studies showed that plastics and microplastics were temporally stored within channel bad sediments or river shore sediments over different time periods (He et al. 2021a; Fischer et al. 2016; Ballent et al. 2016; Klein et al. 2015). Furthermore, microplastics behave differently than natural sediments in terms of settling and erosion under natural flow conditions (Waldschläger und Schüttrumpf 2019a; 2019b). First evidence of an accumulation of microplastics in river sediments (Klein et al. 2015) and the first detection of microplastics in topsoils near rivers in floodplains (Scheurer und Bigalke 2018) indicate that a partial deposition of plastic already takes place within those transport corridors, as is already known with respect to natural sediments. Despite the differences in behavior between plastic and sediment that are already known, the emergence of global transport ideas through river systems has contributed to the idea that plastic can be part of the sedimentary cycle (Zalasiewicz et al. 2016).

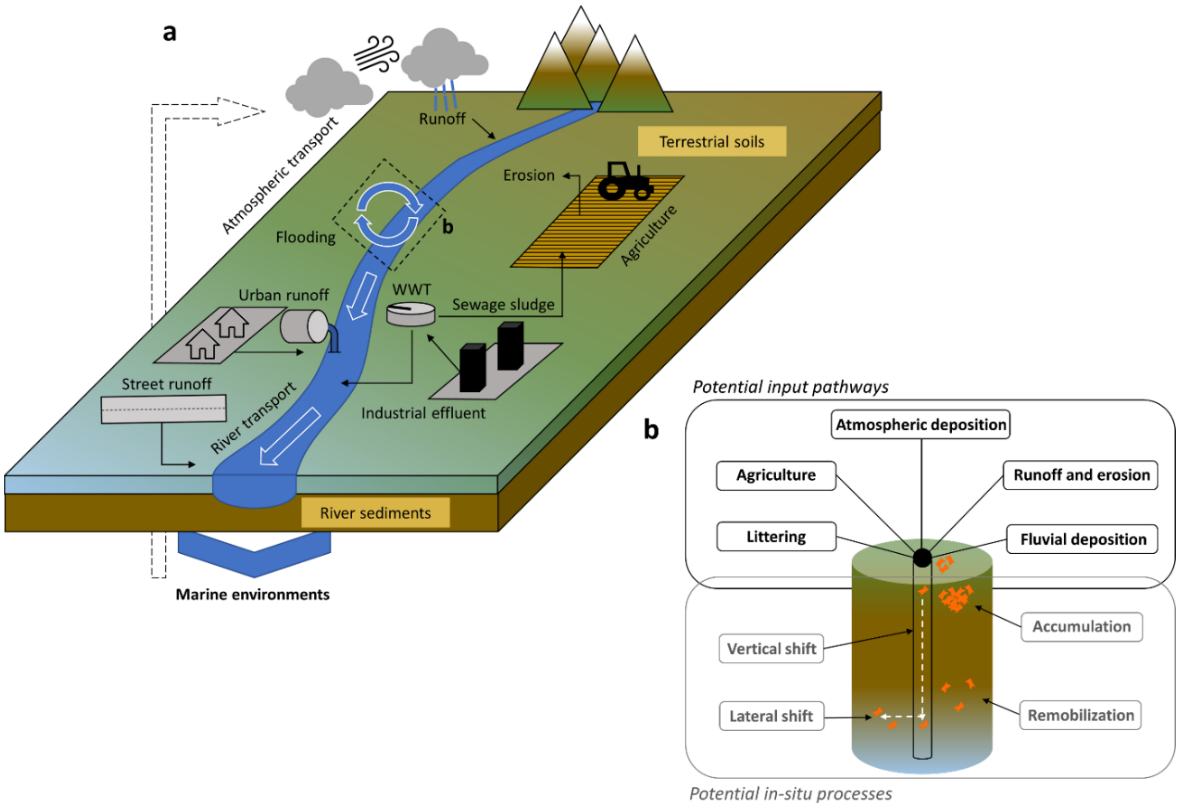

Figure 2: Terrestrial part of the “global plastic cycle” with (a) Simplified scheme of plastic sources, input pathways, and transport through freshwater systems; and (b) potential input pathways and in-situ processes of plastics in soils within the aquatic-terrestrial interface.

Regarding the sedimentary cycle and a geomorphologic perspective, river systems are not solely transport corridors between land and sea. Rather, they are also temporal accumulation sites for sediments that are eroded within the river network catchment and transported by the river water (Bancone et al. 2020; Fryirs und Brierley 2013). Even though sediment deposition is a spatially and temporally complex process, a change of energy from high to low (e.g., flow energy) is necessary for a deposition originating from a previous transport (Bancone et al. 2020). Within natural environments, those high-to-low energy boundaries occur, rarely abruptly, but rather over a transitional environment (Bancone et al. 2020; Edgeworth 2011). Within freshwater environments and the related river networks, floodplains act as a transitional environment at the interface of aquatic and terrestrial systems.

Following known definitions, a floodplain can be described as an “area of sediment accumulation that borders a stream channel, made up from alluvial materials between the channel bank and the valley margins” (Bridge 2003; Fryirs und Brierley 2013). Additionally, floodplains “accumulate sediments during overbank flows, if the transport capacity of the flow exceeds the stream capacity” (Fryirs und Brierley 2013; Bridge 2003). Therefore, floodplains are built up from deposited fluvial sediments and further act as accumulation sites for them. Within floodplains, their properties and morphology are influenced mainly by changes in sedimentation dynamics (e.g., rates, grain sizes), subsequent elevation changes resulting from sedimentation over elements from prior flood regimes (e.g. paleo floodplain surfaces) (Bridge 2003).

In general, lateral and vertical accretion takes place by the deposition of suspended loads resulting in horizontally bedded, fine-grained materials beyond the active channel zone (Bridge 2003; Fryirs und Brierley 2013).

The occurrence of floodplains and associated fluvial deposition depends on several factors. Although sediment deposition is low within the production zone (with 1–2 order rivers, high gradient, and high-flow velocity and power), sediment deposition increases with decreasing flow velocity and power in the transfer and final storage zone of river networks (Huggett and Richard 2007). Previous research suggests that floodplains act as temporary accumulation sites, not only for sediments, but also for nutrients and pollutants (e.g., heavy metals) transported via the river and deposited during flood events (Lair et al. 2009; Hürkamp et al. 2009; Edgeworth 2011). Therefore, floodplains have a natural “sink function,” and through their mainly Pleistocene and Holocene formations also function as natural (sedimentary) archives for major parts of the Earth’s latest history.

Floodplains cover just 0.61% of the global continental land area and around 4.4% of the national area of Germany, with regard to large rivers (>1000 km² catchment) (Nardi et al. 2019). Their role as a transitional environment within the aquatic terrestrial interface makes them important wetland habitats, with important ecosystem function and services (D’Elia et al. 2017; Bridge 2003). Because they are associated with rivers and surround them, floodplains can be considered a landscape connecting area.

Furthermore, based on their “sink function” for nutrients and fine-grained sediments in combination with the availability of groundwater, floodplains with fertile soils are important agricultural production sites (Nardi et al. 2019). Based on the connecting and transport element flood water, floodplain areas act as major flood retention areas and were therefore intensively shaped by humans regarding flood protection measures (Ciszewski und Grygar 2016). For this reason, across Europe, natural or near-natural floodplains do not exist anymore or exist only in small, protected areas that are not continuous (Edgeworth 2011). Large parts of the European floodplains are often intensively used for agricultural production, are isolated from flood dynamics by flood protection. In the meantime, they are also settlement and infrastructural areas. River and floodplain management has led to isolated floodplains built up by legacy sediments (Edgeworth 2011). However, it has been recognized, particularly against the backdrop of climate change and increasing extreme weather events, that flood retention needs to be restored to prevent catastrophic flooding (Masson-Delmotte 2018). This has led to extensive renaturation and revitalization measures in many floodplains (Edgeworth 2011). For example, from 1979 to 2014, 170 greater renaturation projects were conducted within Germany, leading to major gains of recovered active floodplain areas (Bundesministerium für Umwelt, Naturschutz, Bau und Reaktorsicherheit 2015). Main measures include the restoration of lateral and longitudinal connectivity between river and floodplain (e.g., dam removal), levee removal, channel reconstruction, remeandering, and construction of side channels and wetlands (Roni et al. 2019).

When transferring the known sediment transport dynamics and the functions of floodplains to the occurrence of (micro-)plastics in fluvial systems, several common factors arise that contribute to plastic inputs to floodplains: Plastics and microplastics can enter the fluvial system like sediments or pollutants via point and diffuse sources (Bancone et al. 2020; Stock et al. 2019). Even if microplastics seems to have a higher mobility through easy erosion and a different sinking behavior within the water column and flow, controlling factors of transport and deposition could mainly include particle density and shape (Bancone et al. 2020; Waldschläger und Schüttrumpf 2019a, 2019b). Those controlling factors are affected by physical, chemical, and biological factors in the environment, leading to a complex transport and deposition dynamic. In general, plastic transport, temporary storage, release, and reworking are proven or conceivable within active channels and floodplains (Bancone et al. 2020; Scheurer und Bigalke 2018).

The ongoing work of this thesis in 2019 identified evidence for (micro-)plastic transport within river systems and for a temporary storage within active channel sediments (bedload) and shore sediments. The work of Scheurer and Bigalke (2018), including the first detection of microplastics in Swiss floodplain topsoils, opens several questions regarding the possible plastic storage within floodplain soils. Microplastic loads up to 55.5 mg kg^{-1} or 593 p kg^{-1} within near-channel, proximal floodplain topsoils (sampling depth: 0–5 cm) mostly in nature reserves (Scheurer und Bigalke 2018) and has raised the following questions:

- If plastics and microplastic are present in fluvial systems, so far regarded as global transport pathways for plastics, can they also be deposited in fluvial systems?
- If floodplains act as “natural” sinks for sediments and pollutants, and if microplastics are present in proximal floodplain topsoils, could plastics enter the entire floodplain?
- If plastics have entered the environment for the last 70 years, when did they begin to enter floodplains?
- If the connecting medium within the aquatic-terrestrial interface is water and floodplains were built up from flood deposits, could flood dynamics also transport plastic into the floodplain?
- If plastics have been deposited in floodplains, how are depositions spatially distributed, and are they controlled by known factors such as floodplain morphology?
- If plastics meet so far “recognized” geogenic or anthropogenic contaminants (e.g., heavy metals) in floodplains, are there any spatial correlations between different contaminants?

1.2.2 Plastics in soils: The great unknown

Out the outset of working on this thesis, knowledge of microplastics in soils was very limited. After almost five decades of research with a strong focus on first marine ecosystems and second freshwater ecosystems, it was a surprisingly novel finding that microplastics also occur within soils. Recent trends within microplastic publications show a focus on research within marine systems but also an increase of research related to soils beginning in 2018 (Figure 3).

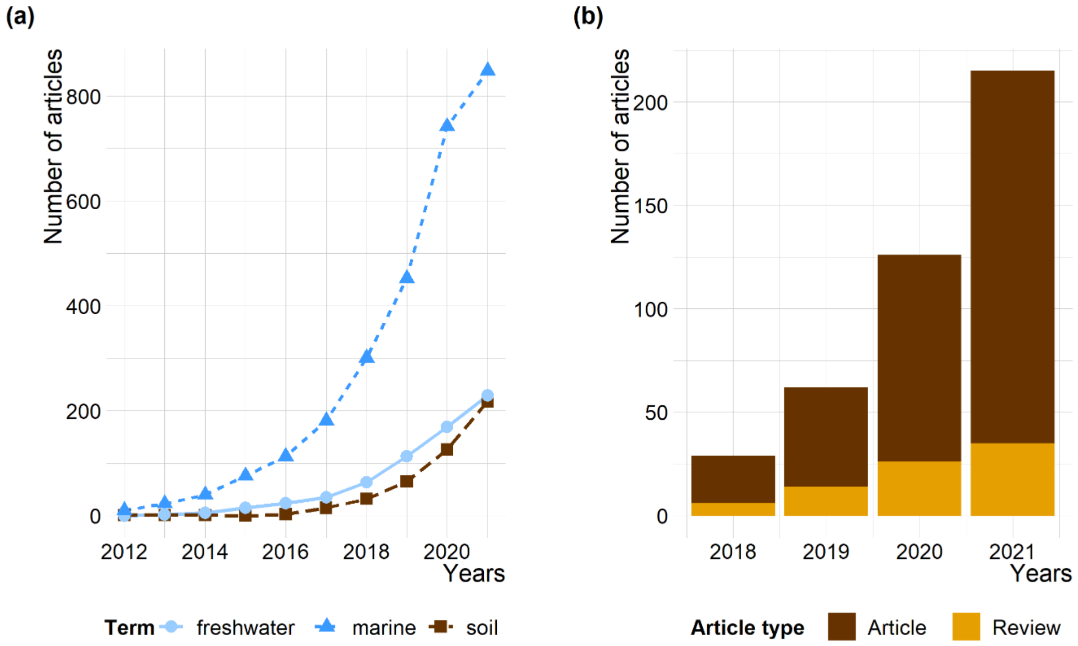

Figure 3: Trends in microplastic publications over the last decade (2012–2021). (a) Number of articles within the field of microplastic research separated by search terms (Data basis: Web of Science hits accessed on 24.02.2022, Clarivate Analytics, search term “microplastic” + “term”); (b) Number of articles within the field of microplastic research in soils separated by article type (Data basis: Web of Science hits accessed on 24.02.2022, Clarivate Analytics, search term “microplastic” + “term” separated by regular articles and reviews).

The first studies of plastics within the terrestrial ecosystem show that plastic is abundant within soils of industrial areas (Fuller und Gautam 2016) and garden soils (Huerta Lwanga et al. 2017). This comparatively late recognition was astonishing since plastics were already considered to be anthropogenic artifacts within soil science (FAO 2006; IUSS Working Group 2015) or were recognized in archaeology as modern anthropogenic disturbances (Zalasiewicz et al. 2016). Nevertheless, with the first evidence of plastics in soils and therefore terrestrial environments, a starting point for a further and rapidly developing field of research was laid (Figure 3). This new research field, developed since 2016 first had to find ways of analyzing plastic in soils. Many of the possible methodological approaches and possible environmental behavior of (micro-)plastics in soils were transferable from previous findings, resulting in a comparatively large review share within soil related articles since 2018 (Figure 3).

Possible sources and input pathways for (micro-)plastics in soils include direct inputs from littering or agriculture and diffuse inputs like depositions from the atmosphere, runoff, or flooding (Figure 2b).

For example, organic wastes such as compost or sewage sludge, widely applied as fertilizers, can contain very large amounts of microplastics (Braun et al. 2021; Brandes et al. 2021; Tagg et al. 2022). The use of agricultural plastics ("plasticulture", e.g., plastic mulching, greenhouses) can also be considered an intensive direct source to soils (Steinmetz et al. 2016). Furthermore, plastics are released into the environment in several ways, including atmospheric (wind) transport, irrigation, erosion, and runoff or flooding, depending on soilscapes and their location (Rezaei et al. 2019; Rehm et al. 2021; Lechthaler et al. 2021).

Once plastics became accumulated in the soil, the synthetic plastic particles became part of a complex, three-dimensional system and matrix, including a mixture of organic matter and mineral components (Bläsing und Amelung 2018). The medium soil therefore allows the adaptation of previous analysis methods, especially from the extraction of plastics from sediments. However, these had to be constantly adapted to the more complex soil properties with regard to SOM, soil aggregates, and pedogenetic features (Möller et al. 2020; Pinto da Costa et al. 2019). The focus of all analytical methods is on the extraction of microplastics from the surrounding soil or sample matrix, which can be achieved in various ways. Furthermore, once incorporated within the soils, plastics could be part of different possible in-situ processes (Figure 2b). Depending on the particle size, shape, and composition, vertical and lateral displacements in the pore space by different organisms are possible by percolating water or groundwater (Rillig et al. 2017b; Yu et al. 2019). Fixation in soil aggregates and thus prolonged accumulation or leaching by groundwater, for example, are also conceivable (Zhang und Liu 2018; Wang et al. 2020).

In 2019, when the work on this thesis began, only seven studies had dealt with (micro-)plastics in soils, focusing on the detection and determination of (micro-)plastic levels in soils. At that time, there was evidence of (micro-)plastics in municipal soils (Technosols) (Fuller und Gautam 2016), garden soils (Huerta Lwanga et al. 2017), proximal floodplain soils (Fluvisols) (Scheurer und Bigalke 2018), and agricultural soils (Entisols, Vertisols, Nitisols, Gleysols) (Zhang und Liu 2018; Liu et al. 2018; Piehl et al. 2018; Corradini et al. 2019). Using different analytical methods, these studies have provided the first evidence of (micro-)plastics in soils. However, these studies only examined topsoil (maximum depth 25 cm) and were exploratory in their search for (micro-)plastics in different soils worldwide. Those first conceptual and methodological approaches to accessing (micro-)plastics within soil systems were reasonable for their initial stage of development. However, the soil as space and spatial interrelationships of soils have not been considered in the process. In general, soils and soil functions can hardly be understood without considering space because soils are spatial phenomena (Weihrauch 2019). According to Weihrauch (2019), soils do not only consist of "stationary matter" but also are a processual phenomenon.

Soils exists within the geographic space and are a result of a specific combination of soil-forming and soil-effecting environmental factors running over time (e.g., weathering, climate, flora) (Blume et al. 2016). Furthermore, soils are strongly shaped by human utilization (Blume et al. 2016). All those environmental and anthropogenic processes act across local spaces (Weihrauch 2019; Willgoose 2018). Therefore, a systematic approach becomes necessary to understand soils as a part of a larger spatial continua within a general landscape or "soilscape" context (Willgoose 2018). With regard to (micro-)plastics as a less "recognized" anthropogenic contamination of soils, systematic approaches that go beyond the evidence of plastic in an isolated soil are required to gain a further understanding of the spatial dynamics. For example, within the proposed global plastic-cycle, terrestrial systems and their soils can only be considered as a single part of a larger interconnected system in which plastics are present (Zalasiewicz et al. 2016).

Furthermore, systematic studies with methodological advances are important to understand the unknown environmental effects of plastics and microplastics within soils. So far, it has become clear that the presence of plastics within soils can have consequences for soil structure, soil organisms, and also plant growth on the soil (Selonen et al. 2020; Lahive et al. 2019; Zang et al. 2020; Rillig et al. 2019; Liu et al. 2017). One of the main problems with plastic in soils, however, is that it will be present for years to decades to possible centuries (Chamas et al. 2020; Napper und Thompson 2019). The low and slow degradation of plastic particles, especially under buried conditions and thus shielded from UV-light, results in a long presence and decomposition into progressively smaller micro- to nanoplastic particles whose environmental impact can be even more significant because of their small size (Napper und Thompson 2019). Furthermore, plastics can carry and desorb or adsorb different other pollutants such as heavy metals or organic pollutants incorporated as plastic additives or present in the soil (Hahladakis et al. 2018; Catrouillet et al. 2021).

With respect to the already known environmental hazards that can emanate from (micro-)plastics within marine and freshwater ecosystems, a variety of these environmental concerns are also conceivable for soils. This is especially problematic since soils are an important but already highly degraded and endangered natural resource that perform the most important functions within natural material cycles, as ecosystems, and most importantly as the basis of all terrestrial plant growth and thus all food chains (Blume et al. 2016). With the emerging threat of (micro-)plastics, an additional human-made risk factor is now entered into soils, whereas humanity basically cannot afford any further soil degradation against the background of global population growth and food insecurity (Food and Agriculture Organization of the United Nations [FAO] 2015; European Commission Q2 2020; European Chemical Agency [ECHA] 22.08.2019). As plastic production and use continues, research on (micro)plastics in soils is still lagging.

Out of this context, the following scientific problems emerged at the beginning of this thesis and partitially remained:

- Despite validated methods developed for the marine environment, there has been and still is a lack of analytical standard protocols and many possible different analytical methods combinations, which hamper scientific comparisons.
- Despite first evidence of plastics and microplastics on and in different soils, there was no evidence of microplastics in subsoils or spatially representative investigation approaches against the background of the soil systems and soilscapes.
- Even if possible input pathways into the soil were known, the contributions of individual input pathways would be unknown.
- Despite first determinations of microplastic behaviour in soil (e.g., mobility), influence of soil on microplastics (e.g., aggregate incorporation), and vice versa (e.g., risks), most environmental drivers and process dynamics have so far only been incompletely understood.

Today, those issues lead to the fact that plastic in soils can still be described as "a great unknown" in many cases today. Nevertheless, the research field of plastics in soils is a rapidly expanding and highly dynamic field, and the state of research is subject to constant and rapid development. Some of the open research questions or unclear to non-existent relations, which emerged at the beginning of the work on this thesis, have been clarified in the meantime. Therefore, the results presented in this thesis, the respective state of research is explained in the introduction of each paper (Chapters 3.1–3.6) and is comprehensively addressed in the synthesis (Chapter 4).

1.3 Unravelling the spatial distribution of plastics in floodplain soils

As outlined in Chapter 1.2, the knowledge and understanding of plastic residues in terrestrial environments is still very limited. The existence of (micro-)plastics within the environment, however, is not a recent discovery within environmental sciences. As stated before, the initial discovery of (micro-)plastics within the environment took place in the 1970s. In the meantime, major developments including the detection of plastic residues within almost all habitats, on all landscapes, and on all continents of the Earth, as well as the further development of analytical methods, have been performed.

With the first detection of (micro-)plastics in terrestrial ecosystems and topsoils, a new branch of research emerged, which pursues a bundle of new research questions and scientific problems. At the same time, the complexity of this research topic and the scientific problems increase with each new detection of plastic in different environmental systems.

However, it has become clear from previous research that (micro-)plastics are transported between the different environmental systems and may even be subject to a global cycle, which is comparable to other known environmental or earth-system cycles (e.g., rocks and sediments, carbon). Assuming a global plastic transport theory, previous research illustrates the role of river systems as main transport routes, but also the possibilities of temporary deposition and thus storage of (micro-)plastics in fluvial and semi-terrestrial settings.

Despite the first detections of microplastics in soils, there is a lack of spatial (micro-)plastic data. Previous research can be defined as mainly explorative, without spatial reference or spatial representative study designs. Within physical geography, the basic understanding and consideration of geospatial aspects and dynamics has the potential to generate spatial data and thus a spatial, environmental, process-oriented understanding of microplastics in environmental systems.

With the onset of research for this thesis in 2019, the formulation of the general scientific problem became simple given the lack of general knowledge about the occurrence of (micro-)plastics in terrestrial and semi-terrestrial environments: Evidence of (micro-)plastics in semi-terrestrial floodplain soils is lacking when it comes to understanding the role of floodplains within a global plastic cycle and possible impacts on floodplain soils. Furthermore, spatial representative data is missing because of the spatial constraints of the previous research. Both issues are especially problematic because plastic does not seem to be a unique problem of isolated or single environments. Possible consequences of plastic contamination for soils and especially floodplain systems could have far-reaching environmental impacts. However, spatial representative data on (micro-)plastics must be gathered before possible environmental impacts can be assessed.

1.3.1 Objectives and hypotheses

The overall goal of this thesis is to unravel the role of floodplain soilscapes as depositional areas for macro- and microplastic debris within the global plastic cycle. Within the framework of this thesis, the spatial distribution of meso- and microplastics in floodplain soilscapes will be investigated to generate a basic understanding of the spatial distribution and spatio-temporal accumulations of plastics in semi-terrestrial ecosystems. Based on the above-mentioned scientific problems and knowledge gaps, the present thesis has the following three major objectives:

Objective 1: To develop a spatial representative and process-oriented sampling approach to quantify the spatial distribution of meso- and microplastics in floodplain soilscapes

Objective 2: To determine environmental drivers of meso- and microplastic distribution from both lateral and vertical spatial distribution patterns in combination with floodplain soil stratigraphy and properties

Objective 3: To establish the temporal enrichment and correlations to other contaminations on the basis of spatial correlations and sediment dating.

To archive these objectives, the present thesis is therefore guided by the following major research questions:

1. What quantities of meso- and microplastics occur in floodplain soils?
2. How are meso- and microplastics spatially distributed within floodplain soilscapes?
3. Which environmental drivers affect the spatial distribution of meso- and microplastics?
4. When did meso- and microplastics enter floodplain soils, and do they remain spatially stable?
5. Are there spatial connections between “new” (plastics) and recognized contaminants (here: heavy metals and metalloids)?

To answer the above-mentioned research questions of this thesis, the following hypotheses were formulated and will be tested:

1. Floodplains are part of a global plastic cycle and act as temporal accumulation sites for meso- and microplastics with considerable concentrations.
2. Meso- and microplastics are widespread within floodplain soilscapes, over the entire catchment area and soil column.
3. Flood-related processes and land use affect the spatial distribution of meso- and microplastics.
4. Meso- and microplastics have been in floodplain soilscapes since the Great Acceleration and are subject to vertical shifts in the soils.
5. Spatial connections between plastics and heavy metal contaminations occur in floodplain soilscapes.

1.3.2 Thesis outline

The thesis commences with the theoretical principles of the environmental plastic problem and the current state of research on plastics in fluvial systems and (semi-)terrestrial soils (Chapters 1.1 and 1.2). The following chapters explain the procedures used to obtain the data for the thesis and the methodological approach on which the research is based. Within two catchment areas and river systems, the implementation of the geospatial sampling approach based on the selection of the study areas and the implementation of the field work (Chapter 2.2.1) takes place. Furthermore, the laboratory analyses for meso- and microplastic detections and analyses of soil properties, heavy metals and metalloid concentrations, and sediment dating are described (Chapter 2.2.2). A physical-geographical, landscape and soilscape based classification of the two river systems is given in Chapter 2.3, followed by a comparison of the two areas.

Within the framework of this thesis, different contributions reaching from conceptual approaches over case studies to viewpoints have been published. The individual contributions follow the previously mentioned hypothesis and the general understanding that spatial dynamics of meso- and microplastics can only be understood against the background of a landscape-oriented and representative study designs. Within this thesis, individual contributions are structured according to conceptual work, case-studies and resultant opinions (Figure 4).

Chapter 3.1 focuses thematically on the methodological concepts that are necessary for investigating spatial dynamics of plastic residues in soils. Based on these underlying considerations, the following chapters focus on investigating the spatial distribution, environmental drivers, and the time period of meso- and microplastic contaminations on the example of the Lahn River (Chapters 3.2, 3.3, and 3.4), while Chapter 3.5 presents the analogy using the example of the river Nidda. Further conceptual developments and approaches based on the former case studies in a broader earth-historical context are summarized in Chapter 3.6.

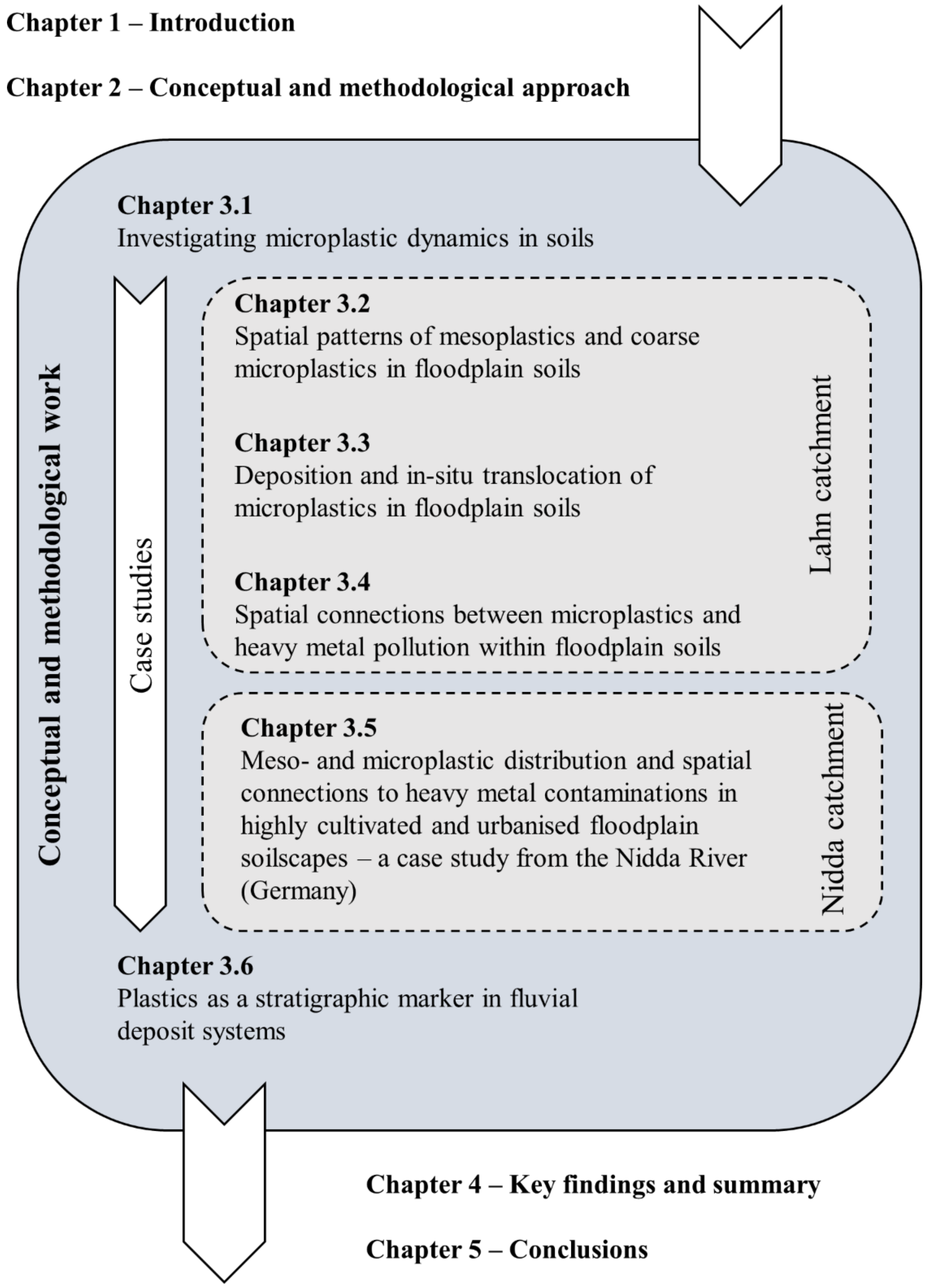

Figure 4: Structure of the present thesis.

The key findings of this thesis and the individual contributions are to be understood as development progress and are therefore summarized and linked to the above-mentioned objectives and hypothesis in Chapter 4. The last chapter discusses the conceptual and methodological approach, gives recommendations and perspectives for further research on (micro-)plastics in soils and floodplains, and makes specific implications for the management of plastic contaminations in floodplain soils by policy makers.

2. Conceptual and methodological approach

2.1 The challenges of detecting meso- and microplastics in soils

With the comparatively new finding of (micro-)plastics in the terrestrial environment, a new and young research field was established in 2016, one that has rapidly adapted and further developed a variety of methodological approaches for the analysis of meso- and microplastics in soils. Many of the analytical methods used today have their origins in microplastics research in marine or fluvial systems, but these methods could not be transferred one-to-one to terrestrial systems and the environmental medium soil (Möller et al. 2020; Thomas et al. 2020).

In contrast to water samples, soil samples are a complex and heterogenous environmental matrix resulting from pedogenesis. Soil itself can be termed heterogenous in their characteristics and structure because of different locations in space and because of interacting environmental processes that affect pedogenesis. With the start of the investigations into plastic residues in soils, there was no information about the spatial distribution of plastic residues in terrestrial systems or a single soil column (Bläsing und Amelung 2018). From knowledge derived from within marine or fluvial sediments, a heterogenous distribution could be assumed in general (Martin et al. 2017a; Cole et al. 2011). Furthermore, it was known that plastics that occur within the environment are highly diverse in terms of chemical composition (polymer-type and additives), particle shapes, and sizes, resulting from production or environmental degradation (Kooi und Koelmans 2019). For this reason, the major challenge of detecting meso- and microplastics in soils can be expressed as detecting heterogenous particles within a heterogenous environmental sample matrix.

Related challenges occur during considerations of sampling strategies and sample handling. Sampling requires an adequate spatial resolution, which is difficult to determine when the spatial dynamics of the substance sought are poorly understood. To tackle this challenge, knowledge about microplastic distributions in other environmental systems must be transferred; additionally, fundamental properties of soils and soilscapes must be spatially considered. Furthermore, sample handling must be oriented to the target substance, here plastics, to detect it within the samples and not contaminate them (Möller et al. 2020).

An assumed heterogenous occurrence within soils can be addressed by sampling large sample volumes, repeating samples, or pooling several individual samples (Möller et al. 2020; Ruggero et al. 2020).

Further challenges occur when considerations and the performance of the meso- and microplastic analysis are pending. The overall aim is therefore to isolate meso- and microplastics from the heterogeneous sample matrix to quantitatively and/or qualitatively determine the plastic components of each sample. To archive this aim, manifold sample separation approaches can be transferred from other environmental media (e.g., water, sediment) to more complex soils. Until now, there has been no standardized method approach or a satisfactory method to perform this comprehensively for all conceivable plastic residues because of their own heterogeneity (Ruggero et al. 2020; Kooi und Koelmans 2019). Therefore, each possible method has its own limitations and analytical constraints, and the selection of a suitable combination of methods must always be hypothesis oriented.

Soil matrices are composed mainly of a mineral phase, an organic phase and the target material (micro-)plastics as a polymeric, non-organic phase. To separate the mineral phase, common approaches like density separations with different density solutions (e.g., water, NaCl, $ZnCl_2$) with different densities (e.g., 1.0 g cm^3, 1.2 g cm^3, 1.6 g cm^3) can be applied within different separation units or devices (Cutroneo et al. 2021). However, this always leaves the organic phase and the polymer phase together because both have the same density range.

To separate (micro-)plastics from the remaining organic matrix, several approaches such as enzymatic digestion, acid and alkaline solution treatments or oxidations, and staining methods or separation based on electrostatic behavior are available (Silva et al. 2018; Möller et al. 2020). After separating the soil phases, sieving and sorting of (micro-)plastics because of the different size definitions (Zhang et al. 2020) and a subsequent quantification and identification often becomes necessary. Here, quantification can be mass or particle based, and identification can be archived by various chemical methods (e.g., FTIR- or Raman-spectroscopy) (Stock et al. 2019; Käppler et al. 2015).

Because of the continuous development of methodological concepts and solutions, it is therefore difficult to specify a longer present “state of the art” for sampling procedures, (micro-)plastic separation and analysis in soil samples. Therefore, each methodological approach must be considered with respect to its limitations and applicability.

2.2 Methods

2.2.1 Geospatial sampling approach

Soils, and more specifically floodplain soils, are three-dimensional spatial phenomena that result from local and regional combination and interaction of environmental factors. Basically, these environmental factors are climate, bedrock, relief, water, flora and fauna, and human influences on or interactions with the soil over time (Blume et al. 2016). For floodplain soils, those environmental factors act locally within the floodplain but are significantly influenced by the entire catchment area of the corresponding river system. Even if floodplain soils and their properties are a local phenomenon, the environmental processes that are responsible for their formation and properties interact between different localities over space and time (Weihrauch 2019). Within soil science in general, a geographical view or an underlying awareness of spatial dynamics and interactions is frequently lacking. As already mentioned, initial studies have exclusively conducted explorative surveys on (micro-)plastic contaminations within topsoils. Such exploratory approaches are carried out without consideration of the geographical space or spatial interactions and dynamics.

In distinction to those explorative study and sampling approaches in (micro-)plastics research, this thesis follows a geospatial sampling approach composed of a spatial systematic and representative sampling concept oriented to different environmental processes and their natural drivers. According to Weihrauch (2019), soils cannot be understood adequately if they are understood as an isolated point within the geographical space. Therefore, within this thesis, the soil and the studied floodplain soils are considered an integrated and influenced part of a larger spatial continuum (here: floodplains, river systems and catchment area) with specific spatial interactions of soil-forming and soil-influencing factors. This soil geographic approach will therefore consider and discuss the studied soils as a three-dimensional part of a soilscape (Willgoose 2018).

Floodplain soils formation is basically a results of fluvial system dynamics like flood water, sedimentation, and erosion under the influence of anthropogenic impacts resulting from a “human-natural entanglement” (Edgeworth 2011). Those fluvial system dynamics and anthropogenic impacts act on local to landscape levels. The geospatial sampling approach presented therefore attempts to integrate both spatial dimensions within a floodplain soilscape. With regard to (micro-)plastic contaminations, it becomes necessary to record and study the environmental processes and drivers responsible for the distribution and spread of these contaminants in floodplains soilscapes. Environmental processes (e.g., flooding) and natural (e.g., bedrock, valley wide) or anthropogenic landscape properties (e.g., land use) could have an influence on the deposition, accumulation, and possible mobilities of plastic particles in floodplain soils.

To understand these processes, the geospatial sampling approach aims to identify suitable and spatial representative sampling sites with different single soil profiles, which are not examined isolated but in the context of the floodplain landscape and its soilcape.

2.2.1.1. Selection of floodplain-cross transects

For the implementation of the approach, two river systems and the associated floodplain soilscapes were selected. The Lahn River and the Nidda River, both located in central Germany, with different catchment characteristics and fluvial system dynamics, but typical for a variety of other river systems in central Europe, were selected (see Section 2.3.). Furthermore, it was evident that, in contrast to the studies carried out so far, soil sections below the topsoil should also be sampled, as the soil, especially in floodplains, cannot be understood holistically without the subsoil (see Section 2.2.1.3.). After these basic considerations, it was necessary to first define spatial criteria for the selection of sampling sites based on the hypotheses and questions formulated at the beginning of this thesis. (Micro-)plastics within floodplain soils should be studied in their vertical and lateral spatial distribution. For the vertical distribution, a maximum sampling depth of 2 meters was selected, with sampling according to fixed depth levels (see Section 2.2.1.3.), considering possible vertical shifts of plastic particles and vertical mobility (Rillig et al. 2017b).

The lateral distribution was conducted on two spatial scales: Level one follows a longitudinal gradient on the catchment scale, and level two follows the floodplain cross-section from proximal to distal floodplain areas. On level one, floodplains and their soilscape formation are affected by changing bedrocks, valley and floodplain extensions, sediment budgets, and flood characteristics and extensions (Brierley und Fryirs 2007; Bridge 2003). On level two, floodplain soilscapes are affected by different valley forms and mostly show a clear geomorphological and sedimentological arrangement, which is mainly shaped by differentiated sediment deposition dynamics between proximal and lateral sites (Fryirs und Brierley 2013). In addition, different groundwater levels occur in the floodplain cross-section, and associated different moisture levels in the soils, affecting current land use (Fryirs und Brierley 2013).

To select a spatially representative set of study sites, a lateral zoning of the river courses was made on spatial level one based on the following factors and their changes along the river courses:

a) Geology of the catchment area and changes in the course of the river
b) Valley slope and valley width, as well as width of the floodplain areas
c) Land use and urbanization

The lateral zoning is based on the basic division of a river system into upstream, middle, and downstream, while considering local and regional landscape phenomena (Figure 5a). Within each identified river zone on spatial level one, comprising of comparable geological, geomorphological and land use properties, representative floodplain cross-transects were identified following the following criteria, which must be fulfilled to investigate the formulated hypotheses of this thesis (Figure 5b):

a) Each cross-transect must be part of a natural flood retention area to allow floodwaters to reach the entire width of the floodplain.
b) Within the cross-transect, no anthropogenic disturbances such as dykes, railway embankments, major roads, land elevations, or buildings should occur.
c) Each cross-transect should include a distinct floodplain morphology with levee, flat area, and backswamp, as well as other natural surface forms (e.g., inactive channels), if applicable.
d) Typical land uses (e.g., riparian vegetation, grassland and pasture, cropland) should occur in each transect.
e) Each cross-transect should not be located in close proximity to potential (micro-)plastics point sources (e.g., garbage dump, WWTPs).

The established criteria were qualitatively tested within a GIS environment based on the available environmental data (see Section 2.2.3.6.). After selecting possible sites in the catchment areas of the rivers Lahn and Nidda, they were inspected in the field to determine the sampling locations. To check the soil properties of each soilscape, a previous soil survey was carried out at each selected site before the regular soil sampling.

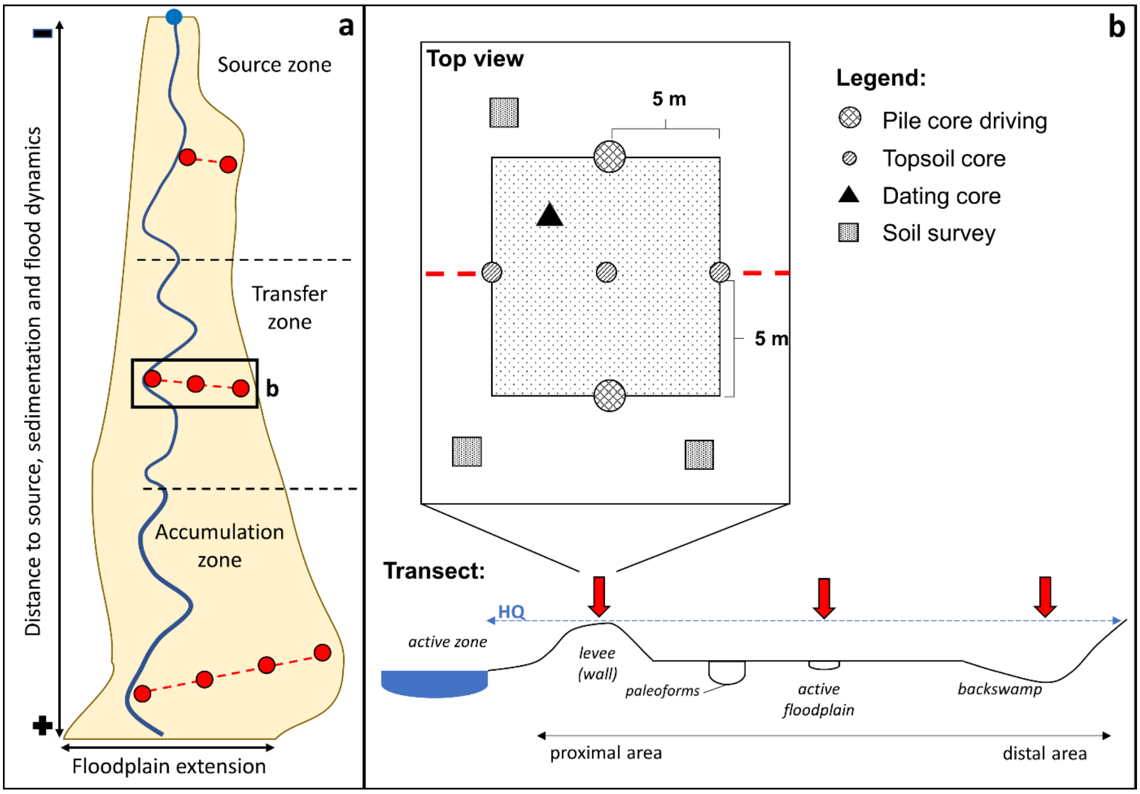

Figure 5: Geospatial sampling approach with (a) transect locations and resolution along the river course and (b) sampling transect and different sampling points within floodplain cross-section.

For the Lahn River catchment and its course, four floodplain cross-transects were established based on land- and soilscape properties introduced in Section 2.3.1. Site ELM (upper reaches) represents the river within the Rhenisch Slate Mountains, smaller floodplain areas that are morphologically strongly characterized with high surface dynamics and young, sandy floodplain soils.

Sites ROT (upper middle reaches) and site STD (lower middle reaches) represents the river within an alternating landscape, wide and flat floodplain valleys, thick loam deposits and alternating urban to rural land uses. Site LIM (lower reaches) resipiscence the wider floodplain valley sections, after a narrow valley, with individual floodplain widenings, alternating flood loam deposits and agricultural land uses.

For the river Nidda catchment and its course, four floodplain cross-transects were established based on land- and soilscape properties introduced in Section 2.3.2. Site NID (upper reaches) represents the river directly after leaving the Vogelsberg mountains, with the first floodplain formation after narrow mountain valleys. Sites MOK (upper middle reaches) and OKA (middle reaches) represents the river within agricultural heartland, with wide and flat floodplain areas under agricultural use. Site FRA (lower reaches) represents the strongly urbanized section of the river in the Rhine-Main agglomeration area.

At each of the selected cross-transects, two to four sampling plots were established between the proximal and distal floodplain areas after previous soil survey. Depending on the metric floodplain width on one side of the river and the soilscape and geomorphological properties, two sampling plots (sites ELM, ROT, NID, FRA), three sampling plots (sites MOK, OKA), or four sampling plots (sites STD, LIM) were established. The first plot was always located on the levee or directly at the beginning of the flat floodplain, and the last one in the floodplain margin (backswamp, or before anthropogenic disturbance). In between, plots were set up at equal intervals between the other plots, as required.

2.2.1.2. Previous soil survey

After the prior selection of suitable sampling sites and floodplain cross-transects, the selected floodplain sections were soil surveyed to make an appropriate determination of the later sampling plots. For this purpose, 5 to 15 hand cores (Pürckhauer, 1 m, Ø 20 mm) were taken over a larger area in the surroundings of each cross-transect and documented according to German soil classification (Ad-hoc AG Boden 2005) and the FAO guidelines for soil description (FAO 2006). The soil properties were examined specifically regarding morphological areas within the floodplain, with a special focus on flow channels and the influence of groundwater.

2.2.1.3. Regular soil sampling

Regular soil sampling was performed between August and October 2019 within both catchments after previous soil survey. At each sampling plot, two soil profiles of 10 m were drilled via pile core driving to a depth of 2 m (Figure 5b). Pile cores were made from stainless steel with a diameter of 100 mm for the upper core (0–1 m) and 80 mm for the lower core (1–2 m).

After extracting the cores by means of a hydraulic lifting unit (Stitz GmbH, Gehrden, Germany) (Figure 6a), the soil stratigraphy and pedogenesis was documented according to the German soil classification (Ad-hoc AG Boden 2005) and the FAO guidelines for soil description (FAO 2006). Soils were classified according to WRB 2015 (IUSS Working Group 2015). Furthermore, soil color was documented according to Munsell charts and carbonate content after reaction with a few drops of 3.23 M hydrochloric acid (HCL) according to Ad-hoc AG Boden (2005).

After soil description, the cores were sampled according to the following depth sections: 10 cm sections for 0 to 50 cm (5 samples), 25 cm sections for 50 to 150 cm (4 samples), and 50 section for 150 to 200 cm (1 sample). Samples were named according to the sampling plot (e.g., ELM-1) and section (e.g., ELM-1-1). Extracted soil material from both cores was pooled and transported in cornstarch bioplastic bags (Mater-Bi bags, Bio Futura B.V., Rotterdam, Netherlands) (Figure 6b). Sampling was carried out with the help of stainless-steel spatulas and hand shovels. To avoid plastic contamination in the field, plastic objects on the equipment used were removed where possible and direct contact between the sample and plastics was avoided.

The regular soil sampling procedure resulted in 211 soil samples (Lahn: 111 from 24 cores, Nidda: 100 from 20 cores) with an average dry sample mass of 1222.5 g with a range of 385 to 3705 g. Because of the very heterogenous occurrence of microplastics in soils and sediments shown in previous studies, those comparatively large sample amounts and the pooling of two cores were applied (Prata et al. 2019; Stock et al. 2019).

2.2.1.4. Soil sampling for dating purpose

Soil samples for dating purpose were taken at the transect sites ELM and LIM within the Lahn River catchment in proximal floodplain positions next to the sampling plots ELM-1 and LIM-1 with the names ELM-D and LIM-D. For this purpose, a single drill core (stainless-steel, Ø 80 mm) was drilled to a depth of 1 m, at site ELM on grassland behind the natural levee and at site LIM on natural riparian vegetation (copses, herbs) (Figure 6c). The drill core was drilled via pile core driving and carefully excavated to obtain an entire soil core free of disturbances as far as possible. Each core was subsequently divided into 2 cm sections. Sample material from each section was extracted in the field and transported in PE-bags resulting in 42 samples from core ELM-D (0–84 cm) and 45 samples from LIM-D (0–90 cm).

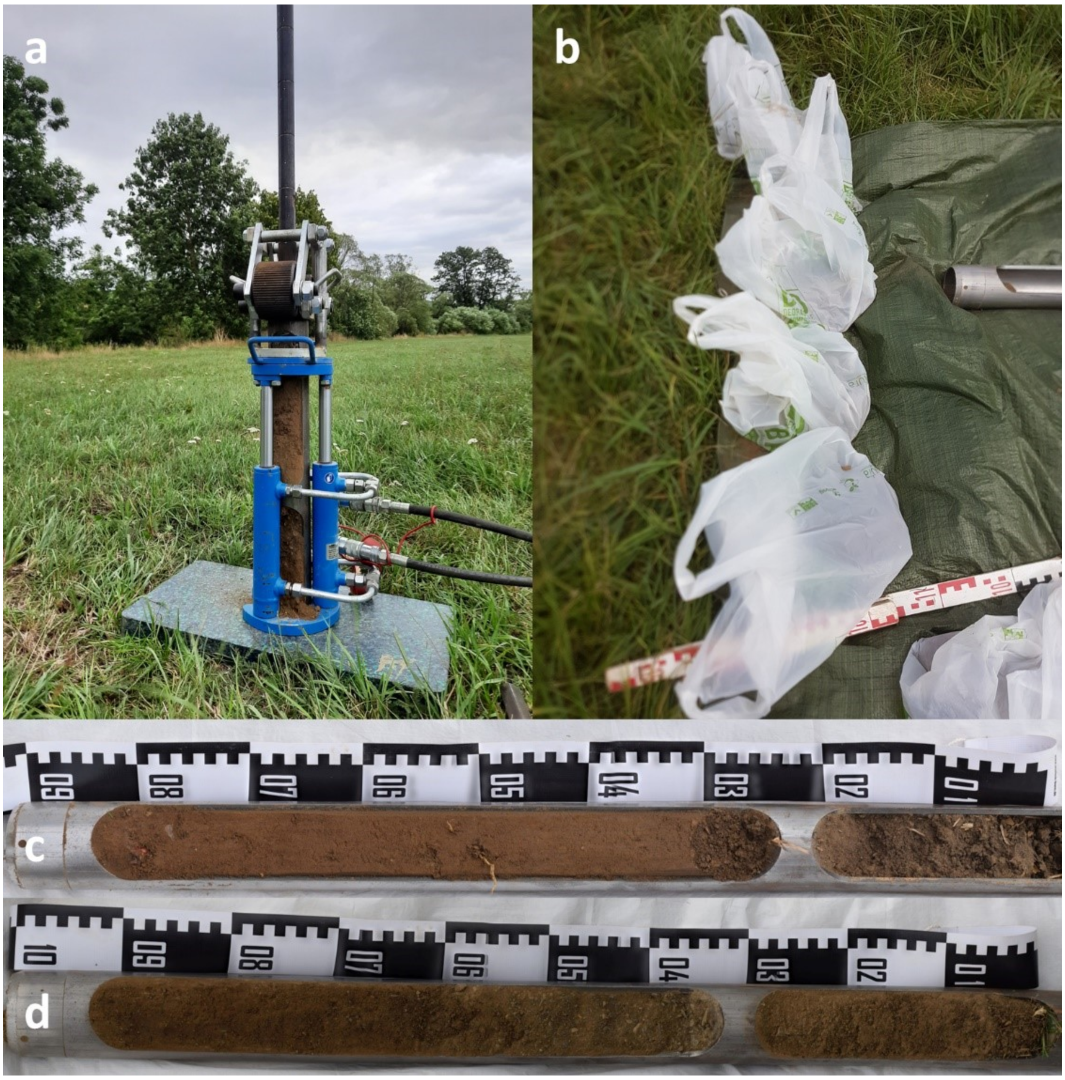

Figure 6: Examples of field sampling with (a) hydraulic core lifter at sampling site ELM (Lahn), (b) corn starch bioplastic bags (Bio Futura B.V.) for sampling storage, (c) drill core LIM-D (riparian), and (d) drill core ELM-D (riparian).

2.2.1.5. Macroplastic sampling on soil surfaces

Where conspicuous macroplastics amounts were visible on the soil surface, additional sampling of macroplastics on the soil surface was carried out. The method was applied to the sampling plots STD-1 (Lahn, lower middle reaches) and OKA-2 and OKA-3 (Nidda, lower middle reaches), both cropland and harvested before sampling. Oriented to the method presented by Piehl et al. (2018), visible plastic fragments were collected on a 20 m² area around the drill points by walking straight lines with two persons (four-eyes-principle). Collected plastic fragments were stored cornstarch bioplastic bags.

2.2.2 Laboratory analysis

Laboratory analysis is based on the following scheme and covers the preparation of the samples up to the data evaluation of the raw data obtained (Figure 7). Sample material from the different field sampling methods (Sections 2.2.1.3 to 2.2.1.5) is transferred to sample preparation and subsequently to the respective analytical methods for plastics analysis, including spectroscopic analysis and heavy metal digestion from plastics, as well as soil properties analysis and sediment dating. Finally, all raw data were processed and transferred to the statistical data analysis.

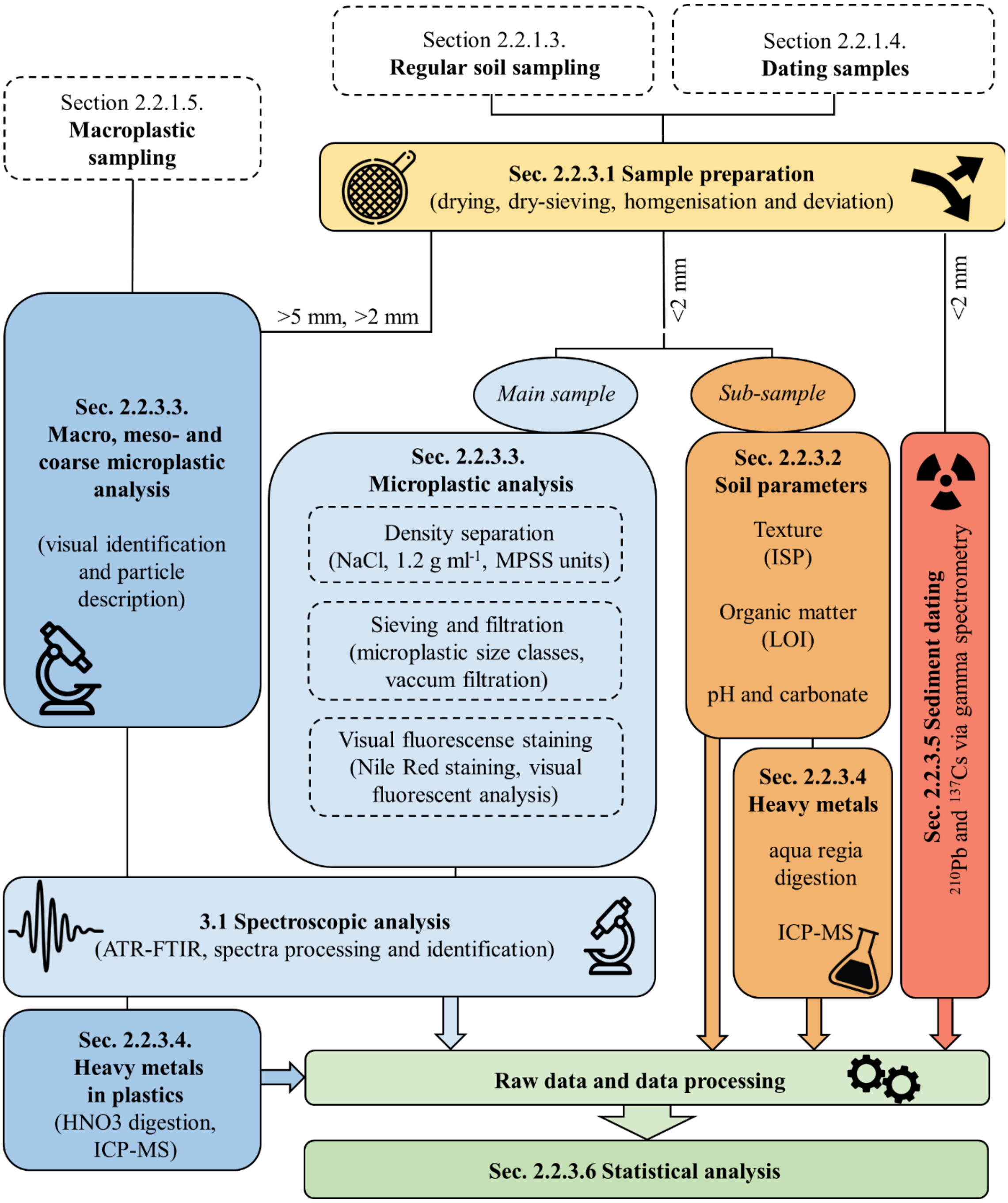

Figure 7: Laboratory analysis scheme with section references for each analysis step.

2.2.2.1 Sample preparation

Sample preparation for regular soil samples was carried out after the samples had been transported from the field. Field fresh soil samples were immediately weighted and dried at 45°C for four days in a closed drying chamber. Subsequently, the dried sample material was carefully mortared (ceramic mortar) by hand to break down soil macro-aggregates and weighted again to document the total sample dry mass. The sample material was than dry-sieved through stainless-steel sieves (Retsch, Haan, Germany), covered with a stainless-steel plate, to the following size fractions: >5 mm (macro- and mesoplastics), >2 mm (coarse microplastics and coarse soil fraction, rock fragments), and >2 mm (microplastics and fine-earth fraction). Fractions >5 mm and >2 mm were weighed and then stored in PE-bags.

The remaining fine-earth fraction was afterwards homogenized in a stainless-steel bowl and divided via a rotary sampler (Retsch, Haan, Germany) to obtain representative sub-samples for soil parameter and heavy metal and metalloid analysis. Sub-samples with an average mass of 130 g (approx. 12.5 % of total sample volume) were stored in PE-bags while the main portion of the sample (Lahn: average 1305.8 g, Nidda: average 1278.5 g) was stored for later microplastics analysis in cornstarch bioplastic bags.

Soil samples for dating purposes were processed in a comparable manner. After drying (45°C, two days, closed drying chamber), the samples were also mortared using a ceramic mortar and dry-sieved into fractions >2 mm (coarse soil and rock fragments) and <2 mm (fine-earth fraction). Samples were weighed at the beginning and dry by fraction to document soil moisture, dry mass, and coarse soil content. Subsequently, the samples were homogenized and divided as described above. Approximately 27 g each were transferred to 50 ml PE containers with screw caps and used for dating.

During sample preparation, various measures were applied to avoid sample contamination by plastics or clothing fibers. In principle, only plastic-free devices were used, which were cleaned with distilled water after each use. Samples were handled in metal or glass containers and stored in plastic only in the case of dating samples and sub-samples for further analysis. A pure cotton lab coat was worn during all work. The exposure time of each sample to the air was also kept as short as possible to avoid air contamination.

2.2.2.2 Soil parameters

Soil parameters were determined from representative sub-samples of regular soil samples (211 samples). For each sample, the soil moisture content was determined from 5.0 ± 0.01 g soil by drying (105°C), and the content of soil organic matter (SOM) was subsequently determined via loss of ignition at 550°C according to DIN 19684–3:2000–08. Both values were recorded as percentage by weight (wt%). Furthermore, pH was measured with a pH 91 electrode (WTW, Weilheim, Germany) in a soil suspension from 5.0 ± 0.01 g with 0.01 M $CaCl_2$ solution (m:V 1:2.5). Soil texture was analyzed via the Integral Suspension Pressure (ISP) Method (Durner et al. 2017) after sample preparation according to DIN ISO 11277:2002–08.

From each sample 30.0±0.01 g or 40.0±0.01 g, depending on the grain size documented in the field, were used for texture analyses. For sample preparation at least 30 ml of hydrogen peroxide (30%, H_2O_2) were added for the destruction of SOM and 20 ml sodium pyrophosphate ($Na_4P_2O_7$) was used as dispersing agent. Recovery of the sand fractions was carried out after the ISP procedure by wet sieving in the fractions >0.63 mm, >0.2 mm, and >0.063 mm (Retsch, Haan, Germany), drying (105°C) and weighing.

2.2.2.3 Meso- and microplastic analysis

The meso- and microplastic analysis was separately performed for (a) meso- and coarse microplastics (>2 mm) and (b) microplastics (<2 mm). Macroplastic particles from soil surfaces were processed like (a) without inspection.

For meso- and coarse microplastic analysis, the respective sieve fractions (>5 mm and >2 mm) of each sample was transferred to a stainless-steel bowl with imprinted grid (1x1 cm grid size). Each grid space was subsequently visually inspected under a stereomicroscope (SMZ 161 TL, Motic, HongKong) with a maximal magnification of 40x. Potential plastic particles were identified according to the criteria introduced by Norén (2007) and own criteria. Particles were counted and picked if (i) no cellular, organic od undissolved soil aggregate structure was visible, (ii) the particle has a homogenous color, and (iii) in the case of filaments the particle is equally thick. The picked particles were cleaned with deionized water and stainless-steel tongs or spatulas, dried (40°C), and stored in glass vessels until further analysis.

For microplastic analysis, a three-step procedure was applied to the respective sieve fraction (<2 mm) to separate the mineral and organic compound of soil samples from microplastic particles: First, the separation of mineral components (sand, silt, and clay particles) was performed with the help of the commercially available “MicroPlastic Sediment Separator” (MPSS) (Hydro-Bios Apparatebau GmbH, Kiel-Altenholz, Germany) (Figure 8a). The special feature of this device is its large size, which allows the separation of large sample volumes, but which also requires long separation times (here: 15 or 19 h) (Imhof et al. 2012). The MPSS unit was filled with a previously sieved (>300 µm) sodium chloride (NaCl) solution. The NaCl solution was adjusted to a density of 1.2 g ml^{-1} and double checked before and after the separation process via pipetting and weighing, as well as with the help of an aerometer (1.900–1.200 g cm^3, Greiner-Glasinstrumente, Lemgo, Germany). With a revolving rotor, the entire sample material (<2 mm) was added, and the dividing chamber of the MPSS unit was closed. The rotor was left running for a total of 60 min to stir up the suspension and the separation process for another 14 h (Lahn samples) or 18 h (Nidda samples). The longer separation time for samples from the Nidda catchment was chosen because of the finer grain size and longer sedimentation time of clays, despite the formation of aggregates of clay minerals present in the salt water (Sutherland et al. 2015).

After the total separation time of 15 h or 19 h, the integrated ball value was closed, and the dividing chamber removed to rinse the separated material (supernatant) into glass bakers with the help of filtered NaCl solution (Figure 8b). The remaining sample material was afterwards separated by wet-sieving (stainless-steel sieves, Ø 75mm, Atechnik, Leinburg, Germany), with deionized water to the following size classes: >1000 µm, >500 µm, and >300 µm (Prume et al. 2021). The lower size limit of the microplastic particles considered is thus 300 µm, a particle size that can still be picked by hand and analyzed via ATR-FTIR. After sieving, the residues were filtered on pleated cellulose filters (Ø47 mm, LLG-Labware, Meckenheim, Germany) via vacuum-filtration and then transferred to glass petri dishes (Ø 90 mm or 200 mm) by rinsing with deionized water and drying at 50°C for two days, according to Prume et al. (2021) (Figure 8d).

Second, to differentiate between organic material and potential plastic particles within the remaining sample material after sieving and filtration, a fluorescent staining procedure was applied. A Nile Red solution with a concentration of 20 µg ml^{-1} Nile Red (Sigma-Adlrich, Taufkirchen, Germany) dissolved in ethanol-acetone (1:1) was applied with the help of a pipette and sprayer to each filter (Konde et al. 2020; Maes et al. 2017) (Figure 9a). Initial dropping with pipette prevents the loss of particle during the subsequent spraying which is necessary for a uniform coverage of all particles on the filter or glass petri dish with the staining solution. Filters were afterwards stained for 10 minutes at 50°C within a drying chamber (Konde et al. 2020). Stained filters or petri dishes were subsequently visually expected inspected systematically under a stereomicroscope (SMZ 161 TL, Motic, Hong Kong), with fluorescence setup (Excitation: 465 nm LED; Emissions 530 nm colour long pass filter: Thorlabs, Bergkirchen, Germany), according to Konde et al. (2020), and transmitted light (Prume et al., 2021) (Figure 9c and Figure 10). This approach allows the visual identification of potential plastic particles but is disrupted by the fluorescence of natural organic components in the red fluorescence range (e.g., chitin shell ants, freshwater mussel fragments), so the exclusion of organic particles must be based on surface structure (e.g., cell structures) or, in case of uncertainty, by later spectroscopic analysis. Each fluorescent, or other potential plastic particle according to the criteria of Norén (2007) was counted, picked, and individually stored in microplates (Brand, Wertheim, Germany).

Figure 8: Density separation procedure with (a) MicroPlastic Sediment Separators (MPSS, Hydro-Bios Apparatebau GmbH), (b) MPSS dividing chamber with integrated ball value, (c) supernatant within dividing chamber after density separation process, and (d) filtrate (>1000 µm) on cellulose filter (with blue plastic film) after sieving and filtration.

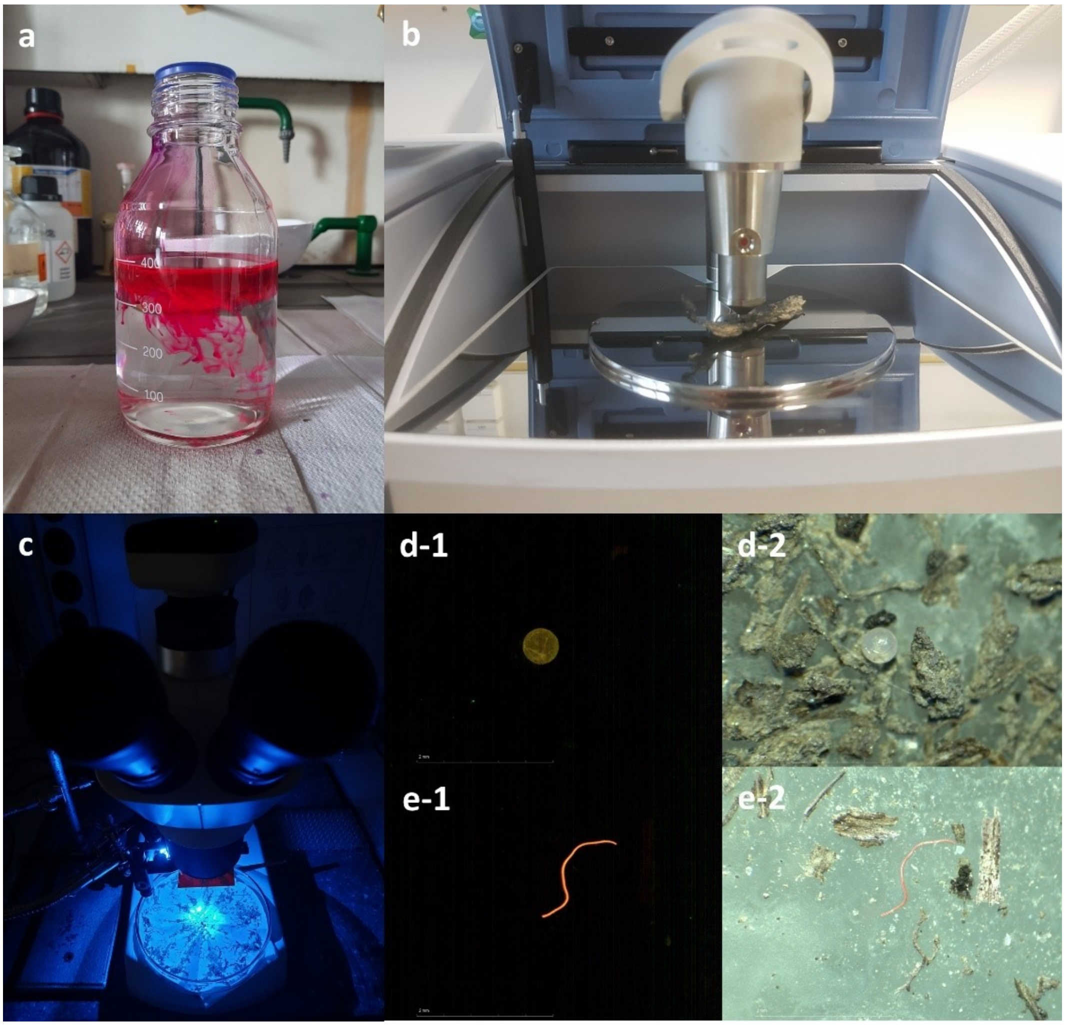

Figure 9: Examples of visual fluorescence staining procedure with (a) preparation of the Nile Red solution, (b) mesoplastic particle during ATR-FTIR measurement, (c) stereomicroscope with fluorescence setup, (d) plastic pallet under fluorescence (d-1) and white light (d-2), and (e) filament under fluorescence (e-1) and white light (e-2).

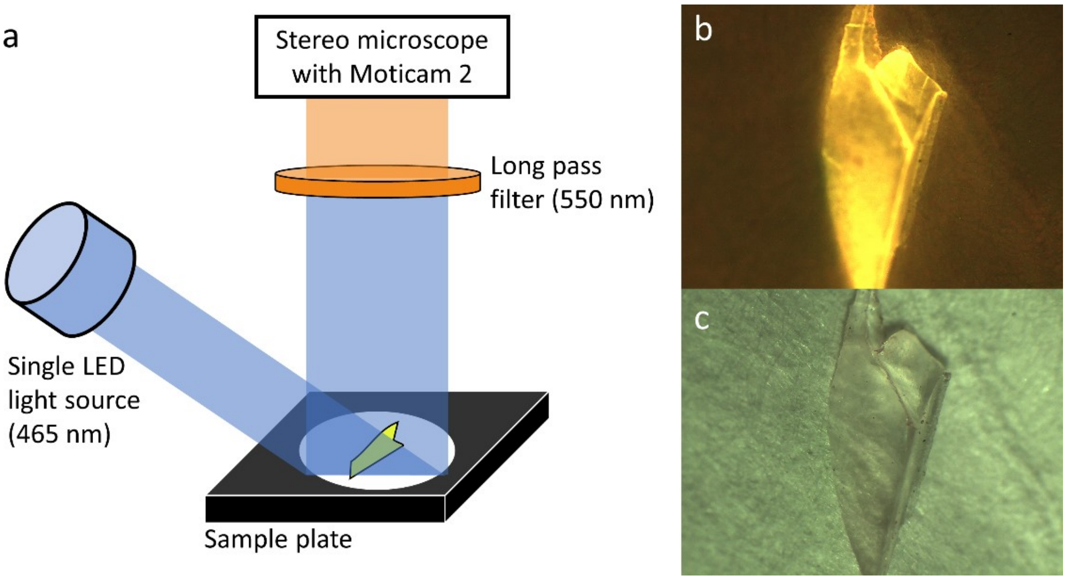

Figure 10: Fluorescence identification with (a) setting of the fluorescence set-up and PE fragment under (b) fluorescence and (c) white light.

Each particle counted and picked from all sieve fractions (>5 mm, >2 mm, <2 mm, >1 mm, >0.5, or >0.3 mm) was classified according to surface characteristics (particle type, shape, surface degradation and color), photographed (Moticam 2, Motic, Hong Kong) and size measured (longest diagonal, Motic Images Plus 3.0, Motic, Hong Kong) (Hidalgo-Ruz et al. 2012).

The third and final analysis step includes the spectrometric analysis of previously visually determined macroplastics from soil surfaces, potential mesoplastic to coarse microplastic particles, and microplastic particles identified via staining-fluorescence procedure. In some cases, adherent soil or organic material was removed from potential plastic particles with stainless-steel tongs and spatulas before spectrometric analysis. Spectrometric analysis was performed via a Tensor 37 FTIR spectrometer (Bruker Optics, Ettlingen, Germany) combined with a Platinum-ATR-unit (Bruker Optics, Ettlingen, Germany). Measurement was carried out using 20 background scans followed by 20 sample scans for each sample, with a resolution of 4 cm^{-1} in a wavenumber range from 4000 cm^{-1} to 400 cm^{-1} (Primpke et al. 2017; Primpke et al. 2018; Jung et al. 2018). Platinum-ATR-unit was cleaned after each measurement with 2-propanol ($CH_3CHOHCH_3$). Because the potential plastic particles had to be placed on the ATR unit by hand with the help of tweezers, the ATR-unit is the limiting factor for the lower size limit of the particles determined.

During meso- and microplastic analysis procedure, contamination prevention was performed by avoiding plastic equipment in the laboratory and the constant wearing of cotton lab coats. All devices used were made of glass, ceramic, or stainless steel and thoroughly cleaned with filtered water (>50 µm) after each use. NaCl solution for density separation or rinsing was filtered before each operation (>300 µm). Corn starch bags were used for sample storage and transport, and their spectrum (ATR-FTIR) was compared with all identification spectra for safety reasons. Furthermore, the sample material was kept under cover whenever possible to avoid air contamination by fibres. During microplastic separation and subsequent analysis steps, contamination control was done by means of blank samples randomly applied during the separation runs.

2.2.2.4 Metal, heavy metal, and metalloid analysis

Pseudo-total concentrations of the metal Fe, the metalloid As, and the metals of interest—named heavy metals V, Cr, Co, Ni, Cu, Zn, Cd, Hg, Pb—were determined from representative sub-samples of regular soil samples (211 samples). For this purpose, 1.0±0.01 g prepared subsample was digested with 20 ml aqua regia (12.1 M HCl and 14.4 M HNO_3, ratio 1:3) according to DIN ISO 11466:2006-12. Elemental concentrations were quantified using inductively coupled plasma–mass spectrometry (ICP–MS, XSERIES 2, Thermo Fisher Scientific, Bremen, Germany). ICP-MS system calibration was conducted with a certified multi-element standard solution (ROTI®STAR; Carl Roth GmbH, Karlsruhe, Germany), whose standard curves were oriented to the background levels for inorganic substances in Hessian soils (Friedrich und Lügger 2011).

Each digest was measured three times and averaged, resulting in converted results given in mg kg^{-1} for elemental concentrations. For further quality control, relative standard deviation (RSD) after threefold measurements, and detection limits resulting from the multiplication of the mean standard deviation of 10 repeated blank measurements by factor 3 were used (Voica et al. 2012; Thomas 2001). Measurements with an RSD ≥20.0% were excluded from further elevation and re-measured. Measurements below the respective detection limits did not appear.

Additionally, analysis of metal(oid) concentrations in macro-, meso-, and coarse microplastic particles, extracted from regular soil samples during meso- and microplastic analysis (Section 2.2.2.3), was performed at the Federal Institute for Hydrology (Koblenz, Germany). For this purpose, 32 plastic particles with a size >2 mm from 9 regular soil samples and a plastic weight of >10 mg were crushed using stainless-steel tongs or CryoMill (CryoMill, Retsch, Haan, Germany).

The comminuted particles were afterwards digested with 6 ml purified HNO_3 (65%) at 260°C and 120 bar for 20 min within acid-cleaned Teflon tubes (Turbowave; MLS-MWS, Leutkirch, Germany) to dissolve adsorbed and additive metals from plastic particles (Catrouillet et al. 2021). Pseudo-total concentrations of the metals Al and Fe; the metalloids As, Sb, and Se; and the heavy metals V, Cr, Co, Ni, Cu, Sn, Cs, and Pb were quantified using ICP-MS (Triple-Quadrupol ICP-MS 8800; Agilent, Santa Clara, CA, USA). Because a representative reference sample for plastics from environmental samples was available, the ICP-MS system was calibrated with certified water samples PS-W1, SPS-W2: Spectrapure Standards AS, Oslo/Norway; TMDA_64.3: CCRMP Canadian Certified Reference Materials Project, Ottawa Ontario/Canada). RSD of the measurement recovery was concisely <10%, and elemental concentrations were reported in ppm.

2.2.2.5 Sediment dating

To date and chronologically classify sediments in different systems, such as marine, lacustrine, or fluvial, different dating methods are available (e.g., luminescence dating, biostratigraphy). For the (micro-)plastic or *Plastic Age* time scale since the 1950s, common chronological approaches are based on radiometric analysis (e.g., ^{210}Pb, ^{137}Cs, ^{241}Am) and can provide accurate dates and robust chronologies depending on the environmental archive studied (Bancone et al. 2020). Despite possible limitations and interferences of radiometric dating (e.g., intensive bioturbation, coarse-grained sediments), the application of the Pb-Cs approach for the floodplain soils of the Lahn (fine-grained sediments) is the best possibility for a chronological classification of the floodplain deposits (Andersen 2017).

To achieve a robust chronology of the ELM-D and LIM-D dating cores, the extracted and preprocessed soil samples, with an average field fresh soil moisture of 12.8% and an average coarse soil fraction of 12.7%, were analyzed at the Gamma Dating Centre, Department of Geosciences and Natural Resource Management at the University of Copenhagen.

To allow a dating of recent sediment depositions, the activity of the naturally occurring lead isotope ^{210}Pb and the artificial isotope ^{137}Cs was measured via gamma spectrometry via an ultralow-background Ge-detector (Canberra, Mirion Technologies, Inc., Atlanta, USA). ^{210}Pb was measured via its gamma-peak at 46.5 keV, ^{226}Ra via the granddaughter ^{214}Pb (peaks at 295 and 352 keV), and ^{137}Cs via its peak at 661 keV. Activities were reported in Bq kg^{-1}.

Chronologies were calculated using a constant rate of supply (CRS) model in which the activity in the lower portion of the cores was calculated on the basis of a regression of the activity of unsupported ^{210}Pb versus cumulated mass depth (Andersen 2017). The CRS model was applied because it can be assumed that both sampling sites receive their ^{210}Pb supply directly from the atmosphere (Andersen 2017). The derived ^{210}Pb chronologies for both cores was verified via the ^{137}Cs peak related to 1963 time-marker as a result of the sharp decline in atmospheric ^{137}Cs fallout following nuclear weapons testing in the 1950s and 1960s. Furthermore, both chronologies were verified via the ^{137}Cs peak related to the regional 1986 time-marker as a consequence of the Chernobyl disaster (Andersen 2017).

2.2.2.6 Statistics and data evaluation

Data handling and processing, basic statistical operations, and data visualizations were conducted using Microsoft Excel (version 290, Microsoft, Redmond, USA) or RStudio (version 1.3.1093, RStudio, PBC, 2020) within an R environment (version 4.0.3, R Core Team, 2020).

All data collected was checked for normal distribution (Shapiro-Wilk test) and variances of variables (Levene's test). Normality and homoscedasticity of the residuals within individual datasets were checked graphically. Comparisons of means was carried out via the Wilcoxon test or Kruskal-Wallis test. To examine dependencies between different data sets and independent variables, linear regression analyses for two variables and areal regressions analysis for three variables were performed. Correlation analysis was performed via Spearman correlation analysis and correlation coefficients (r_{SP}) were interpreted as weak (r_{SP} 0.4 – <0.6), clear (r_{SP} 0.6 – <0.8), and strong (r_{SP} >0.8). Statistical analysis results were interpreted as significant with a p-value ≤0.05. Data visualization and statistical tests were conducted with R standard functions (R Core Team 2020) and the following packages:

- "corrplot" (Wei and Simko, 2017: https://github.com/taiyun/corrplot)
- "ggplot2" (Wickham, 2016: https://ggplot2.tidyverse.org)
- "ggridges" (Wilke, 2020: https://github.com/wilkelab/ggridges)
- "plot3D" (Soetaert, 2019: https://CRAN.R-project.org/package=plot3D)
- "scatterplot3d" (Ligges et al., 2018: https://cran.r-project.org/web/packages/scatterplot3d/index.html)
- "sm" (Bowman and Azzalini 2021: http://www.stats.gla.ac.uk/~adrian/sm/)
- "soiltexture" (Moeys et al., 2018: https://github.com/julienmoeys/soiltexture)
- "vioplot" (Adler et al., 2021: https://github.com/TomKellyGenetics/vioplot)

Spatial data for the pre-selection of the study sites and for the visualization of results were handled in ArcGIS (version 10.8, ESRI, Redlands, USA) and QGIS (version 3.16.15 ‘Hannover’, QGIS Development Team, QGIS Association, https://www.qgis.org). The following datasets (georeferenced raster datasets or shapefiles) with their respective source were used:

- **DLM:** Digital landscape model of Hesse (ATKIS Basis-DLM), Hessian Administration for Land Management and Geoinformation (2019)
- **GK25:** Digital geological maps of Hesse (1:25000), Hessian Agency for Nature Conservation, Environment and Geology (2019)
- **BK50:** Digital soil maps of Hesse (1:50000), Hessian Agency for Nature Conservation, Environment and Geology (2002)
- **LiDAR:** 3-D laser scanning data from Hesse, Hessian Administration for Land Management and Geoinformation (2019)
- **OSM:** River networks and landscape data of Germany, © OpenStreetMap contributors (2019) [http://download.geofabrik.de/europe/germany/hessen.html]
- **ERC:** European river catchments, European Environmental Agency (2019) [https://www.eea.europa.eu/data-and-maps/data/european-river-catchments-1]
- **RND:** River network data (e.g., river courses, river kilometres) and flood data (HQ10, HQ100) of Hesse, Hessian Agency for Nature Conservation, Environment and Geology (2019) [https://wrrl.hessen.de/mapapps/resources/apps/wrrl/index.html?lang=de]

Data processing of FTIR spectra, which were obtained for single macro-, meso-, or microplastic particles during ATR-FTIR analysis, was performed within OPUS (version 7.0, Bruker Optics, Ettlingen, Germany) and Spectragryph (version 1.2.14, Menges 2020, Oberstdorf, Germany). Raw FTIR spectra were processed with atmospheric compensation and baseline correction (concave rubber band method). For spectra identification, the processed spectra were first compared with OPUS band-based standard algorithms to entries within the internal OPUS database (OPUS 7.0 internal database). Because this database contained insufficient entries of plastic products and no entries of non-polymeric natural materials, only identifications with a hit quality >700 were directly recorded. For identifications with a hit quality of 700 to 300, the adsorption bands were manually checked for polymer identification according to the criteria of Jung et al. (2018). Identifications with a hit quality <300 were compered to spectra databases for natural materials provided by Spectragryph (Kimmel_Center: Collection of 363 FTIR absorbance of natural and biogenic material of archaeological interest; provided by S. Weiner from Kimmel Center for Archaeological Science, Weizmann Institute of Science, Israel).

In the case of no sufficient identifications or insecurities, the spectra were finally matched with the database of “Open Specy” (Cowger et al. 2021a) and identifications with a spectral correlation $r^2 > 0.6$ with plastic or non-polymeric natural materials were recorded. In the case of a match with non-polymeric natural materials, potential plastic particles were counted as false-positive results of the staining protocol and were excluded from further analysis.

In addition, for each identified polymer, the “age of earliest possible occurrence” (EPO age) was selected from the following data sets as the first year of worldwide production or first patent application: “History of Plastics” (British Plastic Federation 2020), “Plastikatlas 2019” (Caterbow und Speranskaya 2019), or the works of Zalasiewiccz et al. (2016), Crawford and Quinn (2017), and PlasticEurope (2021).

The concentration of meso- and microplastics were finally calculated and documented as particles per kg soil dry weight (p kg^{-1}) or in size-class dependent sub-concentrations for MEP kg^{-1} (>5000 µm), CMP kg^{-1} (5000–2000 µm), L-MP kg^{-1} (2000–1000 µm), and M-MP kg^{-1} (1000–500 µm). The amount of microplastic concentrations on soil surfaces was documented in the plastic particle quantity per square meter (p m^2). Elemental concentrations of metals, heavy metals, and metalloids from the ICP-MS analysis were documented in mg kg^{-1}. Heavy metal concentrations were compared to legal standards for soils (German national legislation) (Bundesregierung 1998). To allow an effective assessment of heavy metals and related environmental risk, different pollution indices were calculated according to Kowalska et al. (2018). Each of the applied indices allows an assessment of contamination levels and the spatial contamination differences (Kowalska et al. 2018).

To identify heavy metal enrichment compared to natural levels, two indices based on geochemical background levels were calculated. Geochemical background (GB) concentrations of the individual metals and the metalloid As were based on the average values from 341 soil samples (64 floodplain silt substrates, 277 floodplain sand substrates) from Hessian floodplain soils (Friedrich and Lügger, 2011).

To measure the potential impact of anthropogenic heavy metal pollution against geogenic heavy metal contents in floodplain soils, the “Enrichment factor” (EF) was calculated following Eq. (1):

$$EF = \frac{\left[\frac{HM}{LV}\right] sample}{\left[\frac{HM}{LV}\right] GB} \qquad \textbf{(1)}$$

where HM is the concentration of individual heavy metals (mg kg^{-1}), LV is the reference concentration of Fe (mg kg^{-1}) and GB the individual geochemical background concentration (mg kg^{-1}).

For the assessment of spatial contamination differences, the heavy metal “Pollution load index” (PLI) based on “single pollution index” (PI) was calculated following Eq. (2) and Eq. (3):

$$PI = \frac{HM}{GB} \qquad \textbf{(2)}$$

$$PLI = \sqrt[n]{PI_1 \times PI_2 \times PI_3 \times PI_n} \qquad \textbf{(3)}$$

where HM is the is the concentration of individual heavy metal (mg kg^{-1}) and GB the individual geochemical background concentration (mg kg^{-1}).

Environmental risks related to heavy metal and metalloid concentrations were assessed by the calculation of two common environmental risk indices. To access the potential toxicity of heavy metal contamination, the “Contamination Security Index” (CSI) was calculated following Eq. (4):

$$CSI = \sum_{n=1}^{n} w\left(\left(\frac{HM}{ERL}\right)^{\frac{1}{2}} + \left(\frac{HM}{ERM}\right)^{2}\right) \tag{4}$$

where W is the weight of each heavy metal computed according to Pejman et al. (2015), HM is the individual concentration of each heavy metal (mg kg^{-1}), ERM the median value of the effect range, and ERL the lowest value of the effect range calculated according to Long et al. (1995) (Pejman et al. 2015).

For the assessment of potential ecological risks, the “Potential Ecological Risk Index” (RI) (Hakanson 1980) was calculated according to Hakanson (1980) and following Eq. (5):

$$RI = \sum_{i=1}^{n} E_r^i \tag{5}$$

where n is the number of heavy metals and Er is the single index of the ecological risk factor calculated by $E_r^i = T_r^i \times PI$ with T_r^i is the toxic response coefficient according to Hakanson (1980) and PI is the Single Pollution Index according Eq. (2).

2.2.3 Methodological pitfalls and limitations

The methodological approach presented underlies different limitations that occurred first during the geospatial sampling approach and extend into the data analysis.

First, during fieldwork, the spatial representativeness of the selected sampling sites is limited through the restricted number of samples that can be analyzed and the resulting cost and time constraints. The geospatial sampling approach therefore attempts, within this inherent limitation, to provide the most representative sampling oriented towards landscape and soilscape characteristics. Nevertheless, the land use history of each specific sampling site often cannot be traced in detail. This means that past anthropogenic interventions may that lead to disturbances in legacy sediment archives may not be detectable. Furthermore, fieldwork and sampling pose the risk for sample disturbances or contaminations. For example, edge effects such as distortion of the core material during drilling cannot be ruled out despite the comparatively large drilling diameters (>80 mm) (Stock et al. 2019). With regard to potential microplastic contamination during fieldwork, the use of plastic materials during sampling was completely avoided. However, contamination by clothing fibers in the field cannot be ruled out because workwear and outdoor clothing is mainly made of polymer fibers (Song et al. 2015). The used sample bags made of biopolymer made from corn starch has proven to be an effective alternative to conventional PE-bags, although the ATR-FTIR spectra of biopolymer bags were compared with all sample spectra for safety reasons.

Second, during analysis of soil properties and elemental concentrations, possible and well-known limitations are manageable through method standardization. Analysis and sample preparation follow standardized (DIN, DIN ISO) methods, whereby, for example, the (heavy) metal analysis is controlled by standard curves and the exclusion or remeasurement of deviating measurement results (Thomas 2001). The quality of subsequent calculated (heavy) metal pollution indices, in particular EF and PLI, depends on the quality of the database applied to calculate a geochemical background of each (heavy) metal (Kowalska et al. 2018). However, the situation within the study areas is comparatively good because state monitoring measures provide a comparatively good database for calculating geochemical background contents as a function of soil landscape and soil textures (Friedrich und Lügger 2011). In the case of soil texture analysis via the young ISP method, the sample preparation is standardized, but not the measurement of the silt and clay fractions. Here, recent studies indicate that the ISP method may partly overestimate silts and underestimate the clay fraction of the analyzed soil samples (Acevedo et al. 2021).

Third, and most importantly in the very young research field of microplastics in soils, there are several limitations and possible pitfalls in (micro-)plastic analysis. In general, methods and analytical approaches for the analysis of plastic residues within different size ranges are not standardized. The approach of meso- and microplastic analyses introduced above has therefore been compiled from different published methods, adapted and adjusted to the status quo with the start of the work in 2019.

A first pitfall here is the wide variety of size definitions of meso- and especially microplastic particles (Hartmann et al. 2019). Today, a first standardization is made through the ISO/TR 21960:2020, which defines macroplastics (otherwise mesoplastic) with a particle size >5 mm, large microplastics in the range of 5000 to 1000 µm, and microplastics in the range of 1000 to 1 µm. This new classification and former size classifications often specified with a range of 5000 to 1 µm for microplastics and reach their limitation in the pedological context. In soil science, soils are mainly described according to their textures, which are mainly coarse soil (>2 mm) and fine soil (<2 mm) with regard to pedogenesis, pore space, and in-situ transfer processes. Consequently, the class coarse microplastics (5000–2000 µm) was introduced in the context of the thesis, corresponding to coarse soil fraction (Section 3.2).

A second pitfall and limitations are given through the application of density separation methods. Different separation solutions (e.g., water, NaCl, $CaCl_2$, $ZnCl_2$) with different densities (1.0–1.6 g cm^3) allow the separation of different dense polymer sets (Kooi und Koelmans 2019; Li et al. 2018; Cutroneo et al. 2021). Although the common polymers like PP, LDPE, HDPE, PS, or PA show densities <1.2 g cm^3, others like PET or PVC show densities >1.2 g cm^3 (Li et al. 2018). The multitude of existing polymer types and the wide range of potential additives make a full separation with only one separation method almost impossible so far (Andrady 2017). In addition, different devices or laboratory setups exist to perform density separations (Cutroneo et al. 2021).

Within this thesis, density separation was conducted within the commercially available MPSS units, with the special advantage that large sample quantities can be separated. Recovery rates for MPSS were reported with >95% for microplastics down to 40 µm size but with a high material and time requirement (Imhof et al. 2012). Density separation was performed with a NaCl-solution (density adjusted to 1.2 g ml^{-1}), which enables a quantitative separation of common polymers with a density <1.2 g cm^3. Polymers like PET or PVC may not be separated and can be recorded only semiquantitative.

Further limitations arise from the application of the Nile Red staining process. They allow a complete particle-preserving approach in contrast to organic matter oxidation approaches, with recovery rates above 96.9% from marine samples (Maes et al. 2017). However, in the case of calcium-containing shells (e.g., freshwater mussels) or certain organic materials, Nile Red can also bind to these non-plastic organics and hinder visual distinction (Konde et al. 2020). From my own work within this thesis, the staining approach had a false positive rate of approximate 12.0%, which must be verified and controlled by systematic visual examination and a subsequent spectroscopic analysis of fluorescent particles.

A spectroscopic analysis of previous identified potential plastic particles allows a prevention of overestimating fluorescent particles. Because the particle handling is carried out by hand during ATR-FTIR analysis, particles smaller than 300 µm are difficult to handle and often provide insufficient contact area with the ATR crystal. For this reason, the lower limit of the microplastics considered in this thesis was set to 300 µm, although individual measurements of particles <300 µm were possible but require frequent remeasurements. In terms of the microplastic size definition, not all particles down to 1 µm were recorded, which also hinders the comparison with other studies that record smaller particles (e.g., down to 100 µm or 50 µm). The identification of obtained FTIR spectra is also subject to certain pitfalls. Spectra identification works via spectra correlations or other statistical matching procedures, which depend largely on the procedure itself, the quality of the spectra, and the scope of the comparison database (Jung et al. 2018; Käppler et al. 2015). In the case of strong degraded or weathered plastic particles from environmental samples, the quality of the spectra can be insufficient, or identification can be hindered by spectra of fresh industrial plastic particles available in databases (Primpke et al. 2018). Also, adherent organic or mineral material hinders spectral analysis; however, these can usually be solved by cleaning the particles with water (Jung et al. 2018). Furthermore, spectral databases are often only commercially provided. However, an open data spectral database is offered by the OpenSpecy project (Cowger et al. 2021a), which also has spectra of environmental particles and was used in this thesis as an additional identification tool.

During the whole (micro-)plastic analysis approach, there is a risk for sample contamination (Thomas et al. 2020). To reduce and control possible sample contaminations, four measures were implemented: First, the use of plastic equipment was completely avoided, and the work was always carried out while wearing cotton lab coats.

Second, the samples were covered wherever possible and not exposed to the ambient air for a longer period of time to prevent contamination by airborne particles. Third, only filtered water (>50 µm), filtered deionized water (>50 µm), and filtered NaCl solution (>300 µm) was used during analysis and for cleaning of all equipment after each use. Fourth, the analytical process was controlled by blank samples from sample preparation onwards.

Blank control was therefore carried out with five randomly applied blank samples (10 in total) during the MPSS separation runs of each sample set divided according the catchment areas. Blank samples were handled like each regular sample and went through all the operating steps. In total, 10 fragments and two filaments were found in nine of the ten blank samples, resulting in an error of 1.0 to 1.2 particles per sample, which would fall within the range of resulting plastic concentrations. However, in case of the fragments with average sizes of 112.98 µm (sample set Lahn) and 294.9 µm (sample set Nidda), the particle size was below the determination limit of 300 µm. In case of the two filaments, with a length of 1254.5 µm and 449.4 µm, a possible contamination by clothing fibers cannot be ruled out completely. However, only very few fibers were found during the analysis. For this reason and because of the fact that the lower size limit of 300 µm was not exceeded by fragments, sample contamination appears negligible for plastic particles with regard to their size range. The calculated concentrations were therefore not adjusted.

Additional analyses like the ^{210}Pb-^{137}Cs dating of floodplain soils developed within fluvial sediments, pose challenges with regard to potential impacts of the semi-natural sediment archive. Although the measurement of radionuclide activities via gamma spectrometry is considered very robust, the quality of the results depends primarily on the properties of the sampled sediment. In principle, the measurement is only possible in mainly fine-grained sediments, which is why the coarse soil content of the samples was previously controlled (Andersen 2017). Furthermore, bioturbation processes or disturbances of the sample (sample density) during drilling can have a negative influence on CRS model applied (Andersen 2017). Excavating the core, as opposed to pulling it out, was done to obtain an undisturbed sample. Nevertheless, it must be considered that young floodplain sediments are legacy sediments, which means that there can always be an anthropogenic influence on the semi-natural archive dated.

2.3 The studied floodplain soilscapes

2.3.1 The Lahn catchment: Heterogeneous environment

The catchment of the Lahn River is located in Central Germany (Federal state of Hesse, North-Rhine Westphalia and Rhineland Palatinate) between 50° 18’ N (7° 35’ E) and 50° 53’ N (8° 14' E) (Figure 11). The total area of the Lahn River catchment comprises of 5,924 km². Through its location within the Central German low mountain range, the catchment is part of the humid and warm continental climate (Köppen-Geiger: Dfb). Annual mean temperatures range from 7.0°C to 10.8°C (Marburg) or 7.4°C to 11.0°C (Gießen) between 1900 and 2021 (Hessian Agency for Nature Conservation, Environment and Geology 2021b). Annual precipitation ranges from 364 to 991 mm (Marburg) or 326 to 952 mm (Gießen) (Hessian Agency for Nature Conservation, Environment and Geology 2021b).

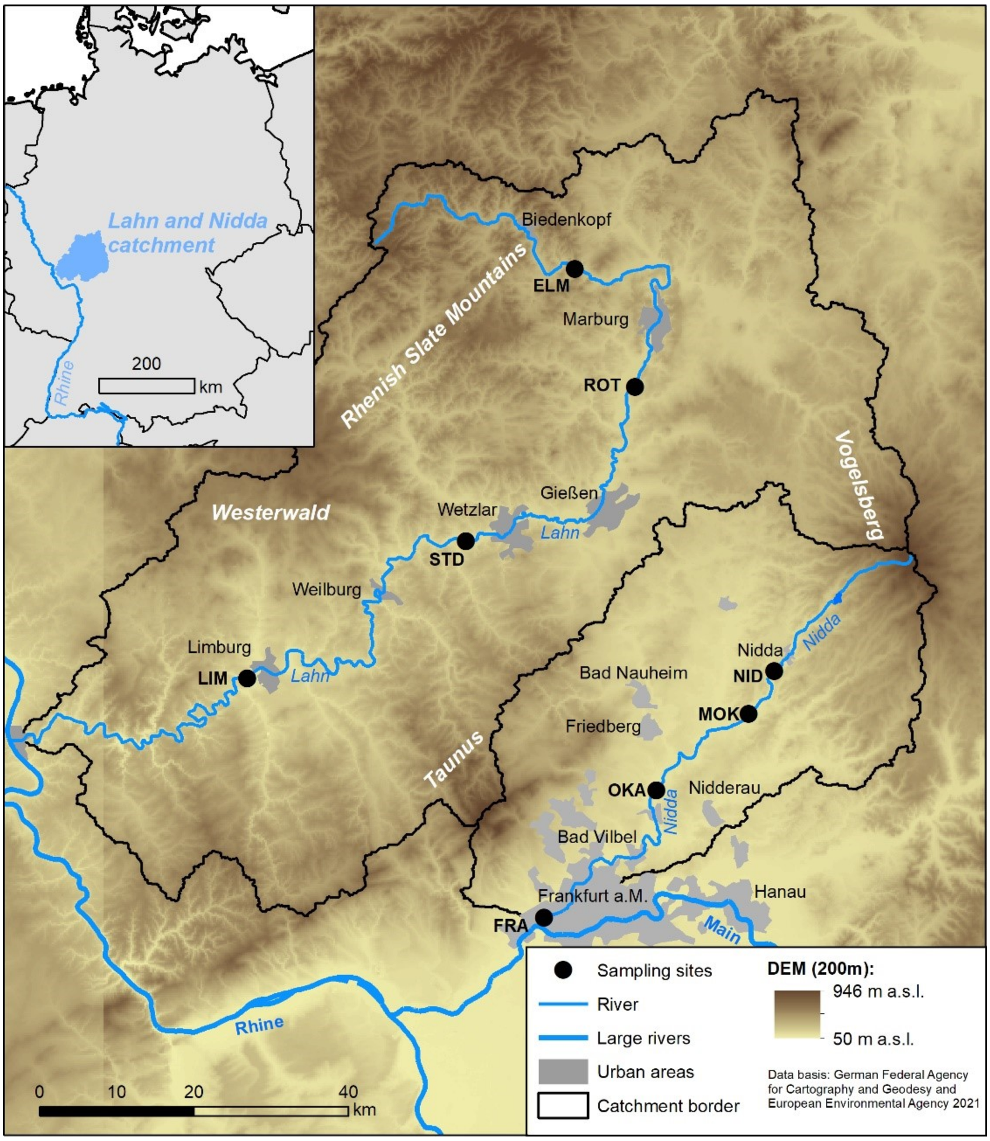

Figure 11: Topleft: General map showing the location of Lahn and Nidda catchment in Germany. Right: Elevation map showing the Lahn and Nidda course with catchment borders, urban areas and sampling sites. Data basis: NUTS 2021 (© EuroGeographics for administrative boundaries), WISE large rivers (© European Environmental Agency, 2021), Digital terrain model 200 (© GeoBasis-DE/BKG, 2021).

With regard to continuing climate change, regional climate projections predict a significant increase in annual mean temperature with an increase in heat and drought extremes, an increase in intensive precipitation events and a slight increase in annual precipitation sums (Masson-Delmotte 2018).

The Lahn River basically flows as follows: Its spring is located within the Rothaar Mountains, part of the Rhenish Slate Mountains, at a height of 603 m a.s.l. The Lahn River flows in easterly direction until it reaches the border of the Hessian Depression landscape. From there, the Lahn flows southwards, passing the urban areas of Marburg and Giessen before the river turns westwards, north of the Taunus Mountain range within its middle reaches. The river then turns southwest between the Westerwald in the north and the Taunus in the south, passes the Limburg Basin and the city of Limburg, and discharges into the Rhine at an altitude of approx. 64 m a.s.l. near Lahnstein.

2.3.1.1 Geology, geomorphology, and landscape evolution

The Lahn River catchment is shaped by different geological units from different geological epochs. The entire upper reaches of the Lahn River are part of the Rhenish Slate Mountains with Devonian and Carboniferous rocks (Meschede und Warr 2019). In its further course, the Lahn is always reached in the west by tributaries originating in the Rhenish Slate Mountains.

To the east and south, the Lahn passes in its middle reaches Permian rocks, the Middle Hessian sandstone formation, and the lower parts of the Tertiary Vogelsberg (basalt). The Lahn then passes between the Tertiary Westerwald mountains (basalt) and the Taunus (Devonian slates and quartzites) (Meschede und Warr 2019). Parts of the Lahn catchment area are also to be designated as depositional areas. The Amöneburg Basin (eastern catchment area), the Giessen Basin (middle course), and the Limburg Basin (lower course) are characterized by the deposition of unconsolidated sediments (sands, gravels, clays) and fluvial gravels and Pleistocene loess accumulations (Tichy 1951).

Geological conditions and tectonic processes are responsible for the course of the Lahn and the development of the river, in addition to climatic changes, especially during the Pleistocene and Holocene (Tichy 1951). Therefore, the present-day Lahn valley mainly follows geological transition or tectonic fault zones and transports sediments of different origins (Tichy 1951; Mäckel 1969). The influence of geology on the morphology of the Lahn valley is illustrated most clearly by the example of the valley widths (Figure 12). The valley formation and the spreading of the Lahn valley are shaped by the resistance of the rocks in the upper and middle reaches and by tectonic processes in the lower reaches. As a result, an alternation of narrow valley sections and wide basin areas has developed.

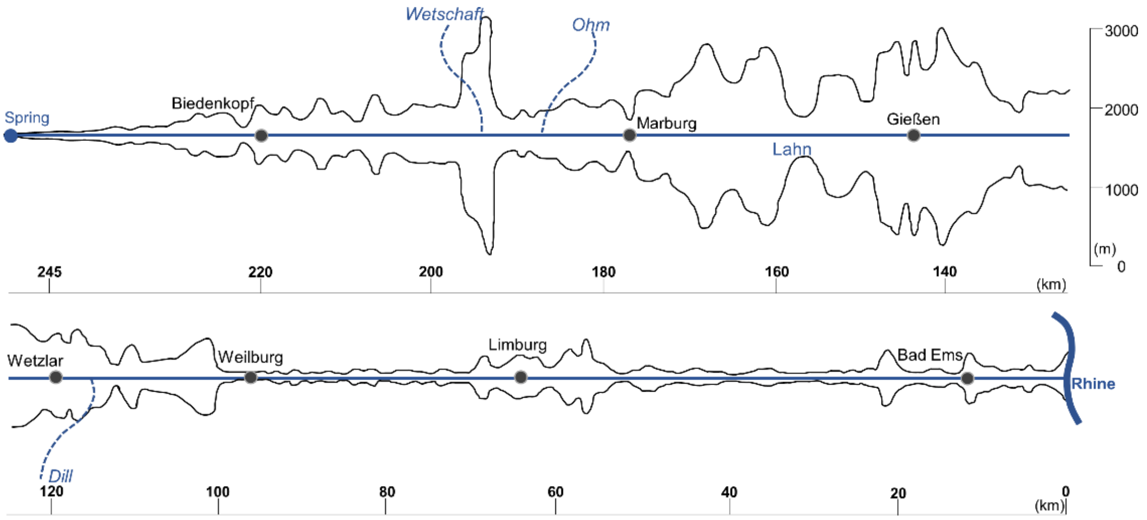

Figure 12: Schematic valley latitudes along the Lahn River course modified according to Tichy (1952).

The landscape evolution within the Lahn catchment area corresponds to the typical one for Central European regions, which are partly located in low mountain areas under continental climate. The Quaternary landscape evolution mainly includes the increased depth erosion and the landscape degradation as a result of tectonic processes, solifluction, and aeolian deposition on slopes during the cold periods and changing vegetation cover (Jockenhövel 1990). With the onset of the Holocene and changing climatic conditions, the landscape in the Lahn catchment area also undergoes substantial changes. Besides the widespread deposition of Laacher-See tephra, following the eruption of the Laacher See volcano for around 13,000 years ago (Reinig et al. 2021) during the transition between Pleistocene and Holocene, also the spread of forests appears during the Preboreal period to the beginning of the Subboreal period (Jockenhövel 1990). Beginning about 5500 BC, the settlement of the area started within the old Neolithic period (Linear Pottery culture). As with other parts of Central Europe, this first settlement is associated with loess rich valleys and basins, which can also be found in the Lahn catchment area (e.g., Limburg basin) (Jockenhövel 1990). For smaller parts of the Lahn catchment area, a more or less distinct settlement continuity can be assumed, as well as in floodplain areas, as demonstrated by the example of the middle Lahn valley south of Marburg (Urz 1995). Subsequent landscape developments within the catchment area will probably be characterized by an increase in deforestation, use of soils (also outside the favorable areas), and, since the Iron Age, the mining of raw materials in low mountain regions (Jockenhövel 1990; Kalias et al. 2003). Consequently, younger alluvial loams were deposited over a larger floodplain area, which contributed to the leveling of the active floodplain and to the formation of the present floodplain morphology (Kalias et al. 2003).

The resulting recent floodplain morphology is diverse and includes all typical surface forms of a floodplain (Fryirs und Brierley 2013; Bridge 2003). The most regular occurrence is a levee (riparian zone), followed by an alluvial flat and one or more alluvial terraces at the floodplain margin. Where flood protection measures occur, dikes are often built directly on the embankment.

Within the alluvial flats, flood channels and paleochannels can occur sporadically. Meander cutoffs occur only very rarely and are mostly anthropogenically influenced. Where no undercutting of the floodplain by anthropogenic measures occurs, back swamps can be present.

Regarding historic land use activities and subsequent impacts on the river landscape, widespread mining holds distinctive importance. Iron ore and other raw materials, which have been mined since the Middle Ages at the latest, are increasingly found within the Rhenish Slate Mountains (Pinsker 1995). During industrialization, mining and heavy industry reached its peak in the 1870 and onward. The surroundings of Gießen and Wetzlar, as well as the tributary Dill, are especially strongly influenced by mining and industry (Martin 2015). However, with the exception of isolated open-pit mines for sand, gravel, and rock extraction, mining has been abandoned throughout the area since the 1980s (Georg 1985), whereas follow-up industries have remained.

Current land use within the Lahn River catchment comprises of 47.0% forested areas, 43.0% agricultural areas including croplands and grasslands, 7.0% urban or traffic areas, and 1.4% industrial area except special uses (Hessian State Office of Statistics 2020). Major catchment parts located within the federal state of Hesse had 1.3 million inhabitants (266 per km²) in 2010 (Hessian State Office of Statistics 2020). The catchment includes three urban centers within the middle reaches having >50000 inhabitants (Marburg, Giessen, Wetzlar) and a concentration of traffic and industry land uses. Within the lower reach, only the city of Limburg and its surroundings can be considered a smaller urban area.

According to geological conditions, valley morphology, landscape evolution, and current land use, it becomes possible to divide the entire Lahn valley along the river course into four different zones:

i. Upper course: Located within the Rhenish slate mountains. Formation of narrow valleys and primarily forested, rural landscape properties, with only small tributaries.
ii. Middle course: In the transition area between different geological units. Formation of wide valleys and agricultural or partwise urban influenced landscape, with large tributaries.
iii. Narrow valley: Between Devonian Taunus and Tertiary Westerwald. Very narrow valley, with rural, agricultural landscape on the surrounding uplands and medium sized tributaries.
iv. Lower course: Located again within the Rhenish slate mountains. Formation of individually valley widenings in basins, mainly agricultural landscapes within the basins and smaller tributaries.

This landscape-based differentiation was used to implement the geospatial sampling approach. After excluding areas where no or only a very small floodplain is present (partly upper course or iii narrow valley), representative study sites were selected for the remaining zones, representing the characteristics of the respective zone.

2.3.1.2 River and floodplain properties

The Lahn is a right tributary of the Rhine with a watercourse length of 245.6 km. It can be described as one of the medium-sized rivers in Germany. The Lahn River shows an average discharge (MQ) of 46.6 $m^3 s^{-1}$ (reference period 1935–2006, Gauge Kalkhofen) (State Office for the Environment Rhineland-Palatinate 2021). In general, the Lahn River is a typical, low-mountain-range river, including slightly to steep inclined sections (Lang und Tönsmann 2002). According to the water structure quality, the Lahn River is classified as “heavily modified”. The water quality is classified as moderate (quality class II-III), with a particular tendency towards eutrophication (Lang und Tönsmann 2002). Point sources of pollutants were not found during official water quality surveys (Lang und Tönsmann 2002).

The main reasons for the river modification are anthropogenic changes such as shortening of the course, riverbed and bank construction, and the creation of weirs. Construction measures, especially to make the lower sections of the Lahn passable for shipping, date back to the 16th century (Gleim und Opp 2004; Lang und Tönsmann 2002). These continued increasingly in the second half of the 19th century because raw materials (iron ore) and metal products could be transported along the waterways (Gleim und Opp 2004; Lang und Tönsmann 2002). The expansion and construction of locks for the lower reaches of the Lahn continued until the 1950s. Although the lower section of the Lahn is currently a federal waterway, it is mainly used for recreational boating, while canoe tourism predominates in the middle and upper reaches (Regional Council Giessen 2015).

The floodplains of the Lahn River catchment occur in different extensions and characteristics within the proposed river and landscape zones. While in the zones (i) upper course and (iii) narrow valley, the floodplains show only a small extension because of the limited valley width; in zones (ii) middle course and (iv) lower course, extensive floodplains occur by valley widths of up to 3 km (Tichy 1951). Land use within the floodplain areas includes mainly meadows and cropland, besides settlement and traffic areas and smallest remnants of floodplain woodland (Lang und Tönsmann 2002) (Figure 13). As in the case of many watercourses in Central Europe, the floodplains of the Lahn are subject to a trade-off between flood protection, agriculture, nature conservation, settlements, and traffic.

In general, the floodplains have been extensively diked in the past and thus disconnected from the flood regime. The intensive diking has been partially removed and modified by flood protection measures or renaturation measures. With regard to flood events, historic and recent floods are documented. Based on archaeological and sediment records from the Niederweimar gravel quarry, high floods may occur already within the early Holocene epoch (Gleim und Opp 2004). Several historic medieval floods are comprehensible, for example within 1255, 1342, 1397, and the 17th and 19th centuries. Since the 1950s, twelve flood events with a discharge >350 $m^2 s^{-1}$ (Gauge Leun, middle reaches) were recorded, with the highest flood event in 1984 (746 $m^2 s^{-1}$, gauge Leun) (Gleim und Opp 2004).

For the Marburg gauge, average flood levels of 503.3 cm (104.3 cm above bank full level) have been measured since the 1960s (Gleim und Opp 2004; Regional Council Giessen 2015). Floodplain areas that are not diked or part of retention areas are flooded, usually annually, while higher flood events effecting wider floodplain areas occur on average every 5.5 years within the Lahn catchment (Hessian Agency for Nature Conservation, Environment and Geology 2021a).

The connection between river and floodplain regarding sediment deposition or erosion can therefore be considered active, in spite of anthropogenic interventions like flood retention basins or dikes. Therefore, an ongoing sediment deposition (e.g., constant deposition of fine sands on riverbanks) or bank erosion can be overserved within the Lahn River floodplains (Martin 2012, 2019). However, these processes are spatially heterogeneous and vary in time and space, depending on flood protection and flood intensity.

2.3.1.3 Composition of the floodplain soils

Floodplain soils directly surrounding the Lahn River comprise an area of 88.9 km² in the Hessian part of the catchment area (HLNUG 2020). In general, the Lahn River floodplains are dominated by Fluvisols, Gleyic Fluvisols or Stagnic Fluvisols, and partly Fluvic Gleysols. The floodplain soils of the Lahn are basically structured stratigraphically from bottom to top as follows:

- Pleistocene strata: Gravel and sand deposits deposited within a Pleistocene river environment. Gravel deposits can be divided into different subunits (Urz 1995; Bos und Urz 2003). Within the gravel deposits, former channels are often visible and filled within the Younger Dryas by gravel and sand deposits (Lomax et al. 2018). The Pleistocene strata is partially terrain forming, especially within the upper reaches.
- Tephra deposits: The border between Pleistocene and Holocene strata is often marked through an incision of Laacher-See-Tephra (LST) deposited during the Younger Dryas (13000 ka) (Reinig et al. 2021). Particularly in the middle Lahn valley, there are partly thick tephra deposits, which have probably been deposited by fluvial processes (Weber et al. 2021a).
- Holocene strata: Floodplain loams, organic-rich with a mainly silty or loamy soil texture, reaching partwise thicknesses >3 m (Bos und Urz 2003; Rittweger 2000). Floodplain loams show a detailed stratigraphy with alternating layers of sand and silt, partwise mixed with LST deposits (Lomax et al. 2018). From the example of the Niederweimar gravel quarry (middle reaches), heavy mineral analysis confirms a deposition of loams after the LST deposition (Lomax et al. 2018).

Predominant soil types such as Fluvisols or Gleysols have developed mainly within the Holocene floodplain loams. The deposition of these loams can be traced to the last 3,000 years in connection with the anthropogenic land use changes (deforestation and subsequent soil erosion) within the entire catchment area (Bos und Urz 2003; Rittweger 2000). As for many other floodplain deposits in Central Europe, the influence of medieval flood events on the share of loam deposition is discussed (Kalias et al. 2003; Huggett. Richard 2007; Bridge 2003).

Information on floodplain soils and their properties were documented during fieldwork (soil survey) and sampling. The related information can be found in Table 6 and Table A 1, as well as in Chapters 3.2, 3.3, and 3.4. For the investigated transects along the Lahn River, floodplain silt loams with a dominant silt fraction (48.03%) followed by sand (32.33%) and clays (19.64%) could be found. While sand content decreases from the upper to the lower reaches, the floodplain loam thickness increases along the river. Within the upper reaches partly only a minor overburden of Pleistocene gravel deposits occurs, which could be attributed to a reduced deposition of loam or an active Holocene erosion as a result of the higher relief energy in the upper reaches (Bridge 2003; Fryirs und Brierley 2013). Furthermore, deviations within the floodplain loam strata occur through single clay layers with maximum clay contents >25% or sand layers with maximum sand contents of >50%. Organic matter content ranges from 1.59% to 21.07%, showing a total average of 5.49%, with highest organic matter loads in topsoils. Deviations occur here as well because of isolated organic rich clay layers (clay mud). Soil pH ranges from 5.11 to 6.94 with moderately acid to neutral pH conditions.

Identified soil horizon sequences contain Ah or Ap (Abp) above combinations of B, Bl, Bgl, Bgr, or Br horizons (Table A 1). Floodplain soil types and horizon sequences are mainly effected by land use, groundwater level (hydromorphic conditions), and portion of coarse soil fragments (gravel), which cause Fluvisols, Halpic Fluvisols, Epi- or Endogleyic Fluvisols, Stagnic Fluviols, or Fluvic Gleysols to occur (Table 6, Table A 1).

Figure 13: Photographs of the terrain situation at the transects of the Lahn River. (a) Transect site ELM, recorded from point ELM-1 (arrow shows location of point ELM-2); (b) Lahn River at site ELM (arrow shows direction to point ELM-1); (c) Transect site ROT (arrow shows point ROT-1); (d) Transect site ROT during spring-flood 2020 (right arrow shows point ROT-1, left arrow point ROT-2); (e) Transect site STD (right arrow shows point STD-3, left arrow point STD-4); (f) Lahn River during spring 2019 (arrow shows direction to point STD-1); (g) Transect site LIM recorded from point LIM-4 (right arrow shows point LIM-3, mid arrow point LIM-2 and left arrow LIM-1); (h) Transect site LIM (arrow shows point LIM-D) with natural riparian vegetation and Lahn River in the background.

2.3.2 The Nidda catchment: From rural to urban areas

The catchment of the Nidda River is located in Central Germany (Federal state of Hesse) between 50° 6’ N (8° 34’ E) and 50° 30’ N (9° 7’ E) (Figure 11). The total area of the Nidda River catchment comprises of 1,942 km² and includes parts of the Vogelsberg and Taunus low mountain range and the Wetterau basin as part of the Hessian Depression in Central Germany. Annual mean temperatures ranged from 7.8°C to 12.9°C (Frankfurt) or 7.4°C to 12.0°C (Bad Nauheim) between 1900 and 2021 (Hessian Agency for Nature Conservation, Environment and Geology 2021b). Annual precipitation ranges from 354 to 957 mm (Frankfurt) or 327 to 939 mm (Bad Nauheim) (Hessian Agency for Nature Conservation, Environment and Geology 2021b). Regional climate projections until 2035 are comparable to the Lahn catchment and indicate an increase in annual mean temperature, extreme heat, and precipitation events (Masson-Delmotte 2018).

The Nidda River springs at a height of 720 m a.s.l. within the Vogelsberg mountains and passes the Vogelsberg in a southwesterly direction. After the first 12 km, the Nidda flows into the Nidda reservoir at an altitude of 235 m a.s.l. Afterwards, the Nidda River leaves the Vogelsberg and continues to pass through the Wetterau in a southwestern direction. After merging in its middle course with the main tributaries (Horloff, Wetter, Nidder), the Nidda reaches the urban agglomeration area of Frankfurt a.M. Within the city area of Frankfurt, the Nidda discharges into the Main at an altitude of approx. 95 m a.s.l.

2.3.2.1 Geology, geomorphology, and landscape evolution

The catchment of the Nidda River is dominated by two major geological units. The upper reaches of the Nidda River are part of Vogelsberg mountains, characterized by Tertiary layered blankets of basaltic and trachytic rocks formed during Tertiary volcanism (20–10 million years ago) (Meschede und Warr 2019). The Tertiary basalts of the Vogelsberg Mountains characterize not only the upper course but also partly the middle course because the Nidda valley is accompanied and framed by the ridges of the Vogelsberg Mountains (Schmidt et al. 2010). After leaving the Vogelsberg mountains, the Nidda River passes through the Wetterau basin. This basin is the southern part of the West Hessian depression and a continuation of the Upper Rhine Graben system (Meschede und Warr 2019). Because of tectonic subsidence in the course of the Vogelsberg volcanism, the Wetterau basin can be considered a tertiary depositional area of marine, limnic, and fluvial sediments (Lang und Nolte 1999). The Tertiary sediments and the basaltic ridges were covered during the Pleistocene with loess deposits, which can reach thicknesses of 10 to 15 meters (Kühn et al. 2017). Middle and lower reaches are therefore dominated mainly by those Pleistocene loess deposits.

River course and valley formation of the Nidda River are mainly affected by the comparatively hard basaltic rocks in the upper reaches, which have led to the development of smaller, shallow valleys on the plateaus followed by a strong deepening in narrow notched valleys and wide valleys partly bordered by basaltic ridges in the middle and lower reaches, through easily erodible loess sediments (Schmidt et al. 2010).

The landscape evolution within the Nidda River catchment correspond mainly to those of the Lahn River introduced before. However, the decisive factor is the aeolian loess accumulation within the Wetterau basin during the Pleistocene periods. During the early Neolithic period, first settlement and human landscape transformation, including forest clearances, are assumed for the Wetterau basin based on palynological and archaeological results and therefore for the Nidda catchment (Jockenhövel 1990). Because of the widespread loess deposits and the associated wide distribution of very fertile soils, the Wetterau can be described as an agricultural heartland, with continuous settlements and land cultivation over the last 7500 years (Kühn et al. 2017). Intensive cultivation of land within the area during the following historical periods is assumed, covering the Bronze and Iron Ages, the special role of Roman influence on the Wetterau, into the Middle Ages and modern times (Jockenhövel 1990).

However, this does not apply to the upper reaches because the low mountain region remains an unsustainable area over extended time periods. Based on the landscape evolution, the morphology of the Nidda catchment outside the Vogelsberg mountains marked from uplands, slopes, and narrow valleys is characterized by elongated basalt ridges and predominantly flat, long slopes, as well as wide river valleys (Kühn et al. 2017; Schmidt et al. 2010; Lang und Nolte 1999). Because of the loess deposits and the long-lasting land cultivation, slopes of eroded, colluvial material predominate. Floodplain morphology follows those characteristics with only small or no floodplain development in the upper reaches and extended floodplain areas after leaving the Vogelsberg and related basalt ridges. Floodplains containing colluvial slopes at the floodplain margins, an alluvial flat and regular levee occurrence at the riparian zone. Alluvial terraces are only rarely relief-forming. Flood channels, paleochannels, and meander cutoffs are rare (Regional Council Darmstadt 2015).

Recent land use within the Nidda River catchment is just as divided as the natural catchment properties: Although the upper reaches are forested (38.7%) or used as farmland (48.6%) with a settlement area of 10.6% and the middle reaches comprise mainly of cropland (53.0%) with a settlement area of 16.1%, the lower reaches are characterized by urban land use with a settlement and traffic area of >58% (Hessian State Office of Statistics 2020). This is also reflected in the population densities, which increase from 72 people per km² to 3077 people per km² from the upper to the lower reaches (Hessian State Office of Statistics 2020).

According to geological conditions, landscape evolution, and cultivation, it becomes possible to divide the entire Nidda catchment and its valley into three different zones:

i. Upper course: Located within the Vogelsberg mountains. Formation of narrow valleys, primarily forested with rural landscape properties and small tributaries.
ii. Middle course: Located within the Wetterau basin. Formation of wide valleys within an agricultural heartland, with main tributaries.
iii. Lower course: Located within the Rhine-Main agglomeration. Originally formation of wide valleys but exaggerated through urban and industrial land use with small urban tributaries.

The landscape-based differentiation was used to implement the geospatial sampling approach within the Nidda River catchment. Representative study sites were selected for each of the three zones, representing the characteristics of the respective zone.

2.3.2.2 River and floodplain properties

The Nidda is a right tributary of the Main River with a watercourse length of 89 km. With an average discharge of 10.7 m^3s^{-1} (reference period 1956–2006, gauge Bad Vilbel), it can be described as a small medium-sized river in Germany (Schweizer et al. 2018; Brettschneider et al. 2019). In general, the Nidda River is a typical low mountain range river with a very characteristic catchment system for Central Europe (Schweizer et al. 2018). Water structure quality of the Nidda River is classified as “heavily modified,” and the water quality is classified as “moderate” (Schweizer et al. 2018; Brettschneider et al. 2019). According to Brettschneider et al. (2019), the river is affected by river engineering for flood protection, which has taken place since the 18th century, along with intense agricultural and industrial activities. Water quality is mainly influenced by municipal and industrial wastewater along the river and its tributaries (Schweizer et al. 2018).

The floodplains of the Nidda River catchment occur in three different extensions and characteristics following the proposed landscape zones: Although the upper course (i) shows only small or partwise non-existent floodplains because of the limited valley widths, the middle course (ii) shows a direct expansion of floodplains after leaving the Vogelsberg mountains, related to an increasing valley width and suddenly less slope of the riverbed. Within the lower course (iii), the floodplain has been extensively altered by urban development (e.g., canalisation) and related flood water protection measures.

Land use within the floodplain areas includes meadows and cropland alongside settlement and traffic areas whose share increases with the course of the river (Figure 14). Parts of the floodplain areas are today part of the landscape conservation area “Auenverbund Wetterau,” resulting in an increasing number of river and floodplain renaturation measures (Regional Council Darmstadt 2015). The Nidda is also subject to a trade-off between different interests, land uses, and nature conservations.

Regarding flood protection, parts of the Nidda floodplain have been disconnected from the flood regime. This mainly affects the urban lower reaches. In the middle and upper reaches, diking is mostly limited to the protection of settlements or infrastructure, which means that large floodplain areas have retained their function as flood retention areas with a total area of 44.8 km^2.

As for other river systems, several historic flood events occurred within the Nidda catchment during the 13th through 19th centuries (Regional Council Darmstadt 2015). Since the 1950s, ten flood events with a discharge >73 m^2s^{-1} (Gauge Bad Vilbel, lower reaches) were recorded, with the highest flood event in 2003 (95.7 m^2s^{-1}, gauge Bad Vilbel) (Hessian Agency for Nature Conservation, Environment and Geology 2022a). For the gauge Nieder-Florstadt (middle reaches), average flood levels of 308 cm (1967–2011) with average flood discharges 9.4 times higher than long-term middle discharge have been measured (Hessian Agency for Nature Conservation, Environment and Geology 2022b).

Except for the lower reaches, the connection between river and floodplain through floods can be considered as active within the Nidda catchment, despite anthropogenic influences. Regarding flood intensity, local deposition of recent legacy sediments and bank erosions can be assumed.

2.3.2.3 Composition of floodplain soils

Floodplain soils of the Nidda River are dominated by Fluvisols, Gleyic Fluvisols, and Fluvic Gleysols. The floodplain soils are basically structured stratigraphically from bottom to top, as follows:

- Pleistocene strata: Gravel and sand deposits deposited within a Pleistocene river environment. The Pleistocene strata is only terrain forming within the upper reaches. Within middle and lower reaches, the Pleistocene strata is covered by younger deposits and thus only rarely relevant for floodplain soil development
- Holocene strata: Floodplain silts and loams, organic-rich with a mainly silty and clayey texture. Floodplain silts and loams showing no distinct stratigraphy. Deposits of sands are rare. Within floodplain margins, floodplain silts and loams are often covered by colluvic material derived from early-Holocene chenozems (today: Luvisols, Regosols) or loess materials.

Predominant soil types such as Fluvisols or Gleysols have developed within those Holocene floodplain silts and loams. The deposition of those Holocene strata can be traced back on the onset of intensive cultivation in the catchment area (Lang und Nolte 1999). The proportion and influence of earlier land use compared to medieval land use on alluvial deposits is also under discussion for this catchment area (Lang und Nolte 1999).

As for the Lahn River catchment, information on floodplain soils and their properties were documented during fieldwork (soil survey) and sampling. The related information can be found in Table 9, as well as in Chapter 3.5. For the investigated floodplain cross-transects along the Nidda River, floodplain silt loams, silty clay loams, and silty clays were the dominant soil textures with average fractions of 55.2% silt, 32.0% clay, and 12.8% sand. Early Holocene or Pleistocene gravel deposits do not occur within the upper two meters of floodplain deposits. Deviations in soil textures occur only in deeper soil layers (>100 cm) with local increases in sand contents (>22.0%). Further deviation within the overall homogenous floodplain deposits occurs through single clay mud layers or deep peat bands.

Organic matter content ranges from 1.57% to 24.91% with an average of 8.33% with highest organic matter loads in topsoils or peat bands. Floodplain soil pH ranges from 4.90 to 7.69, showing moderate acid to weak alkaline pH conditions.

The studied floodplain soils showing soil horizon sequences of Ah with Ap, Ahg, and Ahl, followed by combinations of B, Bl, Blr, Br, and partwise Lhr or Lr horizons. These sequences resulting in Fluvisols, Gleyic Fluvisols, or Fluvic Gleysols. The floodplain soils are often affected by hydromorphic conditions with the occurrence of pedogenic oxides (Fe, Mn) in Bl-horizons and reductive conditions. Distribution of soil types within the floodplain cross-section depend on floodplain morphology and groundwater levels. Within the middle reaches some unidentified anthropogenic artefacts such as pottery shards or bricks were found in the floodplain soils.

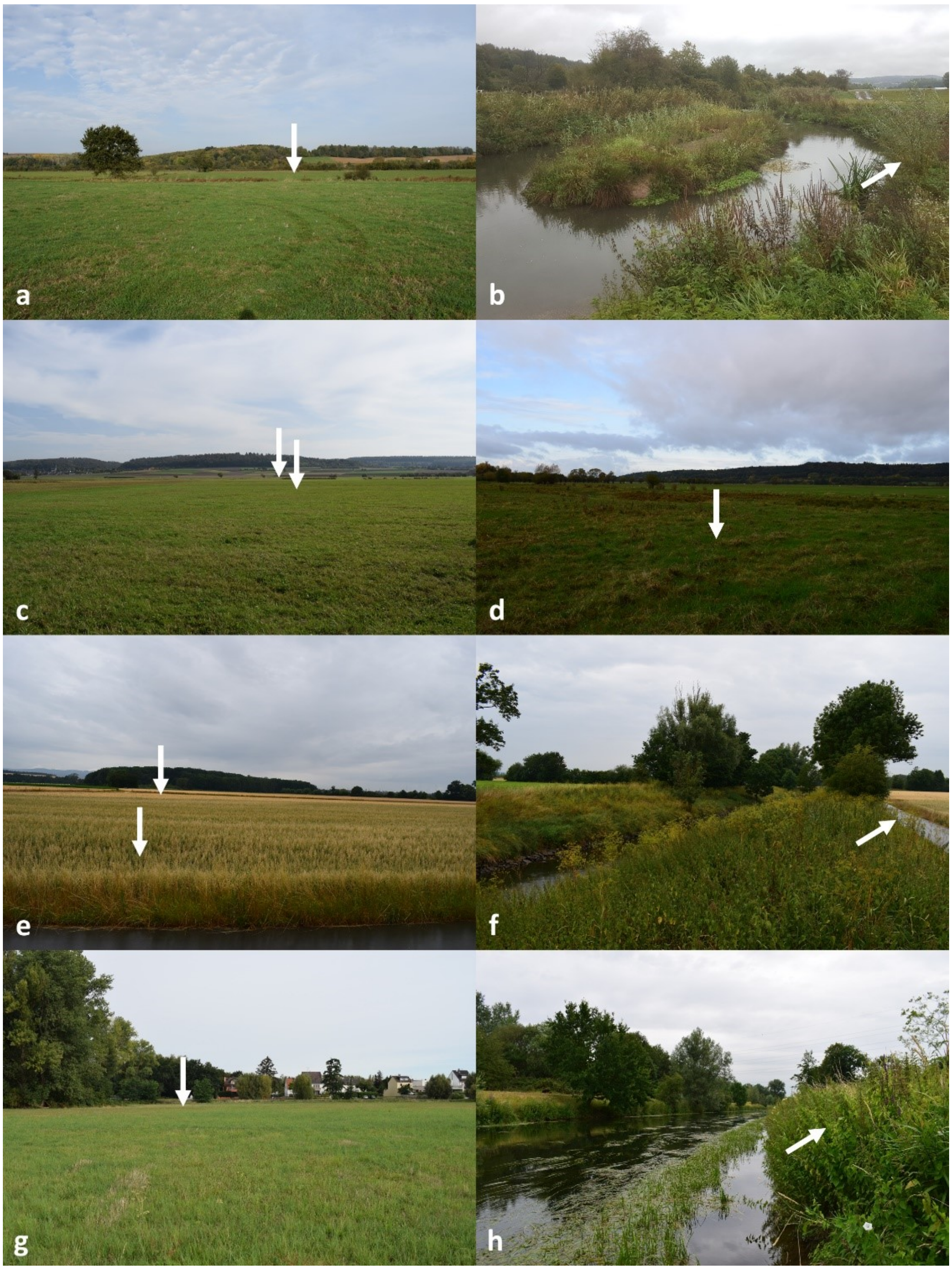

Figure 14: Photographs of the terrain situation at the transects of the Nidda River. (a) Transect site NID, recorded from point NID-1 (arrow shows location of point NID-2); (b) Nidda River at site NID (arrow shows direction to point NID-2); (c) Transect site MOK (arrows shows points MOK-2 and MOK-1); (d) Backswamp at transect site MOK (arrow show point MOK-1); (e) Transect site OKA (arrows shows points OKA-3 and OKA-2); (f) Nidda River at site OKA (arrow shows direction ton to point OKA-3); (g) Transect site FRA, recorded from point FRA-2 (arrow shows location of point FRA-1); (h) Nidda River at site FRA (arrow shows direction ton to point FRA-1).

2.3.3 Land- and soilscape distinctions and similarities

The studied floodplain soilscapes within the catchments of Lahn and Nidda Rivers show several distinctions and similarities with regard to environmental catchment features or floodplain development. First, both catchments and the related river networks are characteristic of a large number of medium sized catchments within Central Europe. Their catchment areas are characterized by different geological conditions, different land uses, and populations (Table 1). Both river systems have been heavily influenced by humans in the past and can therefore no longer be considered near-natural river systems. However, in recent times, both catchments have also been subject to increased renaturation measures, as many rivers within Germany or Central Europe.

Table 1: Comparison of the catchment and floodplain soilscape properties of the Lahn and Nidda Rivers.

Properties		**Lahn catchment**	**Nidda catchment**
Catchment properties	Catchment size and river length	5,924 km^2 and 245.6 km	1,942 km^2 and 89 km
	Geological units	Renish slate mountains, Sandstone formation, Tertiary Vogelsberg and Westerwald	Tertiary Vogelsberg and Wetterau basin
	Dominant landscape properties	Alternation of narrow valley sections and wide basin areas	Narrow valleys in the uplands and wide valleys and flat slopes in the basin
	Land use	Mainly forested (47%) and agricultural (43%) with three urban centers (8.4%)	Reaching from rural to highly urbanized, mainly agricultural 41.8%) and urban (28.4%)
	Population density	266 people per km^2	Range 72–3077 people to km^2
Floodplain soilscape properties	Floodplain soil strata	Holocene alluvial loams over tephra (LST) deposits and Pleistocene sand and gravel deposits	Holocene alluvial silts and clays
	Soil textures	Silt loams (SiL), Loams (L), Sandy loams (SL)	Silt loams (SiL), silty clay loams (SiCL) or silty clays (SiC)
	SOM[a]	organic-rich (1.59%–21.07%, av. 5.49%)	organic-rich (1.57%–24.91%, av. 8.33%)
	pH	moderately acid to neutral (5.11–6.94)	moderate acid to weak alkaline (4.90–7.69)
	Dominant soil types	Fluvisols, Gleyic Fluvisols, Stagnic Fluvisols, Fluvic Gleysols	Fluvisols, Gleyic Fluvisols, Fluvic Gleysols
	Special features	Skeletic Fluvisols in the headwaters or flood channels	Partly anthropogenic artefacts

[a] *Soil organic matter*

Beginning with general catchment properties, both catchments are located within the same humid and warm continental climate. Despite minor local differences, precipitation, temperatures, and the occurrence of extreme weather events and local climate change predictions are comparable. Regarding catchment sizes and river lengths, the Lahn River catchment and course is more than twice as large and long than the Nidda River, and both are classified as medium-sized river systems. Consequently, the mean discharges on the Lahn are greater than those on the Nidda.

A major distinction between both catchments can be made regarding geological properties and landscape properties responsible for the river valley morphology. Whereas the Lahn catchment is characterized by alternating geological units and therefore different rock resistances and sediment origins, the Nidda catchment is clearly dominated by two units comprising of tertiary basalts and Pleistocene loess accumulations. Those geological features cause the Lahn River valley to be characterized by an alternation of narrow valley sections and wider basin areas, whereas the Nidda River valley arises immediately after leaving the low mountain region, with width river valleys.

Furthermore, those geological and landscape evolution features affect historic and recent land use along both rivers. Here, the Lahn River also shows a steady transition from smaller urban to rural areas, connected to the larger basin areas. In contrast, the Nidda River rises in very rural areas, passes through heavily agricultural land, and ends in a major urban agglomeration. This is reflected both in the land use and in the population density and can be partly explained by the historical land use and settlement development following the division into favorable and unfavorable areas in terms of land cultivation.

The floodplain soils developed within both catchment areas differ mainly in their strata, which can be expressed by soil textures (Figure 15). Soil textures of the Lahn River floodplain consists of a diverse compound ranging from loamy sands over loams to silty clays and reflecting the different origins of fluvial sediments from various rocks or sandy sediments in the headwaters and young channel sediments. In contrast, the soil textures of the Nidda River floodplain consist mainly of silty clay loams or silty clays and are therefore clearly finer grained, reflecting the loess-bearing nature of those fluvial sediments. Regarding further soil and soilscape properties, both floodplains show comparable organic matter contents and pH ranges so that they are generally regarded as organic-rich soils with moderate acid to weak alkaline conditions (Table 1). Within both floodplain soilscapes, the occurrence and spatial distribution of different soil types is mainly attributed to the position within floodplains morphology and the influence of groundwater. Within relatively young levee situations, Fluvisols or partwise Gleyic Fluvisols occur. Within the plane area mainly Gleyic Fluvisols or in the case of the Lahn River and related to tephra deposits, Stagnic Fluvisols occur frequently. Fluvic Gleysols are linked to backswamps or depressions where the groundwater influences the upper soil sections. Special soil types such as Skeletic Fluvisols or the occurrence of anthropogenic artefacts are catchment specific with only local occurrence.

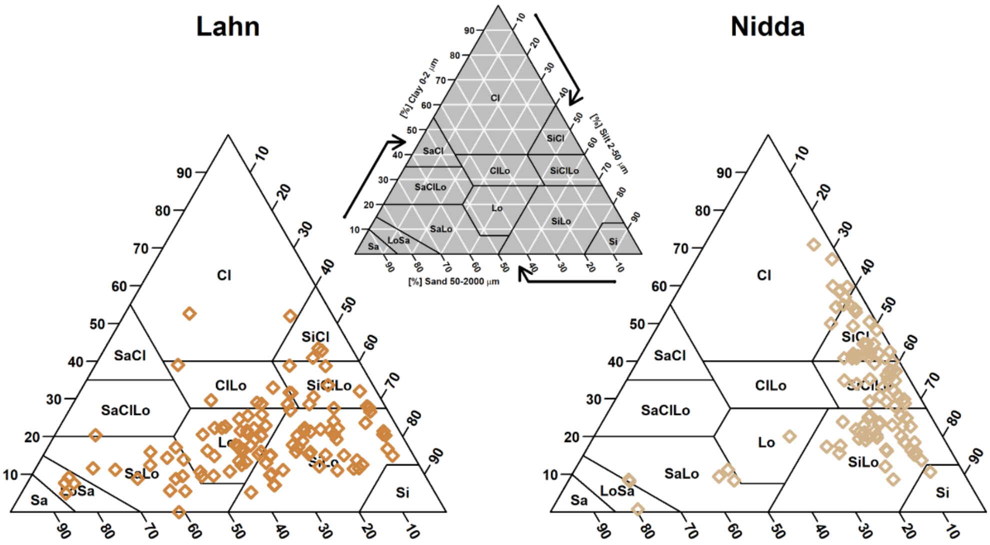

Figure 15: Soil textures of the Lahn (n=111) and Nidda (n=100) floodplain soilscapes.

In conclusion, it can be stated that both catchments and their landscape, as well as floodplain soilscape properties, can be considered typical for Central Europe in terms of similarities and differences. Both natural conditions and anthropogenic influences, as well as current conflicts of use, result in a sufficient model region that can be purposefully investigated to answer the questions raised in this work.

3. Scientific publications

This thesis includes the following publications:

Table 2: Scientific publications within the present thesis.

No.	Titel	Journal	Co-Authors	Status	Own contribution
1	Investigating microplastic dynamics in soils	Land Degradation and Development 2021, 32(1), 270-284, DOI: 10.1002/ldr.3676	Christoph Weihrauch, Christian Opp, Peter Chifflard	Published: 15 January 2020	Main author (60%)
2	Spatial patterns of mesoplastics and coarse microplastics in floodplain soils as resulting from land use and fluvial processes	Environmental Pollution 2020, 267, 115390, DOI: 10.1016/j.envpol.2020.115390	Christian Opp	Published: December 2020	Main author (80 %)
3	Deposition and in-situ translocation of microplastics in floodplain soils	Science of the Total Environment 2021, 152039, DOI: 10.1016/j.scitotenv.2021.152039	Christian Opp, Julia A. Prume, Martin Koch, Thorbjørn J. Andersen, Peter Chifflard	Published: December 2021	Main author (60 %)
4	Spatial connections between microplastics and heavy metal pollution within floodplain soils	Applied Sciences 2022, 12(2), 595, DOI: 10.3390/app12020595	Jens Hahn, Christian Opp	Published: January 2022	Main author (75%)
5	Meso- and microplastic distribution and spatial connections to metals of interest contaminations in highly cultivated and urbanised floodplain soilscapes – a case study from the Nidda River (Germany)	SOIL, preprint soil-2022-1, DOI: 10.5194/soil-2022-1	Christian Opp, Julia A. Prume, Martin Koch, Peter Chifflard	Submitted: January 2022	Main author (60%)
6	Plastics as a stratigraphic marker in fluvial deposit systems	Anthropocene 2021, 36, 100314, DOI: 10.1016/j.ancene.2021.100314	Simone Lechthaler	Published: November 2021	Main author (60 %)

3.1 Investigating microplastic dynamics in soils

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Abstract

Studies on microplastics in soils is currently being established as a new research field. So far, mainly 'explorative studies' have been carried out to detect microplastics in different soil environments. To generate a deeper understanding of microplastics dynamics, 'systematic studies' are required. Such research must built on a targeted sampling strategy and considerate fieldwork and sample handling. From literature enquiry, a five-stage methodological workflow was deduced for studies on micro- plastics in soils. In the present review, the spatial representation of soils/soilscapes with microplastics in soils research is conceptually and practically assessed. We dis- cuss judgmental, randomized, and metric soil sampling strategies. Then, we explain sample pre-processing and give a brief overview of methods for microplastics identification and quantification. We conclude that the establishment of the novel field of research 'microplastic dynamics in soils' requires more intensive consideration of soil sampling strategies. As soil is a complex medium and the soilscape is spatially heterogeneous, we highlight systematic sampling strategies as the best possible options for sophisticated research. However, no overall optimum methodology can be defined because the specific strategy must be in line with the particular research question. For all studies on microplastics in soils, practical improvement is needed to prevent contamination of soil samples with plastics during sampling and sample pre- processing.

Keywords

Field study, Geospatial approach, Pre-processing, Soil sampling, Spatial resolution

3.1.1 An emerging research field and its challenges

Plastics are used in all areas of societal life. Due to the properties of plastic polymers, they are valued for diverse purposes (e.g., in industry, the economy, everyday life). Plastic production and processing are simple and cost-efficient. Hence, plastic production has increased rapidly in the past decades (Andrady 2017). Worldwide, 348 million tons of plastic are produced annually (PlasticsEurope 2018). The major commonly produced polymers are shown in Table 3. In spite of increased recycling or reprocessing of plastic waste and declining land- fill deposition, a large proportion of plastic waste is daily disposed into the environment (Souza Machado et al. 2018a; Karbalaei et al. 2018; PlasticsEurope 2018).

Plastic particles with a size >5 mm are termed macroplastics, mesoplastics, or plastic litter. Particles of 0.01–5 mm are called micro- plastics. Particles <1 µm are termed nanoplastics (Hüffer et al. 2019; Hüffer et al. 2017; Mausra et al. 2015; Zhang et al. 2020). Despite various attempts at forming a definition, this terminology has been most widely adopted (Möller et al. 2020; Rillig et al. 2019; Silva et al. 2018; Stock et al. 2019; Zhang et al. 2020). Genetically, we distinguish between two types of microplastics: (a) primary microplastic manufactured at the <5 mm size range often used in cosmetic and cleaning products, and (b) secondary microplastic resulting from physical comminution and/or chemical degradation of originally larger plastic particles (Andrady 2017; Barnes et al. 2009; Napper und Thompson 2019).

Environmental research into microplastics was first carried out in coastal waters (Carpenter und Smith 1972; Carpenter et al. 1972), later in the oceans worldwide (Karlsson et al. 2017; Martin et al. 2017a; Nuelle et al. 2014; Phuong et al. 2018; Stock et al. 2019; Taylor et al. 2016; Wright et al. 2013). A detailed database on microplastic abundance and behavior in marine ecosystems, and the endangerment of aquatic organisms was established (Cole et al. 2011; Martin et al. 2017a; Taylor et al. 2016; Wright et al. 2013). However, microplastics are not only present in the oceans. Because plastics are produced, processed, and used on land as man-made materials, microplastics are transported from land to sea. Rivers are the main transport corridors for microplastics as water moves from land to ocean (Alimi et al. 2018; Blettler et al. 2017; Liu et al. 2019; Siegfried et al. 2017; Xiong et al. 2018). Therefore, not only marine/aquatic but also semi-terrestrial ecosystems are affected by microplastics (Liu et al. 2019). In addition to translocation and transport by water, microplastics also appear to be transportable by wind (Abbasi et al. 2017; Rezaei et al. 2019). These findings enable us to hypothesize that microplastics can spread farther in the landscape than previously assumed. Especially, since they are preserved for a long time in various environ- mental media (Chamas et al. 2020). After almost five decades of research, the environmental effects of microplastics for terrestrial ecosystems are now increasingly investigated (Engdahl 2018; Rillig et al. 2019; Rillig et al. 2017b; Rillig et al. 2017a; Selonen et al. 2020; Verla et al. 2019; Yu et al. 2019).

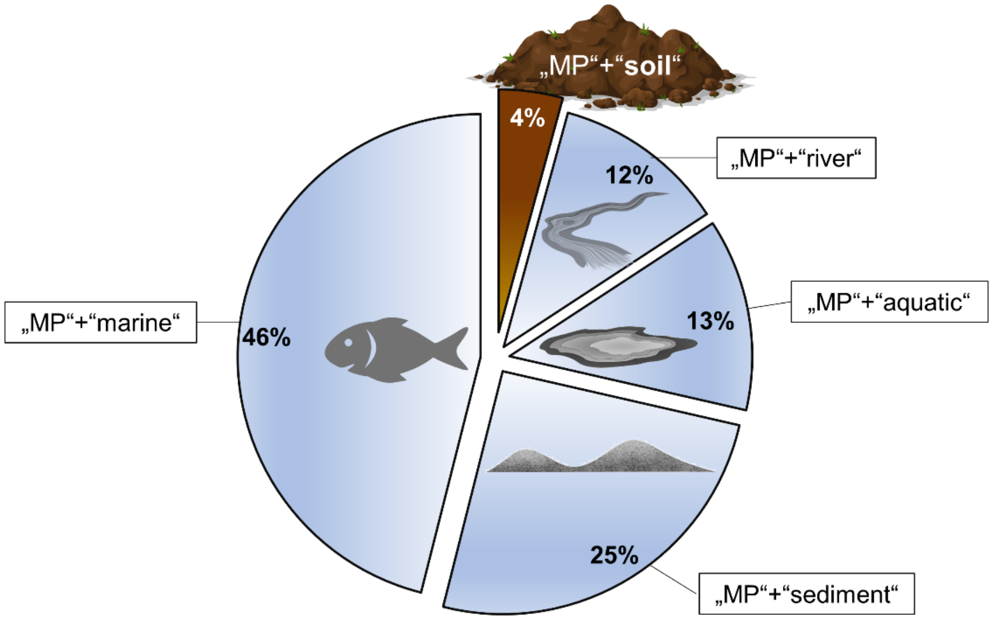


Figure 16: Results of a quantitative literature enquiry on microplastics-related publications on the Web of Science between 2014 and 03/2020. Specification and percentages of microplastic-related studies according to different search terms and combinations in the titles (MP = microplastic; n = 639).

Surprisingly, it is a relatively novel finding that plastic occurs or is deposited in soils (Huerta Lwanga et al. 2017). Research into microplastics in soils is young and studies are still scarce. A quantitative review of the recent publications on microplastics reveals a strong increase in articles since 2014. However, only 4% of the papers are on microplastics in soils (Figure 16). These are largely 'explorative studies' seeking microplastics in certain soil environments, with a focus on microplastics occurrence and abundance. Studies have shown that microplastics occur in agricultural and strongly anthropogenically influenced soils, as well as in floodplain soils (Corradini et al. 2019; Huerta Lwanga et al. 2017; Piehl et al. 2018; Scheurer und Bigalke 2018; Zhang und Liu 2018). For topsoils under agricultural use, microplastic contents between 0.34 and 42.960 microplastic particles per kg of soil (mpp kg^{-1}) were reported (Zhang und Liu 2018; Piehl et al. 2018). With regard to polymer types, studies were only able to identify some of the commonly produced plastics, because methods for the analysis of microplastics in soils are in their infancy (Table 3; Liu et al., 2018; Piehl et al., 2018; Scheurer and Bigalke, 2018).

Methodological advances are needed to evaluate the presently unknown environmental effects of microplastics in soils. Impacts on soil organisms are possible, including nanoplastics-uptake by plants resulting in entry into the food chain (Huerta Lwanga et al. 2017; Rillig et al. 2019). To evaluate and restrict negative impacts of micro- plastics in soils, a better understanding of the microplastic-related processes is required (e.g., transport routes and vectors). This can hardly be achieved by 'explorative studies' but requires 'systematic studies' focusing on microplastics' integration in and interaction with their spatial surroundings (i.e., landscape/soilscape). To conduct such studies, we still need to develop methodological foundations for precise and internationally comparable sampling, microplastic detection, and quantification.

Table 3: Plastic polymers in the focus of past studies on microplastics in soils.

Ranking by production[1]	Common plastic polymer types[2]	Corradini et al. (2019)	Liu et al. (2018)	Piehl et al. (2018)	Zhang & Liu (2018)	Scheurer & Bigalke (2018)	Huerta Lwanga et al. (2017)	Fuller & Gautam (2016)
1	**PP** (polypropylene)	Polymer type not reported	x	x	Polymer type not reported	x		
2	**PE** (polyethylene)		x	x		x	x	x
3	**PVC** (polyvinyl chloride)			(x)		x		x
4	PUR (polyurethane)							
5	PET (polyethylene terephthalate)							
6	**PS** (polysterene)			x		x	x	x
7	ABS (acrylonitrile butadiene styrene)							
7	SAN (styrene acrylonitrile resin)							
8	**PA** (polyamide)					x		
9	PC (polycarbonates)							
10	**PMMA (**polymethyl methacrylate)			(x)				
11	POM (polymethylene)							
12	**PES** (polyethersulfones)		x					
13	**SBR** (styrene-butadiene)					*x*		
14	**Latex**					*x*		

[1] EU28+NO/CH plastic converter demand according to PlasticEurope (2018), [2] Frequently produced and consumed plastic polymer types according to PlasticEurope (2018), (x) = detected only as microplastic (>5 mm)

Table 4: Text shares informing about the methodological stages distinguished in the present paper as represented in reviews on microplastics in soils (December 2017 until March 2020).

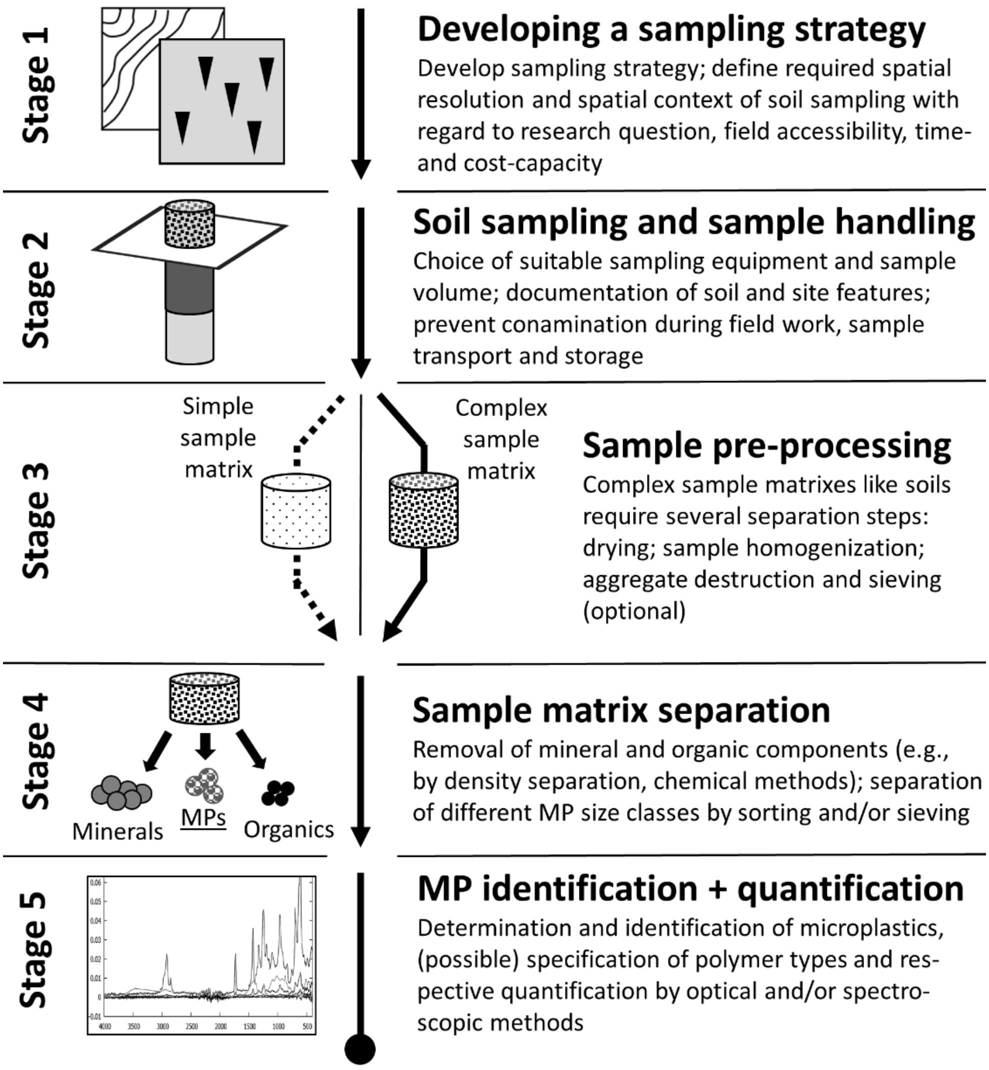
Review	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**	**Stage 5**	**Background on environmental MP pollution**
	Developing a sampling strategy	Sampling and sample handling	Sample pre-processing	Sample matrix separation	MP identification /quantification	
Möller et al. (2020)	3 %	10 %	1 %	46 %	27 %	13 %
Ruggero et al. (2020)	0 %	0 %	0 %	41 %	59 %	0 %
Zhang et al. (2020)	0 %	0 %	1 %	11 %	13 %	75 %
Pinto da Costa et al. (2019)	0 %	8 %	0 %	9 %	24 %	59 %
Qi et al. (2019)	0 %	2 %	0 %	14 %	2 %	82 %
J. Wang et al. (2019)	0 %	0 %	0 %	0 %	0 %	100 %
W. Wang et al. (2019)	0 %	0 %	0 %	18 %	15 %	67 %
Xu et al. (2019)	0 %	0 %	0 %	1 %	2 %	97 %
Bläsing & Amelung (2018)	0 %	0 %	2 %	13 %	8 %	77 %
He et al. (2018)	0 %	1 %	1 %	17 %	12 %	69 %
Silva et al. (2018)	0 %	*5 %	0 %	5 %	67 %	23 %
De Souza Machado et al. (2017)	0 %	0 %	0 %	5 %	8 %	87 %
Total	**0.5 %**	**2 %**	**0.5 %**	**15 %**	**20 %**	**62 %**

Calculated on the basis of word count of thematic text (excluding titles, abstract, introduction, conclusion, figures and tables)
*MP = microplastics; * considering sampling of water and sediments*

Several authors have already dealt with microplastics in soils through reviews (Table 4). However, these publications largely focused on background information on environmental microplastics pollution or on the procedures of microplastics identification/quantification. By contrast, the establishment of adequate sampling strategies, soil sampling, and sample pre-procession has largely been neglected. These aspects are different for soil-related studies than for studies on microplastics in waters. Furthermore, they are crucial if one wants to conduct systematic research on microplastics dynamics in soils. Hence, the present review aims to make three contributions:

(a) to differentiate conceptually between explorative and systematic studies to enable the establishment of research on microplastic dynamics in soils; (b) to elaborate on strategies for creating adequate spatial representation in the empirical designs of studies on micro- plastics in soils; and (c) to critically discuss related sample handling and pre-procession.

From our literature enquiry, a five-stage workflow was deduced for studies on microplastics in soils, which is reflected in the present review's structure (Figure 17). With regard to the focus of the other topic-related reviews, we deal in particular with the so far underrepresented Stages 1–3 of the Workflow. Still, a short overview of analytical and quantification procedures is given, in combination with a reference list, which might lead the interested readers to further information.



Developing a sampling strategy
Develop sampling strategy; define required spatial resolution and spatial context of soil sampling with regard to research question, field accessibility, time- and cost-capacity

Soil sampling and sample handling
Choice of suitable sampling equipment and sample volume; documentation of soil and site features; prevent conamination during field work, sample transport and storage

Sample pre-processing
Complex sample matrixes like soils require several separation steps: drying; sample homogenization; aggregate destruction and sieving (optional)

Sample matrix separation
Removal of mineral and organic components (e.g., by density separation, chemical methods); separation of different MP size classes by sorting and/or sieving

MP identification + quantification
Determination and identification of microplastics, (possible) specification of polymer types and respective quantification by optical and/or spectroscopic methods

Figure 17: Five-stage methodological workflow for studies on microplastics dynamics in soils, as derived from literature enquiry (MP = microplastics). (Stages 1–3 are detailed further in the respective sections of the present paper. For Stages 4 and 5, an overview is given).

3.1.2 A geospatial approach to microplastic dynamics in soils

To understand microplastic dynamics in soils from a system perspective, we must consider the spatial contexts of microplastics in soils. First of all, this requires developing a suitable strategy for study site selection and the sampling procedure, in line with the respective research question. Such spatial considerations are significant for investigating possible displacement, transport routes, or environmental risks of microplastics in soils.

The dynamics of microplastics in soils theoretically encompass different interdependent process types (e.g., physical translocation by soil water, chemical reactions with the soil matrix, biochemical processes during mineralization). Due to their complexity, microplastic dynamics are not well understood. Thus, microplastic dispersion and potential negative effects cannot be prevented or limited effectively.

Presently, the dynamics of microplastics in soils are also too technically demanding to investigate under field conditions. Hence, it is a challenge for microplastic research to generate a process for understanding microplastic dynamics in soils. As a possible solution, we propose a geospatial approach to microplastic dynamics in soils. As microplastic dynamics lead to a certain spatial distribution of microplastics in soil profiles and soilscapes, we can study this spatial distribution in the field and deduce on the processes that formed this distribution. This was proposed by Weihrauch (2019) to investigate soil phosphorus dynamics. In the present paper, we transfer this 'geospatial approach' to microplastic research.

3.1.2.1 Developing a sampling strategy

A systematic investigation of the spatial microplastic distribution in soils requires an adequate spatial resolution. Such is achieved when the soil samples sufficiently represent the investigated two- or three-dimensional spatial unit (e.g., a surface area or a soil profile). Spatial resolution encompasses three aspects (Figure 18a): (a) the positioning of sampling sites; (b) the number of soil samples; and (c) the spatial distribution of the samples over the investigated area/volume they shall represent.

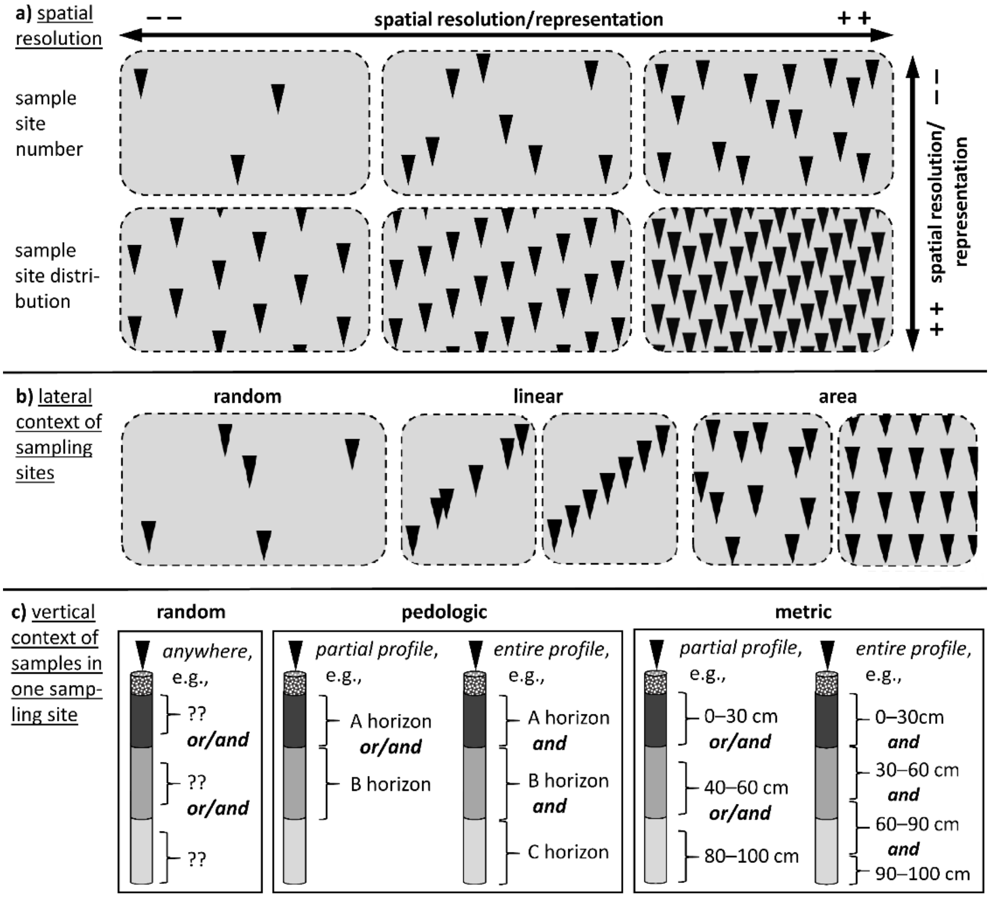


Figure 18: Aspects to be considered for developing a suitable sampling strategy for studies on microplastics dynamics in soils. (a) Soil sampling-based spatial resolution/representation of study areas as a function of sample site number and sample site distribution (triangles mark sample sites). (b) Possible lateral contexts of sampling sites. (c) Possible vertical contexts of samples within one sampling site. Vertical sampling resolution significantly depends on whether one or several samples are taken per sampling site. (Here only shown for mixed sampling

from a larger vertical soil section combined into one sample; e.g., 0–20 cm. Alternatively, local samples can be extracted, which relate to a specific soil depth; e.g., 25 cm).

(1) Sampling sites might be positioned in the landscape according to (a) subjective interpretation (judgmental sampling), (b) spatial randomization, or (c) metric criteria.

(a) If sampling sites are chosen on the basis of interpretation (e.g., background knowledge, visual evaluation of the landscape), they often occupy particular locations related to specific research questions or hypotheses (e.g., depressions, road- side areas as potential zones of microplastic accumulation) (Möller et al. 2020; Wells 2010). The correctness of the results generated at these locations thus strongly depends on the correctness of the underlying hypotheses plus the validity of the spatial interpretation. Due to the complexity of the soilscape, the latter might introduce significant bias into interpretative soil sampling. Moreover, on the basis of spatially specific hypotheses, one might probably only be able to support or reject the assumptions but not to make systematic unexpected findings.

(b) Randomized sampling means the distribution of several sampling sites within a defined (i.e., limited) area under the premise that all sites have equal opportunity to be selected and that they are selected independently from each other (Wells 2010; Möller et al. 2020). The positions of the sampling sites depend on a chosen area (mostly on the basis of interpretation or landscape evaluation, e.g., land use) but not on site or soil features of the concrete sites. The respective study area is thus treated as homogeneous with regard to soil and site features. This is conceptually critical especially because microplastics distribution is unlikely to be homogeneous (Möller et al. 2020). Anyways, this form of spatial generalization might be sufficient for studies, which aim at results representative for certain areas or landscape sections (e.g., comparison of microplastic pollution of two agricultural fields). It might also be plausible when certain statistical tests are planned (e.g., correlation analyses) as the resulting statistical sample will consist of independent data (Wells 2010). However, randomized sampling is rather inadequate for studies on microplastic dynamics in soils as it ignores the highly relevant landscape and soilscape particularities.

(c) Metric sampling means the positioning of sampling sites on the basis of distances. This type of sampling also ignores particular site and landscape features. It might be useful to generate a good representation of an area or landscape section unbiased by interpretation or subjective landscape evaluation. By contrast to randomized sampling, it is also favorable for the comparison of different areas or landscape sections unbiased by divergent metric dimensions. It is thus favorable for studying and comparing gradients or spatial patterns (e.g., of increasing microplastic accumulation, microplastic hotspots). However, metric sampling might lead to the integration of uninteresting sites. Moreover, the resulting statistical sample would not consist of independent data. Thus, certain statistical procedures would not be available for data evaluation (Wells 2010). In consequence, it strongly depends on the research question and the desired form of data evaluation which type of empirical design should be chosen for positioning the sampling sites.

(2) Another important aspect is the number of soil samples. Generally, larger sample numbers lead to higher spatial resolution (i.e., better spatial representation). The best possible spatial representation is achieved when all sampling sites are at an equal distance from each other, that is, when the not investigated spaces in between are smallest. Hence, a sampling strategy must be designed not only just according to the research question but also according to the size of the investigated spatial unit. One option to achieve adequate spatial representation of a particular study area could be the prior calculation of the sample number required for the specific research question and the planned statistical tests on the basis of pilot-sampling and geostatistical analyses (Li 2019; Li et al. 2020a). However, to date, such strategies have not been transferred to research on microplastic dynamics in soils, probably because analytical methods are still very costly. Thus, logistical aspects (e.g., costs, site accessibility) also have to be considered as they would, in most cases, probably decrease spatial resolution. The first studies on microplastics in soils (Fuller und Gautam 2016; Huerta Lwanga et al. 2017) did not report the spatial context of the investigated soils. The more recent studies document the spatial sample contexts but not systematically (Corradini et al., 2019; Piehl et al., 2018; Scheurer & Bigalke, 2018; Zhang and Liu, 2018; Table 4). Hence, as a reader, it is difficult to evaluate if and how well the examined soils represent the respective study areas. Furthermore, it is evident from publications on microplastics in soils that often relatively small sample numbers are processed because the respective analyses are rather cumbersome (see following chapters). For instance, Scheurer and Bigalke (2018) used 87 samples to represent the whole floodplain soils in Switzerland. By contrast, Corradini et al. (2019) processed 90 soil samples to represent an area of 10 km^2. Hence, spatial resolution is different in studies on micro- plastics in soils and requires reflection in the present review.

(3) To develop a suitable sampling strategy, two dimensions of spatial resolution should be considered, the lateral (i.e., soilscape) and the vertical (i.e., soil profile; Weihrauch, 2019). Soils result from and are shaped by pedogenic and environmental processes, which do not just affect one location (i.e., one spot in coordinate space) but larger spatial areas (e.g., landscape sections). Hence, soils are no isolated phenomena but are parts of soilscapes and must be understood in their landscape context (e.g., slope position). This can hardly be achieved, when one single soil is investigated. For instance, the effect of erosion on soil formation cannot be elucidated from one soil on the topslope alone. Several soil profiles along the slope would be required that have a lateral context with each other. Weihrauch (2019) proposes three options for the lateral context of soil sampling sites: (a) no lateral context (i.e., samples are taken randomly and not interpreted in a genetic context with each other), (b) a linear context (e.g., in transects/catenae), and (c) a two-dimensional context (e.g., mapping of a surface area; Figure 18b). Of the seven published field studies on microplastics in soils, five are based on random sampling, one on transects, and one on area mapping (Table 5). A trend shows for researchers to favour sampling without lateral context. This might suffice for explorative studies. However, systematic studies should rather be based on a linear or two-dimensional lateral sampling site context (according to the research question).

Table 5: Overview of the seven studies on microplastics in soils: sampling site properties and soil sampling methods.

Investigated soils	Land use	Sampling context lateral / vertical	Spatial resolution of sampling	Sampling tools	Sample integrity	Sampling depth [volume]	Sample storage	Reference
Agricultural soils [Entic Hapoxerolls]	Cropland, treated with sludge over the last ten years	Random /metric	Three randomly placed sampling sites, three samples on each field (30 fields in 10 km² area)	Metallic auger	Disturbed (i.e., not in initial stratification)	0 - 25 cm [*Not reported*]	PP bags, PET jars	*Corradini et al. (2019)*
Agricultural soils [*soil type not specified*]	Suburbs and country -sides with vegetable cropland	Random / metric	20 sampling sites, three samples at 0.5 m² large randomly placed sample plots	*Not reported*	Disturbed	0 - 3 and 3 - 6 cm [1 kg]	Aluminum box	*Liu et al. (2018)*
Agricultural soils [Entisols, Vertisols]	Cropland (barley and regularly ploughed, without agricultural plastics)	Linear / metric	14 sample plots (32 x 32 cm) located on two transects in the center area of farmland	Metal spatula	Disturbed	0 - 5cm [5120 cm²]	PE barrels	*Piehl et al. (2018)*
Agricultural soils [Nitisols, Gleysols]	Cropland with plastic-greenhouse vegetable production	Random / metric	Two study sites, six randomly placed samples with in five 150 m² large plots at each sampling site	Metal spatula	Disturbed	0 - 5, 5 - 10 cm [*Not reported*]	*Not reported*	*Zhang & Liu (2018)*
Floodplain soils [*soil type not specified*]	River floodplains (grassland and wetlands)	Area / metric	29 study sites, three mixed samples from three river-parallel transects (length: 16 m, distance: 1 m) at each site	Steel tools	Disturbed	0 - 5 cm [320 cm³]	Aluminum box	*Scheurer & Bigalke (2018)*
Garden soils [*soil type not specified*]	Home gardens	Random / metric	*Not reported*	*Not reported*	*Not reported*	0 - 10, 10 - 20 cm [50 g]	*Not reported*	*Huerta Lwanga et al. (2017)*
Municipal soils [Technosols]	Waste facility and industry surroundings	*Not reported*	*Not reported*	*Not reported*	*Not reported*	*Not reported* [*Not reported*]	*Not reported*	*Fuller & Gautam (2016)*

To depict vertically oriented processes (e.g., related to soil water movement or soil horizons), sampling sites need to be investigated by more than just one sample per site. The vertical resolution increases with the vertical sample number per site. The first study on micro- plastics in soils did not report the vertical sampling context (Fuller und Gautam 2016). From the other studies, three are based on one sample and three studies are based on two samples per sampling site (Table 4). Hence, the vertical representation of soil profiles has generally been rather poor so far.

There are three options for the vertical context of soil samples within one site (Figure 18c). (a) Samples can be taken randomly, with- out regard of their depth or pedogenic background (e.g., no attribution to a certain soil horizon). (b) Samples can be taken according to pedogenic characteristics (e.g., soil horizons), either from selected soil sections or from the entire profile (i.e., all soil horizons). (c) Samples can be taken from defined metric depths or depth sections, either for some selected depth sections or for all sections of a profile.

No study on microplastics in soils applied a pedogenic vertical sampling strategy (Table 4). Hence, questions regarding soil stratification and effects on vertical microplastic distribution could not be evaluated in past research. The six studies, which report their vertical sampling context, took soil samples according to soil depth. Two studies focused on the upper topsoil (0–5 cm), one on the plough layer (0–25 cm). Three studies took samples from two depth sections (0–3, 3–6 cm; 0–5, 5–10 cm; 0–10, 10–20 cm). These authors do not explain the rationale behind their choice of sampling depths.

For the few studies on microplastics in soils, a clear trend shows for favoring investigations of topsoils. Topsoils have specific features and represent a soil profile neither quantitatively nor qualitatively adequately (Weihrauch 2019). Topsoils are particularly critical to study due to a multitude of land use-based alterations (e.g., on agricultural fields), which might distort data comparison between sites, depths, or even across a plot (Li et al. 2010). Hence, results generated from topsoil studies are specific and do not draw a holistic picture of microplastics distribution and dynamics in soils. For instance, a vertical translocation of microplastics (e.g., to the groundwater) can presently not be excluded as there are no studies yet that examine subsoil microplastic pollution. Hence, even for explorative studies, a topsoil focus does not seem favorable in all cases.

3.1.2.2 Soil sampling and sample handling

For understanding soils in the landscape/soilscape context, a systematic documentation is required for: (a) sampling site features (e.g., relief, vegetation, land use history) and (b) specific soil features (e.g., soil type, horizons, respective standard features; Möller et al., 2020). In the examined studies on microplastics in soils, this information is not reported and probably was not obtained during sampling. Hence, no information on microplastics dynamics can be deduced from the studies' results, only the occurrence and abundance of microplastics.

Soil and site feature documentation is, for example, explained and standardized in the “Guidelines for soil description" (FAO 2006) and "World reference base for soil resources" (WRB) for the international context (IUSS Working Group 2015). Conventional soil sampling (e.g., for standard parameter analyses) is largely standardized by national standards, environmental laws, and administrative proceedings. However, it is known from marine research that artificial sample contamination with plastics during sampling, sample transport, and storage is a problem (Cole et al. 2011; Fischer et al. 2016; Horton et al. 2017). Thus, artificial plastic contamination must be considered and excluded for soil sampling in microplastics research.

In all previous studies, topsoil samples were taken using steel sampling equipment (Table 5). All authors document the equipment used, as it is clear that plastic equipment should not be applied to avoid contaminations. Because samples were taken up to a maximum depth of only 25 cm, no drilling methods were necessary and samples could be taken out of a shallow pit or directly with a spade.

Furthermore, the type of soil samples must be considered. Soil can be sampled locally, that is, at a defined position in three- dimensional coordinate space. The respective results then relate to a certain geographical location, possibly even to a certain soil depth at this location. Alternatively, composite samples could be created by mixing soil material from several sampling sites (Möller et al. 2020). It is only plausible to mix samples from sites relatively close to each other, which are characterized by comparable site and soil factors. The respective results are regionalized and inform about a certain area in the soilscape. Which type of soil samples should be chosen strongly depends on the research question. Localized samples are suitable for investigating spatial patterns and dynamics of microplastics in soils, where spatial heterogeneity is informative. Instead, composite samples are plausible for studies where representative regional information is wanted (i.e., without small-scale spatial heterogeneity), for example, for research related to land use practices or for studies based on experimental designs with plotting. Hence, composite sampling was often used in explorative studies on microplastics in soils (Corradini et al. 2019; Liu et al. 2018; Zhang und Liu 2018; Scheurer und Bigalke 2018). Currently, no recommendation can be given regarding how many samples should be combined into one composite sample (Möller et al. 2020).

The type of soil samples taken relates to the resulting mass or volume of soil material available for further analysis. In the field studies, different sample amounts are documented. The documented sample masses reach from 50 g (Huerta Lwanga et al. 2017) to 1000 g (Liu et al. 2018). The sample volumes reach from 320 cm^3 (Scheurer und Bigalke 2018) to 5,120 cm^3 (Piehl et al. 2018) of moist unprepared soil. The relatively large amount of sample material is logistically needed due to the further analysis steps, especially with respect to the separation of microplastics from the soil matrix (Figure 17).

Probably, larger amounts of soil material were so far also processed, because it has originally not been known if there were any microplastics in the investigated soils and how they were spatially distributed within the material. Hence, large samples could enlarge the probability of finding microplastic particles at all or in significant number.

If large sample quantities are required, these can only be gathered easily for topsoils (as they are logistically convenient to reach). To get samples from deeper soil sections, a more intensive interference with the soil is necessary (e.g., drilling). In microplastic studies, drilling methods have already been used for sediment sampling but not in studies with a soil focus (Ballent et al. 2016). Many drilling devices (e.g., augers of Pürckhauer type) only extract small soil quantities. Hence, to result in sufficiently large soil samples, several drilling cores would have to be gathered adjacent to each other and the respective samples would have to be mixed (e.g., the B-horizon material from adjoining drill cores).

Alternatively, pile-driving probes with a larger diameter could be used, which would make sampling more time-consuming and cost-intensive. It is recommended to pay attention to the contamination by plastic components (e.g., plastic caps on pile-driving probes, splinters of plastic hammers) when using drilling equipment. Many of these components can be removed before sampling. Certain textiles might also pose a risk of contamination (e.g., clothing fibers). Contamination can be avoided by reducing contact (quick storage after sampling) or by wearing cotton clothes.

Plastic particles may not just detach from our equipment during sampling but also during transport, and might artificially enrich our samples with external plastics. This means that no plastic bags or other plastic materials should be used during sampling and further processing. Especially, PE bags are often (Corradini et al. 2019; Piehl et al. 2018). However, if plastic bags are used for soil sampling in microplastic studies, this should only be done if no determination of materials similar to the bags' plastic type is planned and the possible contamination by the bags (e.g., through abrasion) is comprehensively controlled.

Alternatives to PE bags can be metal cases or buckets made of aluminum and glass jars. When plastic jars are used for sample trans- port and storage, they should be handled carefully and with low abrasion to minimize contamination. The use of metal vessels can be critical when the examination of microplastics is combined with the examination of other pollutants, like heavy metals. An alternative could be the use of biodegradable plastic bags, as long as the polymer types of these bags are known and are not the study's focus.

Finally, the samples have to be stored until the next methodical stage or for longer time. Samples should always be stored in closed containers to prevent contamination by the ambient air (e.g., dusts).

If the samples should be stored in plastic containers such as PE bags or PET jars, they should be stored as dry, cool, and dark as possible to prevent potential degradation of the plastics (Napper und Thompson 2019). In the case of biodegradable bags, it must be examined whether long-term storage is possible. In general, the polymer type of all plastic containers used should be known, the samples should be handled carefully and blank samples should be used as a control to verify any contaminations.

3.1.2.3 Sample pre-processing

A main challenge in the analysis of microplastics from environmental media is the separation of microplastics from their respective medium (e.g., water, soil material). The analysis of water samples can usually be carried out by sieving and filtration methods. For soils and sediments, the separation of microplastics from other matter is required. Various methodological approaches for the analysis of marine, aquatic, and limnic sediments were recently transferred to extract micro- plastics from soil samples (Bläsing und Amelung 2018; He et al. 2018a; Liu et al. 2018). However, it should be considered if a simple (e.g., beach sands) or a complex sample matrix (e.g., soil material) is at hand (Figure 17). As a result of pedogenesis, the biogeochemical properties of soil samples differ from, for example, beach sediments and form a more heterogeneous sample matrix comprised of several different components (e.g., mineral, organic, and microplastic particles).

In soil science, samples are usually dried before analysis because the results (e.g., heavy metal contents) are mostly reported in relation to soil weight (e.g., in SI of soil). For many questions, it is plausible to use the soil's dry weight. The weight of moist soil is largely influenced by weather conditions (e.g., precipitation). Thus, it gives different results with regard to the timing of soil sampling. Such results would be relative: For instance, element concentrations would appear higher in dry times (because it is related to lower dry weight) than in moist times (because it is related to higher moist weight). To come to absolute (i.e., generalizable) results, the soil moisture is thus eliminated by drying. This is done by air-drying at room temperature or in drying furnaces at temperatures between 50 and 70°C (Corradini et al. 2019; Piehl et al. 2018; Pinto da Costa et al. 2019). The application of drying furnaces significantly accelerates the drying process. However, excessively high temperatures can negatively influence plastics. Polymer melting temperatures range between 20 and 60°C for PE, 20 and 30°C for PET, 30 and 80°C for PP and PS, and 85 and 120°C for PC, depending on the production properties of each polymer (PlastikCity Ltd 2019). The decision to perform either low- or high-temperature drying depends on the respective research question and the further scope of the investigation. Drying temperatures within the ranges of the melting temperatures of different polymers could alter the polymer surfaces or could cause unwanted reactions between polymers and the soil matrix.

After drying, the soil aggregates should be crushed to prevent microplastics from adhering to mineral components or from being enclosed in soil aggregates.

Without this treatment, microplastics within soil aggregates could not be extracted and would be neglected in further analyses. Hence, it is important to disjoint soil aggregates as they are shown to contain microplastic particles and fibres (Zhang et al. 2019).

In addition to manual sample homogenization by manually crushing the aggregates with pestle and mortar, it is also possible to use ultrasound techniques, which might be necessary for strongly aggregated soils with high clay contents (Piehl et al. 2018). The manual method cannot destroy microaggregates satisfactorily (Pinto da Costa et al. 2019). Treating samples with ultrasound enables to reliably disjoint both macro and microaggregates. However, at too high ultrasound or attrition energies, plastic particles could be fragmented during crushing. This secondary fragmentation of microplastic particles must be reflected in studies concerning the size, shape, and surface texture of microplastics.

3.1.2.4 Sample matrix separation

In contrast to microplastic analyses in water and sediment samples, processing soil material faces the challenge of separating several components. Presently, no satisfactory methods exist for this purpose. As sample separation can hardly be achieved in one preparation step, a suitable and standardized workflow is required. Three steps of micro- plastic extraction can be differentiated, which can be applied individually, partially, or consecutively: (a) the removal of the mineral phase, (b) the removal of organics, and (c) the size classification of microplastic particles by sorting and/or sieving. It is crucial to make sure that soil samples are not contaminated with external plastic (clothing fibres, plastic equipment) at any stage of this workflow.

3.1.2.4.1 Removal of mineral phase

In most studies on microplastics in soils, the principle of density separation is used to remove the mineral phase from the pre-processed samples. The separation of the heavier mineral components (i.e., sand, silt, finally clay), that sink to the bottom, from the lighter components (i.e., microplastics, organics), that float up, depends on the density (ρ) of the separating solution and the density of the assessed plastic polymers (Durner et al. 2017). Different separation solutions are currently applied (e.g., NaCl, demineralized water, NaI, $ZnCl_2$, $CaCl_2$) (Claessens et al. 2013; Huerta Lwanga et al. 2017; Imhof et al. 2013; Liu et al. 2018; Scheurer und Bigalke 2018; Zhang und Liu 2018).

A new approach is the application of castor oil for separation. The method was tested with recovery rates of 99 ± 4% for PP, PS, PMMA, and PET, but samples with a high content of organic material require additional treatment for organic matter decomposition (Mani et al. 2019). Independent of the sealing solution, the verification, and correct adjustment of the desired density must be ensured during laboratory analyses because it depends on the room temperature and chemical processes (e.g., solubility of chemicals) (Crichton et al. 2017).

Density separation can be conducted in different vessels. Beakers, separation cylinders, and centrifuges made of glass or plastic are used. Because the duration of sedimentation is 25–48 hr., the use of a centrifuge, additionally coupled with a rubber disc, can significantly accelerate the process and make it much more time-efficient (Pinto da Costa et al. 2019; Scheurer und Bigalke 2018).

An alternative to open vessels or centrifuges is the application of closed sedimentation cylinders with a separation chamber. Devices like the Munich Plastic Sediment Separator (MPSS) (Imhof et al. 2012) or the Sediment-Microplastic-Isolation (SMI) unit (Coppock et al. 2017) enable the separation of the floating micro- plastic particles from the sunk soil particles.

Because the sedimentation process takes a long time, partly more than 24 hr., an acceleration by centrifugation is possible (Scheurer und Bigalke 2018; Zhang und Liu 2018). In this case, the use of lower sample amounts (e.g., 5–20 g) is required depending on the centrifuge size. However, several repetitions are needed to minimize the number of particles lost in the instruments (e.g., attached to inner vessel walls) (Corradini et al. 2019; Scheurer und Bigalke 2018). A direct separation of microplastics from the mineral and organic soil particles presently only exists for the smallest microplastic particles (<30 µm). For this purpose, a pressurized fluid extraction with methanol and dichloromethane is used (Fuller und Gautam 2016). However, this method can only be applied for specific research questions.

3.1.2.4.2 Removal of organics

Organics (e.g., humus, peat particles, and plant/root fragments) mostly have a density comparable to microplastics. Thus, density separation usually results in organic components being extracted along with microplastics (Corradini et al. 2019; Felsing et al. 2018; Zhang et al. 2019). In order to isolate the microplastic particles, they can be removed manually using a stereomicroscope with respect to the detection limits/magnification of the microscope (Crawford und Quinn 2017; Song et al. 2015). Alternatively, organics and microplastics can be separated technically.

As in marine and aquatic research, enzymatic digestion may be applied using a variety of enzymes in combination with a subsequent H_2O_2 treatment (Löder et al. 2015; Mintenig et al. 2017). During this procedure, plastic is not degraded. However, the method is time-consuming and still has to be tested for the successful application to soil organic matter (Bläsing und Amelung 2018; Pinto da Costa et al. 2019; Prata et al. 2019). Furthermore, different acid and alkaline solution treatments exist (e.g., with 65% HNO_3, 96% H2SO$_4$, mix of 69% HNO_3 + 70% $HCLO_4$ (4:1)). With all acid treatments, a rapid removal of the organic components is observed (Enders et al. 2016). However, structural degradation of plastic particles was often observed.

In contrast to acid treatments, alkaline treatments influence neither the microplastic particles shape nor surface properties (Enders et al. 2016). The treatments apply NaOH, KOH, or both in combination. Both chemicals are suitable for biological samples but have not been applied to soil samples. Although these treatments do not degrade plastics, the methods are unable to remove alkali-insoluble organic matter from soil (Bläsing und Amelung 2018). Therefore, humins probably remain in the samples after the alkaline treatment, which complicates the later identification of the microplastic particles (Dehaut et al. 2016).

Furthermore, the oxidation of humus is sometimes applied to remove organics (e.g., 30% H_2O_2) (He et al. 2018a; Liu et al. 2018). The oxidation can be improved by adding a Fe(II)-containing solution (e.g., $FeSO_4$) as a catalyst for the reaction (Fenton reagent). Restrictions may arise here for calcareous soils, because the Fenton reaction could be impeded by carbonates (Liu et al. 2016). Removing organics with just H_2O_2 causes a digestion of PE and PP (Silva et al. 2018). No negative effects are reported for the application of the Fenton reagent.

Next to the enzymatic and chemical treatments, a separation based on the different electrostatic behaviour of organic and plastic particles was developed (Felsing et al. 2018; Hidalgo-Ruz et al. 2012). This method has no negative effect on microplastic particles. However, it was tested only for various sands and sediments, where it gave reliable results in the separation of organic material. The method should be validated for the application to soil samples (Felsing et al. 2018).

3.1.2.4.3 Sieving and sorting of separated microplastics

After microplastics have been separated from the mineral and organic matrix, it is useful to characterize the plastic particles further according to size by sieving and/or sorting. According to the above- mentioned definition, microplastics range between 0.01 and 5.0 mm in diameter (see first chapter 3.1.1). Considering this wide range, the question arises if these thresholds are also plausible in soil science. Instead, microplastics could further be separated into larger and smaller microplastics (>2 and <2 mm, respectively) according to the soil scientific differentiation between fine and coarse soil components. The determination of microplastic size classes can provide important insights into possible transport processes, as well as the physical and chemical degradation in soils.

Generally, macro- and microplastics can be separated with sieves with a mesh size of 5 mm. Particles <5 mm are often further subdivided using specific series of sieve mesh sizes (e.g., <1.0, 1.0–3.0, 3.0–5.0 mm; 1.0–0.25, 0.25–0.05 mm; 5–1 mm) (Liu et al. 2018; Zhang und Liu 2018; Piehl et al. 2018). For particles <1 mm, a filtration with various pump systems (e.g., vacuum) and glass fibre filters is often used (Klein et al. 2015; Scheurer und Bigalke 2018).

Sieving can be conducted after drying and crushing, or intermediately during analysis (i.e., after density separation as dry or wet sieving). For soil samples with a high clay content, a pre-treatment might be needed to disaggregate the soil material (e.g., with H_2O_2, $Na_4P_2O_7$) (Piehl et al. 2018). The effective size separation during sieving also depends on whether the soil aggregates have been crushed properly (Zhang und Liu 2018).

To enable a quantification and identification of the separated microplastics, the manual sorting and counting of the detected particles is established. This process can be facilitated by staining the sample material with Nile Red tracer (Maes et al. 2017).

Depending on the size class, microplastic particles are counted and documented by eye using a binocular or stereomicroscope. In addition to taking photographs, the documentation includes the classification of the particles according to different features, which were mostly adopted from marine research (Baldwin et al. 2016; Fischer et al. 2016; Nor und Obbard 2014). Shape, surface texture, colour, and luster are documented (Nor und Obbard 2014; Horton et al. 2017). Furthermore, the surface area and length of the particles are determined in some studies using various imaging software (Lorenzo-Navarro et al. 2018).

Pre-treatments of soil samples for studies on microplastic dynamics could be remedied by automating the sorting and classification. Because most studies produce images of the microplastic particles, microplastics placed on filters after separation can be photographed at the appropriate resolution. Based on different colour and shape features, machine learning could then be used for automatic counting and classification (Lorenzo-Navarro et al. 2018). In addition, automatic image analyses from Fourier-transform infrared spectroscopy (FTIR) microscope images combined with an automatic database analysis have already been performed (Primpke et al. 2017; Primpke et al. 2018). Because these are also suitable for complex sample matrixes, an application to soil samples would be useful and should be developed in further studies.

3.1.2.5 Microplastic quantification and identification

The final step in the analysis of microplastics in environmental samples is the quantification of the microplastic components, and, in most studies, the identification of the polymer types. Both sieving and sorting, as well as automatic sorting methods, allow us to calculate a value for the proportion of microplastic particles in soil samples. However, current studies reveal a wide range of detection limits related to the minimum size of the detected particles. Depending on the applied method, the detection limit varies from 1 to 1000 µm, whereas in some cases, a large part of the small microplastic particles could not be detected and a comprehensive quantification was difficult (Huerta Lwanga et al. 2017; Liu et al. 2018; Piehl et al. 2018; Scheurer und Bigalke 2018; Zhang und Liu 2018).

The detected amount of microplastics can be quantified by counting the particles and putting them in relation to the mass or volume of the original soil sample. At present, the unit mpp/kg is mostly used to report results (Pinto da Costa et al. 2019; Prata et al. 2019; Silva et al. 2018). Still, the unequal size of the microplastic particles complicates the comparability when using this unit. Alternatively, by weighing the micro- plastic particles, it is possible to derive the mass-based unit 'mg per kg soil' (mg/kg), which increases the comparability with other soil analysis results (e.g., elemental concentrations) (Möller et al. 2020; Qi et al. 2020; Wang et al. 2019; Wang et al. 2020). However, the exact determination of the microplastics' weight is currently difficult, because of the low density and small particle sizes (<500–300 μm). Moreover, the selection of the unit to report the results might depend on the research question. For studies on the general occurrence and abundance of micro- plastics in the environment, a mass-related specification (e.g., mg kg^{-1}) seems to be sufficient and plausible.

Instead, when effects on soil functions, relocation processes, or modeling are in focus, informations on particle number (e.g., mpp/kg), size, shape, and type become relevant. For approaches such as simplifying the complex diversity of MP particles through a three-dimensional dimension, also size, density, and shape of each particle is required (Kooi und Koelmans 2019).

After the visual identification of microplastics, an identification of the polymer type might be wanted in some studies, for example, to deduce on the plastics' provenience. This can be achieved by various chemical methods whose applicability and limitations have already been reviewed in the literature (e.g., Pyrolysis-gas chromatography– mass spectrometry, ToF-SIMS, Raman spectroscopy with μRaman, and FTIR with μFTIR) (David et al. 2018; Du et al. 2020; Dümichen et al. 2017; Hermabessiere et al. 2018; Pinto da Costa et al. 2019; Renner et al. 2018).

The increasing number of samples and possibly high numbers of microplastic particles in soils lead to large amounts of data, which can be processed in an automated way (image analyses or automatic spectral analysis with databases) (Primpke et al. 2017; Primpke et al. 2018). The application of spectroscopic methods for the analysis of plastics has already been discussed in other soil specific reviews as well as reviews of the material sciences and in marine research (Elert et al. 2017; He et al. 2018b; Pinto da Costa et al. 2019; Prata et al. 2019; Renner et al. 2018; Ruggero et al. 2020; Silva et al. 2018; Zhang et al. 2020) and is not further elaborated in the present review.

The methods commonly applied for soil scientific studies have in common that the heterogeneous soil sample matrices require a more or less complex sample preparation or separation. First approaches to reduce this effort are the pre-scanning of the sample without chemical treatment, based on near-infrared spectroscopy (NIRS) detection (Paul et al. 2019). Moreover, a direct quantification of heterogeneous sample matrices by the combination of thermogravimetric analyses (TGA) with thermal desorption system coupled with gas chromatography–mass spectrometry (TDS-GS-MS) and the application of twisters as solid-phase absorbers was demonstrated for PE particles (Dümichen et al. 2015; Dümichen et al. 2017). Despite the diversity of identification procedures and their different applicability to soil samples, there is still a large demand for research to validate, improve, and develop suitable, comparable, cost- and time-efficient methods particularly regarding pre-scanning methods.

3.1.3 Conclusions

The discovery of microplastic particles as new pollutants in the environment opens up a novel field of research for soil science. Potential hazards posed by microplastics and nanoplastics in soils (e.g., uptake by plants and introduction into the food chain) are theoretically plausible. However, a better understanding of microplastic dynamics is needed to systematically evaluate the effects of soil- bound microplastics pollution (e.g., on biota and the food chain) and to develop targeted mitigation strategies. Regarding the current trends in environmental microplastics research, we think that it is specifically required to transition from solely explorative micro- plastics studies to more systematic investigations. This would especially call for a more intensive consideration of spatially adequate sampling strategies than documented in previous studies. The proposed geospatial approach might thus enable further more sophisticated research.

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3.2 Spatial patterns of mesoplastics and coarse microplastics in floodplain soils as resulting from land use and fluvial processes

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Abstract

Plastic, and especially microplastic, contamination of soils has become a novel research field. After the detection of microplastics in soils, spatial distribution and dynamics are still unknown. However, the potential risks associated with plastic particles in soils cannot be sufficiently assessed without knowledge about the spatial distribution of these anthropogenic materials. Based on a spatial research approach, including soil surveys, this study quantified the mesoplastic (MEP, >5.0 mm) and coarse microplastics (CMP, 2.0–5.0 mm) content of twelve floodplain soils. At four transects in the catchment area of the Lahn River (Germany), soils down to a depth of 2 m were examined for plastic content for the first time. MEP and CMP were detected through visual examination after sample preprocessing and ATR-FTIR analyses. Average MEP and CMP concentrations range between 2.06 kg^{-1} (±1.55 kg^{-1}) and 1.88 kg^{-1} (±1.49 kg^{-1}) with maximal values of 5.37 MEP kg^{-1} to 8.59 CMP kg^{-1}. Plastic particles are heterogeneously distributed in samples. Both plastic size classes occur more frequently in topsoils than in soil layers deeper than 30 cm. The maximal depth of CMP occurrence lies between 75 and 100 cm. Most common CMP polymer type was PE-LD, followed by PP and PA. MEP and CMP particles occur frequently at near channel sides and more often on riparian strips or grassland than on farmland. Vertical distribution of CMP indicates anthropogenic relocation in topsoils and additional deep displacement through natural processes like preferential flow paths or bioturbation. By comparing sedimentation rates of the river with the maximum age of plastic particles, sedimentation as a deposition process of plastic in floodplains becomes probable. From our findings, it can be concluded that an overall widespread but spatial heterogenous contamination occurs in floodplain soils. Additionally, a complex plastic source pattern seems to appear in floodplain areas.

Keywords

Microplastic, Contamination, Vertical transfer, Geospatial approach, Spatial distribution

3.2.1 Introduction

Worldwide, a large proportion of plastic waste, especially microplastics, is disposed into the environment (Barnes et al. 2009; Karbalaei et al. 2018; Souza Machado et al. 2018a; PlasticsEurope 2018). Plastic production has rapidly increased since its serial production in the 1950s, and today 348 million tons of plastic are produced each year (Andrady 2017; PlasticsEurope 2018). Research on plastic and microplastics has demonstrated the occurrence of plastic particles in different size ranges all around the world and in several ecosystems (Allen et al. 2019; Emmerik und Schwarz 2020; Peeken et al. 2018). Soils, as terrestrial ecosystems and fundamental resources of the global food security system, are also affected by plastic pollution (He et al. 2021b; Souza Machado et al. 2018b; Rillig 2012; Wang et al. 2019; Zhang et al. 2020). Despite the limited number of studies on meso- (MEP) and microplastics (MP) in soils, it could be proven that, in particular, microplastic have various effects on soil biota, soil physical, and chemical properties, as well as plant growth (Engdahl 2018; Hüffer et al. 2019; Rillig et al. 2017a; Rillig et al. 2017b; Rillig et al. 2019; Yu et al. 2019). Because one of the hot- spots of plastic pollution is located in the oceans (Martin et al. 2017b), the transport of plastic by rivers could be seen as a major source of plastic distribution (Alimi et al. 2018; Liu et al. 2019; Siegfried et al. 2017; Tibbetts et al. 2018; Xiong et al. 2018). Immediately beside these main land-to-sea transport paths are floodplains, which are semiterrestrial ecosystem. The first study on microplastics in floodplain topsoils in Swiss nature conservation areas reveals the abundance of microplastic in these ecosystems (Scheurer und Bigalke 2018). Because floodplains are mainly sedimentation and flood retention areas, a systematic accumulation of plastic particles is conceivable in floodplains.

Microplastics as anthropogenic materials are defined with a currently implemented definition of a size spectrum between 1 and 5000 mm (Mausra et al. 2015). This defined size range reaches its limits if studying environmental processes in a soil context (e.g., transport or transfer processes) because, in the case of particles, these processes are also size dependent (Blume et al. 2016; Rillig et al. 2017b; Yu et al. 2019). In soil science, a differentiation is made between different grain sizes and coarse gravel (2–6 mm) or very coarse sand and coarse sand (> 2000 μm) against textural sand classes (< 2000 μm) (FAO 2006; IUSS Working Group 2015). Differentiation between coarse and fine soil/earth has already been used for a long time to describe soils and pedogenesis, and makes a significant distinction for in situ transfer processes (e.g., macropores; Blume et al., 2016). As microplastic particles within the size range of coarse sand fraction can be assumed to be difficult to relocate in situ, soil context research should specify these size classes. The present study distinguishes between macroplastics (> 25000 μm, 25 mm; abbreviated as MAP), mesoplastics (> 5000 μm; abbreviated as MEP), and coarse microplastics (abbreviated as CMP) with a size range of 5000 to 2000 μm.

For the deeper understanding of spatial plastic dynamics in soils, more systematic studies in contrast to the so far established "explorative studies" are required (Weber et al. 2020).

Hence, the present study uses a geospatial approach to investigate the spatial dynamics of MEP and CMP in floodplain soils to answer the following research questions:

(1) What are the levels of MEP and CMP pollution in floodplain soils in an entire catchment area?
(2) Is the lateral distribution of MEP and CMP a function of river section, land use, or distance to water body?
(3) Are MEP and CMP involved in the sedimentation processes and/or vertically displacement processes?

This is intended to achieve the objective of an improved understanding of spatial plastic dynamics inside the three-dimensional system of the soilscapes and enable further targeted research about responsible processes in landscapes.

3.2.2 Material and methods

3.2.2.1 Study area

The investigation was performed in floodplain areas of the Lahn River located in the central German low mountain range (Hesse, Germany; Figure A 1). The Lahn River, with a length of 245.6 km, drains a catchment area of 5924 km^2 (Regional Council Giessen 2015). The geology of the Lahn River catchment consists principally of different rock types from the Paleozoic age, tertiary basalts and sandstones (Meschede und Warr 2019). The Lahn Valley reaches a maximum with of ca. 3.0 km (Tichy 1951). According to hydrological, geological, and landscape properties, the Lahn Valley can be divided into four zones: (A) upper course (Rhenish Slate Mountains, smaller floodplain), (B) middle course (wide valley with wide floodplain), (C) narrow valley (almost without distinctive floodplain), and (D) lower course with individual valley widenings and floodplains.

The floodplains beside the Lahn River and surrounding valleys are built up from organic-rich silt and loams, reaching a thickness of 3.0 m, which was deposited during the late Holocene (Bos und Urz 2003; Rittweger 2000). Even if early Holocene depositions occur, the main sedimentation process occurred over the last 3000 years in connection to anthropogenic land use change (reclamation) (Andres et al. 2001; Bos und Urz 2003; Delorme und Leuschner 1983; Kalias et al. 2003; Rittweger 2000).

These Holocene strata are on top of Pleistocene gravel and sand deposition, which are partially terrain forming in the upper reaches (Bos und Urz 2003; Mäckel 1969). The border between Pleistocene and Holocene depositions is marked in the middle reaches between the cities of Marburg and Wetzlar through an incision of the LST during Younger Dryas (Laacher See tephra; Bos and Urz, 2003). Floodplain surface morphology consists of river banks, plain areas with conserved forms (e.g., former loops or meander bends, channels), and back swamps. Different soil types, like Fluvisols, Gleysols, and Stagnisols, have developed in the deposited river sediments (Table 6).

Table 6: Sampling site features.

Sampling Area	Catchment properties			Sampling site	Floodplain properties			Soil properties	
	Catchment zone	River km[a]	Width of flood area		Morphological unit	Land use	Distance to channel (m)	Sampling depth (cm)	Soil type (WRB[b])
ELM 50.865345 8.618088	Upper course	201.9	617.7	ELM-1	Riparian	riparian vegetation	8.8	100	Skeletic Fluvisol (Technic, Arenic)
				ELM-2	Plane	farmland	500.6	100	Endogleyic Skeletic Fluvisol (Anthric, Siltic)
ROT 50.734907 8.733830	Middle cource	168.3	1543.2	ROT-1	Riparian	grassland	15.5	200	Halpic Fluvisol (Arenic)
				ROT-2	Plane	grassland	462.5	200	Stagnic Fluvisol (Anthric, Tephric, Loamic)
STD 50.552517 8.451405	Middle cource	121.0	689.4	STD-1	Riparian	farmland	50.0	200	Fluvisol (Anthric, Arenic)
				STD-2	Plane	grassland	228.9	200	Skeletic Fluvisol (Loamic)
				STD-3	Plane	grassland	433.3	200	Epigleyic Fluvisol (Silitc)
				STD-4	Backswamp	grassland	622.7	200	Fluvic Gleysol (Clayic)
LIM 50.389916 8.039374	Lower cource	57.0	420.4	LIM-1	Riparian	riparian vegetation	12.2	200	Haplic Fluvisol (Arenic)
				LIM-2	Plane	grassland	82.9	200	Endogleyic Fluvisol (Silitc)
				LIM-3	Backswamp	grassland	251.1	200	Fluvic Gleysol (Loamic)
				LIM-4	Low terrace	farmland	383.2	200	Skeletic Stagnic Fluvisol (Densic, Clayic)

[a] according to WRRL-Viewer Hesse; [b] = World Reference Base for Soil Recourses (2015)

The current land use in the main Lahn River catchment is 7.0% urban and traffic, 1.4% industry, 43.0% agriculture (crop- and grassland), and 47.0% forested (Regional Council Giessen 2015). As of 2010, the Hessian catchment parts had 1.3 million inhabitants (266/km^2; Regional Council Giessen, 2015). The water body of the Lahn River can be named urbanized only in the direct surroundings of the cities Marburg, Giessen, Wetzlar, and Limburg (Martin 2012). Floodplains are under mainly agricultural land use (crop- or grassland), excluding riparian strips (channel bank) and small amounts of urban areas. As the lower Lahn River reaches were used for shipping, the river is deepened and channelized (Martin 2012; Regional Council Giessen 2015).

Similar to other rivers in central Europe, different medieval flood events are documented for the Lahn River (e.g., 1255, 1332, 1552) (Gleim und Opp 2004). Over the past 100 years, flood events with a discharge >400 m^3 s^{-1} (Station Leun) and water levels >450 cm (Station Marburg) occur frequently, with a century high-flood event in 1984 (Gleim und Opp 2004). Different flood water management measures (e.g., flood retention basins, dikes, return of flood retention areas) were established inside the catchment. However, recent flood events have not eroded or deposited high loads of sediments, and local erosion and deposition of fine sands appears (Martin 2012, 2015, 2019).

3.2.2.2 Soil sampling

The spatial distribution of MEP and CMP was investigated on four sites representative for zones A (upper course), B (middle course) and D (lower course) with extended floodplains. In order to investigate the spatial dynamics of MEP and CMP inside the floodplain system, each site was selected according to the following criteria: (1) location inside a natural flood retention area with frequent flood events, (2) sequence of different morphological units and soil differentiation, (3) land use differences in floodplain cross-section, and (4) no direct MP sources (e.g., highways, industrial plants). A soil mapping was carried out on each of the four sites in order to obtain an overview on soil scape properties and set each transect representative for a larger floodplain area with comparable soil properties (Weihrauch 2019).

Floodplain cross-section transect, containing two or four sampling sites, were established at each site according to the above-mentioned criteria. The distance between the sampling sites depends on the width of the floodplains. Two soil profiles at a distance of 5 m to each other were sampled down to a depth of 2 m through pile core driving (core diameter: 100 mm and 80 mm) and then sampled in sections of 10 cm (0–0.5 m depth), 25 cm (0.5–1.5 m depth), and 50 cm (1.5–2.0m) depth. Sample mass ranged between 388 g and 3225 g (mean 1150 g) of dry soil material including coarse soil fractions and organic material. Samples were transported and stored in corn starch bioplastic bags (Mater-Bi bags, Bio Futura B.V., Rotterdam, Netherlands). A total of 120 samples (10 samples per soil profile) were taken at four sites between August 12, 2019 and August 23, 2019. Additional plastic fragments on topsoil surface were sampled if the number of plastic fragments around the drill hole was noticeable.

On sampling site STD (Profile STD-1), visible plastic fragments (macroplastic: >25000 µm, MAP) were collected on a 20 m^2 area next to the drill point. This sampling of plastic particles from soil surface was only used on this site because there was a conspicuous amount of visible plastic fragments. MAP surface samples were handled in accordance with sample handling of soil samples.

The stratigraphy and pedogenesis of the sampled floodplain soils was documented according to the German soil classification (Ad-hoc AG Boden 2005) and the FAO Guidelines for soil description (FAO 2006) and were classified according to WRB 2015 (IUSS Working Group 2015). Soil color with Munsell charts and the carbonate content after reaction with a few drops of 3.23 M hydro- chloric acid (HCl) according to Ad-hoc AG Boden (2005) was determined in field.

Contamination prevention during soil sampling was performed by the general renouncement of plastic tools. This includes the removal of plastic parts on the pile cores, the sample material removal with stainless steel spatulas, and the final transport of samples in bioplastic bags.

3.2.2.3 Laboratory analysis

For each soil sample, a five-step procedure, including sample preprocessing and analyses, was applied (Figure A 2). Samples were short-time stored in corn starch bags and then dried at 45°C in a dying chamber (step 1) for a maximum of four days. After drying, samples were carefully crashed with pestle and mortar (step 2) to solve soil macroaggregates. Step 2 is important because CMP can be embedded in soil macroaggregates (250–2500 µm) and additional microplastic in microaggregates (20–250 µm) (Amelung und Zech 1999; Zhang und Liu 2018).

According to the size classes of MEP (> 5000 µm) and CMP (> 2000 µm), soil samples were dry sieved (step 3) through a 5 mm- and 2 mm-wide mesh, stainless-steel sieve (Retsch GmbH, Haan, Germany). During the sieving process, the sieves were covered and shaken. Each fraction was then weighed and stored again in fresh corn starch bags. A sample proportion < 2000 µm was saved for later analysis of microplastics, which is currently in progress. During sample preprocessing, the exposition time of each sample was reduced as much as possible to avoid air contaminations (e.g., clothing fibres). Both fractions of each, single sample were then visually determined (step 4) for the MEP and CMP content. Plastic particles found in the sieving fraction > 2000 µm were counted as CMP, whereas particles found in the fraction > 5000 µm were counted as MEP. MAP particles could be detected only from the surface samples of side STD. Therefore, each fraction was transferred to a stainless-steel bowl with imprinted grid (1x1 cm grid size), and each grid space was inspected under a stereomicroscope with 40x maximal magnification (SMZ 161 TL, Motic, Hong Kong).

Potential plastic particles were identified under application of criteria for visual determination of microplastics introduced by Noren (2007).

A particle was picked if (a) no cellular, organic or undissolved soil aggregate structure was visible, (b) the particle has a homogenous color, and (c) in case of filaments, the particle is equally thick. Subsequently, each identified particle was classified into different categories according to Hidalgo-Ruz et al. (2012), photographed (Moticam 2, Motic, Hong Kong), and stored in glass vessels until further analysis (Hidalgo-Ruz et al. 2012). Even if several authors suggested that visual identification of microplastic is prone to serious errors, this conclusion depends on the particle size (Andrady 2017; Hidalgo-Ruz et al. 2012; Song et al. 2015). For CMP particles with a size > 2000 µm, identification by microscope seems to be suitable with a low risk of underestimating the total particle number (e.g., in case of transparent or yellow-weathered shapes) (Song et al. 2015). Additionally, the MAP samples from site STD were also visual determined, photographed, and stored in glass vessels.

For final identification and to avoid overestimation, all visually identified CMP, MEP, and MAP particles were analyzed with a Tensor 37 FTIR spectrometer (Bruker Optics, Ettlingen, Germany) combined with a Platinum-ATR-unit (Bruker Optics, Ettlingen, Germany). In the case of very dirty particles, these were carefully cleaned at the measuring point using steel tools (tweezers, spatula). The Platinum-ATR-unit, in the case of particles with strong adherent soil material, was cleaned with 2-propanol ($CH_3CHOHCH_3$). The measurement of each particle was performed with 20 background scans, followed by 20 sample scans. Spectral resolution was set to 4 cm^{-1} in a wavenumber range from 4000 cm^{-1} to 400 cm^{-1} following the suggestions of Primpke et al. (2017) and Primpke et al. (2018).

3.2.2.4 Statistics and data evaluation

Basic statistical operations were performed in Microsoft Excel 2013 (Microsoft; Redmond, WA, USA), in R (R Core Team, 2020), and RStudio (Version 3.4.1; RStudio Inc.; Boston, MA, USA). Depth variation of particles was illustrated using a “vioplot” package and comparison with sedimentation rates using “sm” package (Adler et al. 2019; Bowman und Azzalini 2018).

Data processing of FTIR spectra was performed in OPUS 7.0 (Bruker Optics, Ettlingen, Germany). Each spectrum was compared with the entries in OPUS 7.0 internal spectra database. Quality for identifying a polymer was a hit quality of > 300 (Lorenzo-Navarro et al. 2018; Primpke et al. 2017; Primpke et al. 2018). Each particle that did not achieve a hit quality above 300 was measured twice after additional carefully cleaning. Additional FTIR spectra analyses and plotting was performed in Spectragryph (Version 1.2.14; Menges, 2020; Oberstdorf, Germany). Previously unidentified particles were additionally compared with spectra database of natural and biogenic materials.

MEP and CMP concentrations are reported in particles (MEP or CMP) per kilogram soil dry weight (MEP kg^{-1}, CMP kg^{-1}). The concentration of surface MAP particles is given in absolute numbers. For comparison of CMP abundance in floodplain soils and sedimentation rates, the following procedure was performed:

(a) For each FTIR-identified particle, the age of earliest possible occurrence (e.g., year of first production or patent application) was chosen from “History of Plastics” (British Plastic Federation 2020) and/or “Plastikatlas 2019” (Caterbow und Speranskaya 2019). (b) Sedimentation rates and sediment ages (Quartz OSL/14C) from all available regional studies were compared. Finally, the sedimentation rate of 0.07 cm per year (cm/a) calculated by Lang & Nolte (1999) for the Wetter river floodplain was chosen (Lang und Nolte 1999). This value is closest to the calculated average (0.11cm/a) of three rivers (Amöneburg Basin, Wetter River, Dill River) and is most comparable in morphological terms (Lang und Nolte 1999; Martin 2015; Rittweger 2000). (c) Age of earliest possible occurrence was multiplied by sedimentation rate and compared to sample depth.

3.2.3 Results and discussion

3.2.3.1 Meso- and coarse microplastic abundance in floodplain soil

Inside the floodplain areas of the Lahn River, plastic particles were found at each transect site. Overall, 14 MEP particles (10 significant FTIR identified) and 78 CMP particles (40 significant ATR-FTIR identified) were documented. On site, STD-1 additional 16 MAP particles (13 significant ATR-FTIR identified) were collected on a 20 m^2 area next to the drill hole. Even if this result is only representative for a single area, a value of 6500 particles per hectare can be calculated. Piehl et al. (2018) documented a value of 206 MAP per hectare for an agricultural field (Piehl et al., 2018). In comparison with this study and due to the limited area representativeness, the sampling point STD-1 could be considered a MAP hotspot.

The MEP concentration in soil samples ranges from 0.62 to 5.37 MEP kg^{-1} (median 1.62 MEP kg^{-1}, mean 2.06 MEP kg^{-1}). For visual identified CMP, the concentration lies between 0.31 and 8.59 CMP kg^{-1} (median 2.25 CMP kg^{-1}, mean 2.87 CMP kg^{-1}) and for additional ATR-FTIR-identified CMPs between 0.37 and 6.06 CMP kg^{-1} (median 1.37 CMP kg^{-1}, mean 1.88 CMP kg^{-1}; Figure 19a). The difference between the clearly visually identified number of CMP and the FTIR identified CMPs could be explained by the strong surface degradation of weathered particles. Additional degraded particle surfaces allow a better adhesion of dirt (e.g., minerals, organic matter), which facilitates cleaning and identification using a spectra database based on fresh particles (Primpke et al. 2018).

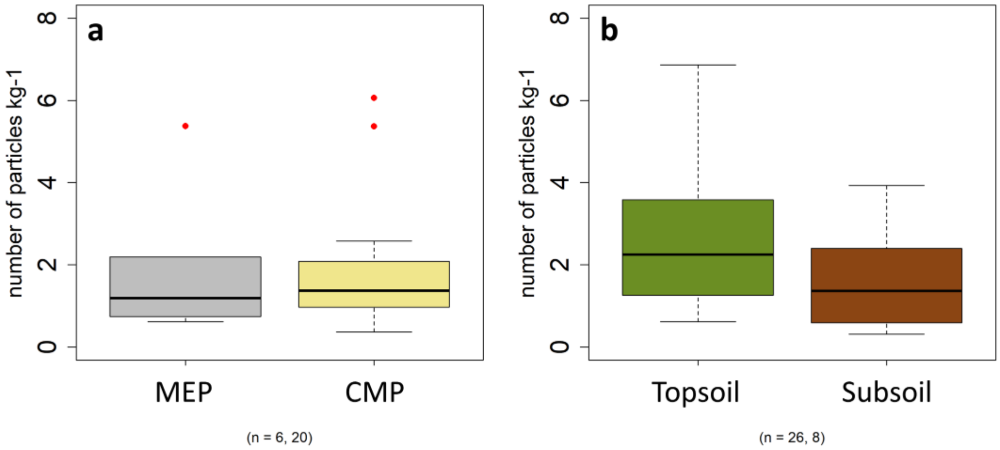

Figure 19: Overview of number of MEP and CMP particles per kilogram soil dry weight. a) MEP and CMP loads at all sampling sites. b) MEP and CMP loads in topsoil (depth: 0-30 cm) and subsoil (depth: >30 cm).

Because there are currently only a few quantitative studies on micro-, meso-, and macroplastics in soils, each reporting different quantitative values, interpretation and discussion is limited. In a comparison of the results of this study with the results of Liu et al. (2018) and Zhang and Liu (2018) for agricultural topsoils, their microplastic load range within 78.00 ± 12.91 particles kg^{-1} (respectively 7100 p kg^{-1}) and 62.50 ± 12.97 particles kg^{-1} (respectively 42.96 p kg^{-1}) (Liu et al. 2018). These values clearly exceed the concentration of the recent study. In contrast, the range of mesoplastics reported by Liu et al. (2018) with 6.75 ± 1.51 to 3.25 ± 1.04 p kg^{-1} corresponds to the concentrations documented by this study (Liu et al., 2018). Another microplastic and meso- plastic concentration, reported for Swiss floodplain topsoils in nature reserves by Scheurer and Bigalke (2018), is given with a maximum of 592 p kg^{-1} (55.5 mg kg^{-1}) and an average of 5 mg kg^{-1}. A comparison with the only other study on floodplain soils is complicated by the use of the mg kg^{-1} unit. However, assuming that the maximum is approximately 11 times higher than the average value and that 88% of total microplastic load occurs in a size <500 µm, the concentration of CMP could be comparable (Scheurer und Bigalke 2018).

Dominant identified polymer type is PE-LD with 5 MEPs and 16% of total CMP particles (Figure 20). In CMP fraction PP (6%), PA (5%), PS (4%), POM (4%) and PET (3%) form the majority together with single others. Collected surface samples from Site STD-1 consists of PE-LD, PE-HD, PVC, PP and PS. These findings are clearly comparable to other studies of microplastics and MP in soils. PE and PP seem to represent the majority of plastic particles in soils (Liu et al. 2018; Piehl et al. 2018; Scheurer und Bigalke 2018; Zhang und Liu 2018). This finding is not unexpected because PP, PE-LD, and PE-HD are the most frequently used polymer types and show the largest production quantities (Andrady 2017; Ellen MacArthur Foundation 2017; PlasticsEurope 2018).

Strong degradation of particles and poor surface properties (e.g., strongly adherent soil material) leads to a huge amount of not clearly identified particles (49% of total CMP particles). Additional cleaning of larger particles with distilled water is possible but difficult for fragile pieces and must be carried out carefully.

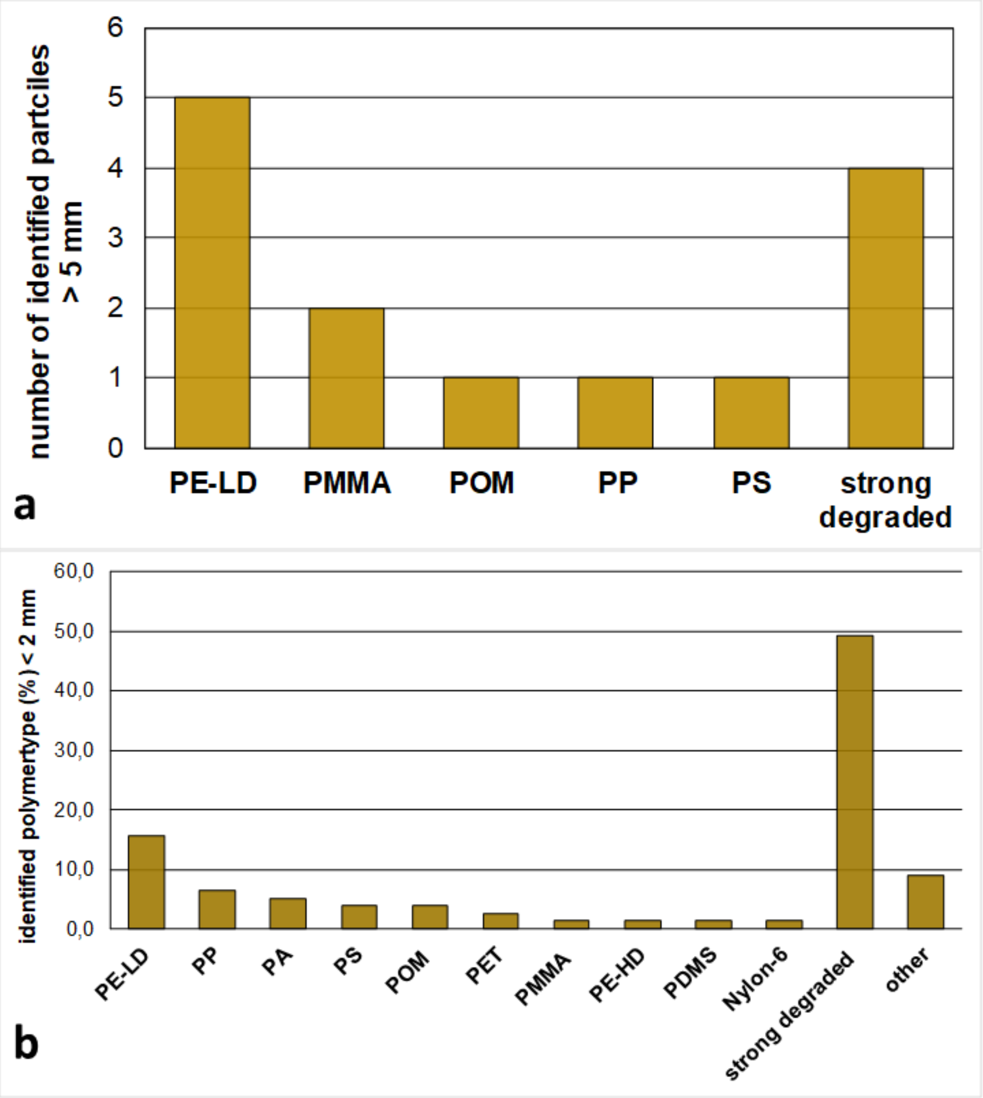

Figure 20: ATR-FTIR identified polymer types in floodplain soil samples. a) Absolute number of identified MAP particles. b) Polymer type percentage of identified CMP particles (n = 78).

3.2.3.2 Characteristics of plastic particles

The detected MEP and CMP occur in different forms. Examples for particle forms are given in supplementary material (Figure A 4). The predominant forms were fragments (32%) and films (32%), followed by filaments (19%; Figure 21a). A new class was built for “fiber balls” (11%) because fibers were often found in a tangle. This class contains fiber balls that consist of several fibers of the same color and shape, usually in a bunch or bound to a single soil macro aggregate.

Foamed or other particle forms occur least. In case of the particle shape, irregular (48%) and regular (32%) shapes are most common (Figure 21b). This seems to be contrary, but fragments and films occur in both shape forms. Other studies noted fibers (equivalent of filaments) as the most common shape form followed by fragments or films in the microplastic size class (Corradini et al. 2019; Liu et al. 2018; Zhang und Liu 2018). In contrast, MEP films and fragments represent the main share of particle shapes (Liu et al. 2018; Piehl et al. 2018). This comparison is limited by the fact that all mentioned studies investigates topsoils or plastic surface accumulations on agricultural land. For MEP and CMP in floodplain soils under agricultural use, films (46%), fragments (31%), and filaments (23%) arise as documented for MEP by other authors. Unlike this, soils under grassland use or in riparian sites fragments (32%) building the majority and filaments are just 17%. In addition, the condition of particles, forms, and shapes indicates primarily weathered (68%) or very degraded (5%) conditions (Figure 21c). This could indicate that the majority of particles have been in the environment for a longer time. Both chemical and physical degradation processes, like UV-radiation or mechanical crushing, could lead to the degradation of the particles over time (Song et al. 2015). Out of this indication, these particles could be named as old. Unweathered or fresh particles (25% in sum) indicate that fresh and/or young particles are also present. In comparison with land use, fresh and unweathered particles occur more often on cropland (38%) than on grasslands or riparian (22%). This may suggest a permanent input of fresh MEP and CMP through agricultural practices and a slow degradation (Corradini et al. 2019; Hurley und Nizzetto 2018; Napper und Thompson 2019).

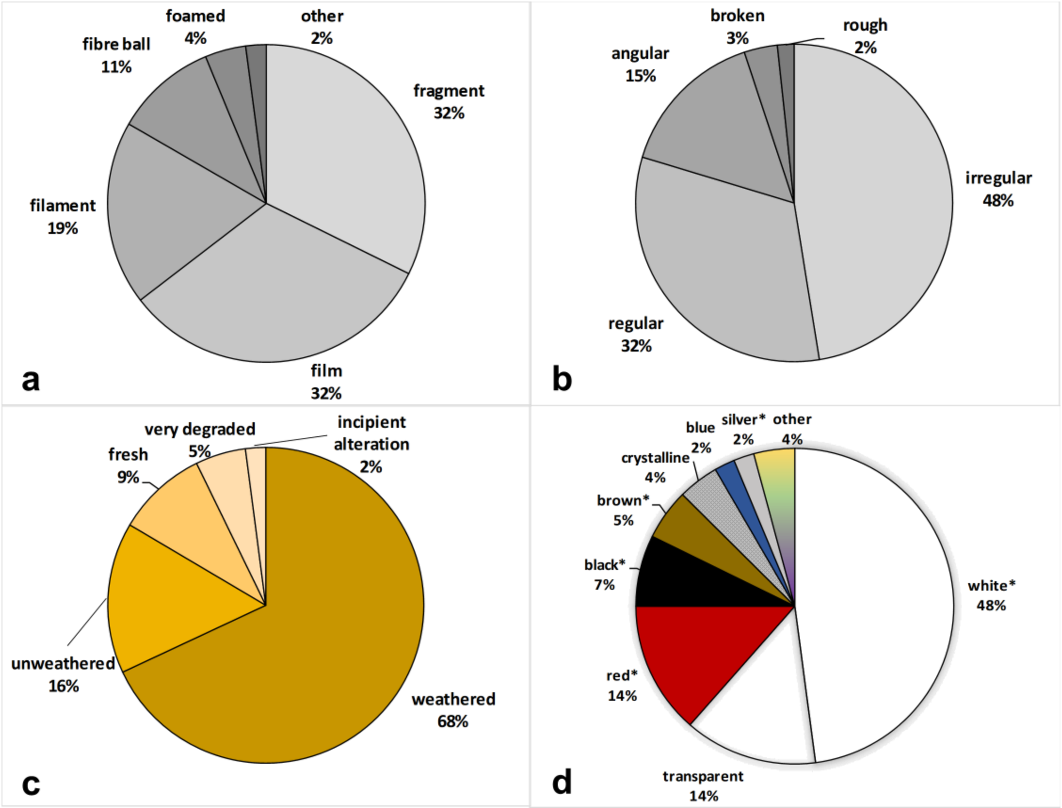

Figure 21: Shape and surface characteristics of MEP and CMP particles. a) General form of MEP and CMP particles according Hidalgo-Ruz et al. (2012). b) Shape form of MEP and CMP particles according Hidalgo-Ruz et al. (2012). c) State of shape, form and colour conservation according Hidalgo-Ruz et al. (2012). d) Surface colour of MEP and CMP particles.

A comparable finding shows the observation of the particle color. MMP and CMP occur first of all in white (48%), transparent (14%), and red color (14%), followed by minor represented colors (Figure 21d). The white and transparent color classes also include slight discoloration, often associated with yellowing or bleaching. As this result indicates, strong and fresh colors are minor, whereas bleached colors are widespread and indicate particle weathering (e.g., though UV-radiation; Song et al., 2015). Piehl et al. (2019) documented white and transparent colors as major shares for MEP on agricultural soil surfaces. Other studies note main shares of black or transparent colors in cropland topsoils comparable to the strings or shedding films from agricultural plastics (Liu et al. 2018). In the present study, no difference in particle color shares between land uses could be found. Therefore, the composition particle color share seems to be a question of MMP and CMP source, especially on agricultural soils.

3.2.3.3 Lateral particle distribution

The lateral spatial distribution of plastic in floodplain soils can be captured on two levels. Level 1 represents the floodplain catchment area, subdivided in up- and downstream areas, and level 2 represents a detailed differentiation of land use and flood dynamics on transect sides. With increasing flow length and catchment area size, the number of possible plastic sources (e.g., urban areas drainage, agricultural land use) increases (Ballent et al. 2016; Fischer et al. 2016; Klein et al. 2015; Tibbetts et al. 2018).

The presence of MEP and CMP at all floodplain transects indicates a widespread occurrence of plastics in soils. Sampling site ELM, representing the upstream course of the Lahn River catchment, shows an CMP average of 1.51 mg particles kg^{-1}, whereas site LIM located in the downstream course shows a higher CMP average of 2.66 mg particles kg^{-1}. In contrast, sampling sites ROT and STD, representative for the middle course, range between 1.22 and 1.36 particles kg^{-1} (CMP average). A continuous increase relative to the flow length cannot be observed. Nevertheless, significantly higher maximum values occur at the down- stream sites (STD: 2.57 particles kg^{-1} CMP; LIM: 6.06 particles kg^{-1} CMP). A higher abundance of MEP and CMP near urbanized areas or behind those in flow direction, found for different MP loads in river waters worldwide, could not be approved for floodplain deposits (Xiong et al. 2018). However, the increase in maximum values suggests that an increase in possible plastic sources leads to an increase in MEP and CMP concentrations, as demonstrated for Swiss floodplain soils by a correlation with population (Scheurer und Bigalke 2018). It can be concluded that the basic distribution of plastics in floodplains seems to be diffuse, based on the multitude of input paths (Blettler et al. 2017; He et al. 2021b; Karbalaei et al. 2018).

The spatial sampling approach in floodplains cross-sections allows a data evaluation on level 2: Considering flood dynamics as a possible transport mechanism of plastics in fluvial systems, each floodplain area could be divided into a proximal area (near to channel, high flood probability) and a distal area (distant to channel, lower flood probability) (Bridge 2003; Fryirs und Brierley 2013). Superordinately, 75% of MEP and CMP particles occur in near channel samples, whereas 25% occur in a larger distance to the channel (Figure 22b). As near channel sites including riparian strips (riparian vegetation) and grassland, both land use types contain 87% of MEP and CMP particles in sum (Figure 22a).

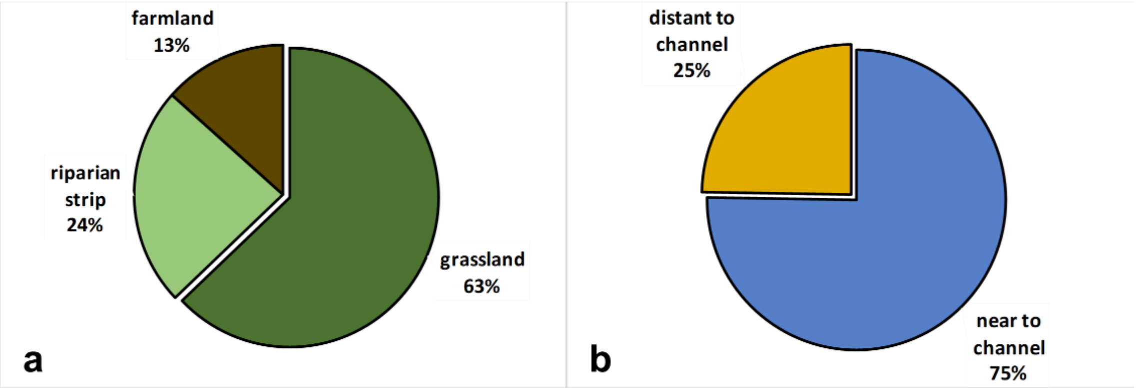

Figure 22: Lateral MEP and CMP distribution according to sampling sites in floodplain areas. a) According to land use (n = 26). b) According to channel distance (reported in Table 1) (n = 26).

The high loads of MEP and CMP in near channel sites could be explained by the frequent occurrence of flood dynamics at those floodplain parts and the facilitated deposition of plastics through higher vegetation roughness. Only 13% of the total MEP and CMP amount were detected on farmland sites, although this was the second-most frequent land use of sampling sites (Table 6).

Therefore, the agricultural land use and cultivation practices, often suggested as a major source of plastic contamination of soils, could not be seen as the primary source (Bläsing und Amelung 2018; Corradini et al. 2019; Piehl et al. 2018). However, MEP surface enrichments, like onsite STD-1, may be traced back to sewage sludge application or degradation of microplastic debris (Corradini et al. 2019; Piehl et al. 2018).

The identified lateral distribution pattern of plastics in floodplain soils leads to the conclusion that flood dynamics could build a link between the aquatic and terrestrial system. Plastic loads in river waters and sediments could be transported or deposited not only in riparian sediments but also in floodplain soils. MAP, MEP, and CMP deposition on soil surfaces was observed in the surroundings of all sampling sites after flood events (Figure A 6). The occurrence of MEP and CMP in distal floodplain areas and on farmlands indicates that several factors interact in the same area. Therefore, a bunch of potential plastic sources could play a role for plastic abundance. Because flood dynamics and deposition, cultivation practices, and the degradation of microplastic debris in direct surroundings could be considered key processes, a complex source pattern has to be assumed (Scheurer und Bigalke 2018; Wang et al. 2019; Zhang et al. 2020). This can include both point or diffuse sources and small-scale hotspots (e.g., waste debris) in aquatic and terrestrial systems. Future research should therefore increasingly differentiate the possible sources to develop strategies against a progressive increase of plastic contamination of soils and the environment.

3.2.3.4 Vertical dynamics of coarse microplastics

When studying microplastics or CMPs in soil, the vertical distribution is important because the majority of environmental processes in soils also cover deeper sections than the topsoil. Vertical displacements of MP in soils have already been demonstrated by Rillig et al. (2017a, 2017b) and Yu et al. (2019). Further displacement processes are therefore expected. As far as we know, no other study has dealt with samples from a depth greater than 25 cm (Weber et al. 2020).

In comparing MEP and CMP values in topsoil (0–30 cm) and subsoil (30–200 cm), the topsoils contain an average of 2.94 particles kg^{-1}, whereas the subsoils indicates lower average values (1.62 particles kg^{-1}; Figure 19b). A decrease in depth is also observed on agricultural soils (Liu et al. 2018; Zhang und Liu 2018). Liu et al. (2018) report an average number of mesoplastics between 6.75 particles kg^{-1} in shallow soil to 3.25 particles kg^{-1} in deep soils. However, Zhang and Liu (2018) studied agricultural soils, and Huerta Lwanga et al. (2017) studied garden soils, and neither declared significant difference between two soil layers because of cultivation practice. Unfortunately, a comparison is difficult, despite the few studies available, because only depths of 3–6 cm (Liu et al. 2018), 5–10 cm (Zhang und Liu 2018), and 10–20 cm (Huerta Lwanga et al. 2017) are regarded as deep-soil layers. The comparison is therefore insufficient because these depths are considered topsoils both on agricultural soils and under grassland. The vertical distribution of MEP and CMP is heterogeneously similar to the lateral distribution.

As an example, in profile LIM-1 (riparian zone), 10 CMPs occur in the upper 30 cm (0–10 cm: 4 CMP, 10–20 cm: 1 CMP, 20–30 cm: 5 CMP) and a single particle in a depth of 75–100 cm. The maximum depth at which CMP (single PA particle) was found is 75–100 cm below the surface at the above-mentioned sampling site LIM-1. A difference between visual- and polymer- type identified particles in the maximum depth could not be detected (Figure 23). The majority of particles found in subsoils is related to proximal floodplain (near channel) sampling sites (Figure 23). The vertical distribution of MEP and CMP particles for all sampling sites shows that the maximum reached was between 20 and 30 cm depth.

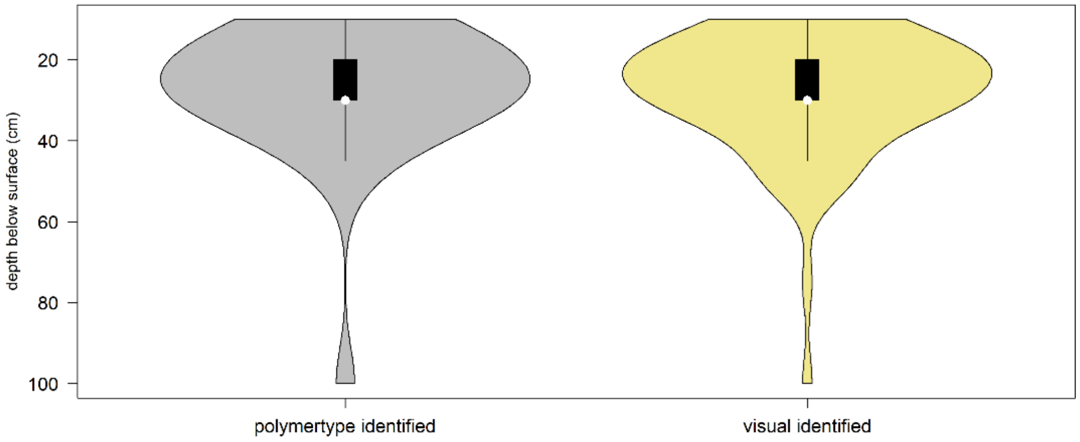

Figure 23: Depth distribution of MEP and CMP particles for polymer type identified particles (n = 53) and visual identified particles (n = 94).

Comparing depth distribution to land use classes, maximum depths are reached under grassland (60.0 cm) and riparian (87.5 cm; Figure 24). Under farmlands, the maximum depth of plastic abundance is strongly correlated with the frequent working depth of cultivation (approx. 30 cm). However, those differences in depth distribution compared with distance to channel are linked to the land use because farmlands are more frequent in the distal floodplain area. A vertical displacement of the CMP is conceivable only through a few processes, as in situ transfer is particle-size dependent (Blume et al., 2016). The clear depth limit under arable land use indicates that CMP does not penetrate through the frequent compaction under the cultivated topsoil (Blume et al. 2016). In addition to anthropogenic relocation (e.g. by ploughing), further deep displacements by preferential flow paths (e.g., coarse pores, earthworm tunnels) or bioturbation are conceivable (Lahive et al. 2019; Rillig et al. 2017b; Selonen et al. 2020; Yu et al. 2019).

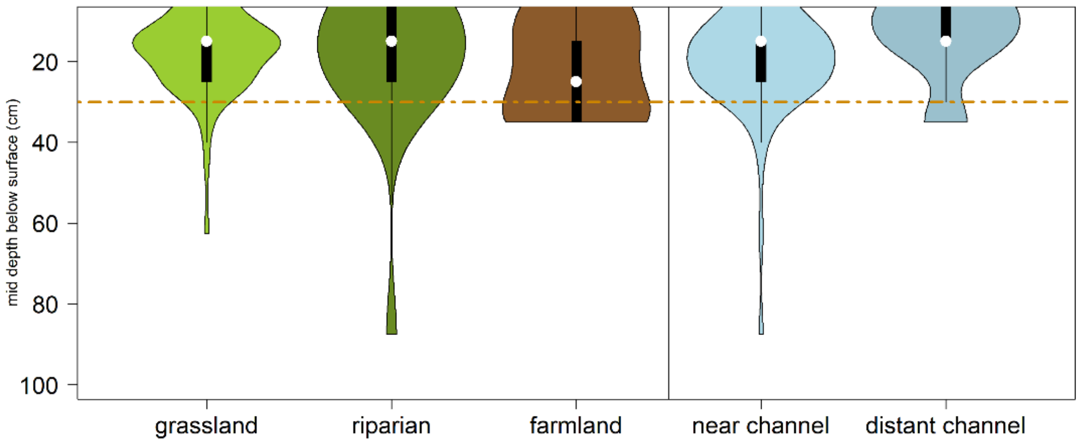

Figure 24: Depth distribution of visual identified MEP and CMP particles differentiated by land use and channel distance (both parameters reported in Table 1 for each sampling site). Grassland: n = 61, riparian: n = 23, farmland: n = 12, near channel (< 100 m): n = 72, distant channel (> 100 m): n = 24. Maximal soil cultivation depth (approx. -30cm) added with orange dotted line.

On the other hand, the high contents and maximum depth in riparian zones may indicate direct sedimentation or younger relocation of sediments containing plastics (e.g. bank erosion) (Klein et al. 2015). Comparing the real CMP depth distribution with the expected CMP depth distribution, calculated by earliest occurrence of identified plastic type and catchment sedimentation rate per year, CMP occurs at much greater depths than could be achieved by sedimentation processes alone (Figure 25). The average mid-depth where MEP was detected is 14.0 cm (22.4 cm for CMP). Based on sedimentation rates an average mid-depth of 5.2 cm for both MEP and CMP was calculated. Therefore, CMP occur 4.3 times deeper than assumed by sedimentation rates.

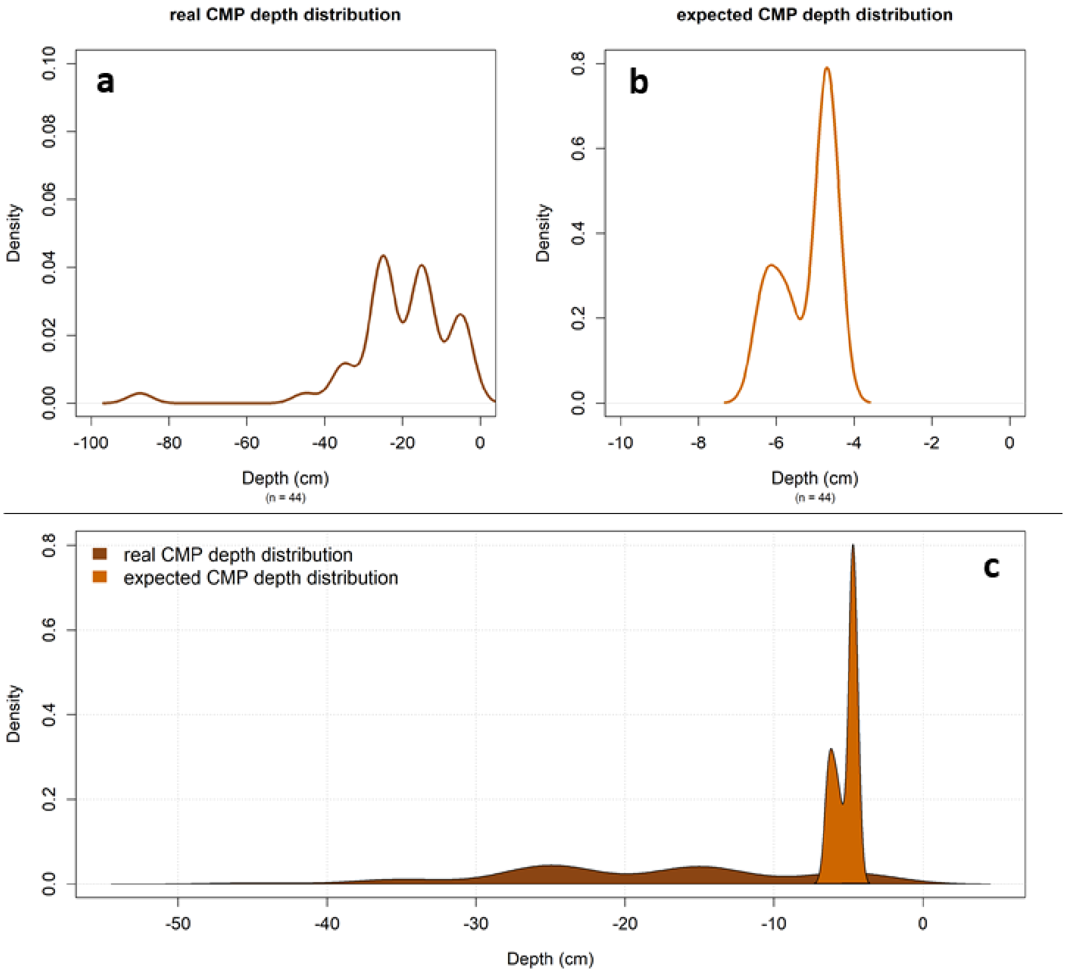

Figure 25: Depth distribution of CMP in a) real floodplain samples (n = 40) and b) expected depth distribution according plastic age and sedimentation rates (n = 40). c) Density plot of the value distribution for both, real and expected values, by depth.

As most identified particles have a date of earliest occurrence within the 1930se1950s, the calculated sedimentation rate can become even smaller because the increase in global plastic production started at the end of the 1950s (Andrady 2017; Heinrich-Böll-Stiftung und Bund für Umwelt und Naturschutz Deutschland (BUND) 2019). However, this result indicates that sedimentation could not be the main driver for MEP and CMP deposition in deep floodplain soils. To enable CMP to reach such depths, vertical transport processes must take place in the soil. While our results can provide indications merely through the vertical distribution, other authors have examined vertical displacements more closely. Rillig et al. (2017) have demonstrated vertical displacement by earthworms even for particles of a size from 2360 to 2800 µm (i.e., partly in the CMP size range). For microplastics with a size less than 2000 µm, which are not included in this study, an in situ vertical transfer through soil pore space should be easily conceivable (Engdahl 2018). Other authors suggest that sedimentation is also not a major source for MP and MEP loads in floodplain soils or riparian sediments based on correlation with grain size data (Scheurer und Bigalke 2018). However, this comparison is only possible to a limited extent, as the authors examined topsoils in the direct riparian zone which cannot be regarded as representative of the sedimentation dynamics in the entire floodplain.

However, the major concentration of MEP and CMP in upper soil layers at riparian zones and local meso- and macroplastic accumulations (Figure A 5a, Figure A 6a, and Figure A 6b) after floods indicate that this highly dynamic source cannot be excluded here. Flood events can deliver plastic of different sizes. Nevertheless, environmental degradation processes (e.g., chemical or physical alteration) and relocation processes seem to play a key role for the heterogenous distribution of plastic in the floodplain soils. In order to understand vertical processes and dynamics more clearly in future, in addition to the expanded use of laboratory experiments (e.g., column experiments), more field studies with a vertical context are recommended. High-resolution vertical sampling, in connection with the recording of soil parameters such as density, pore fraction or pore size, and also the dating of sediment layers could provide information about these in-situ processes.

3.2.3.5 Plastic contamination in floodplain soils

If microplastics are considered an environmental pollutant, then it must be assumed that, in contrast to other pollutants (e.g., heavy metals), no natural or geogenic background value exists. It must be anticipated, first, that plastics are purely anthropogenic substances that have been present in the environment for only a short period of time (Andrady 2017; Zalasiewicz et al. 2016). Second, the variety of occurring particle shapes, the type of plastics reinforced by the variety of additives, make a comprehensive pollution assessment complex (He et al. 2018b; Wang et al. 2020; Zhang et al. 2020). Several studies on the effects of plastics and microplastics in soils show that microplastics pose an emerging threat to soil biota and plants (Rillig et al. 2017a; Rillig et al. 2019; Xu et al. 2019). By plant uptake of micro- and nanoplastics, food production and human health could be affected (Rillig et al. 2017a; Rillig et al. 2019).

Overall, the abundance of MEP and CMP in floodplain soils of the Lahn River is significantly smaller than in contaminated soils, agricultural soils, river sediments, and river waters (Corradini et al. 2019; Fuller und Gautam 2016; Klein et al. 2015; Liu et al. 2018; Piehl et al. 2018; Zhang et al. 2019; Zhang und Liu 2018). However, the relatively small amount of MEP and CMP is in line with the findings from other soil-related studies, which state that the number of plastic particles in increasing with decreasing size (Corradini et al. 2019; Huerta Lwanga et al. 2017; Liu et al. 2018; Scheurer und Bigalke 2018; Zhang et al. 2019; Zhang und Liu 2018). This could also indicate that the contamination levels of the smaller microplastic particles (< 2000 µm) inside the floodplain soils of the Lahn River could be considerably higher. Assuming the spatial distribution that proves the occurrence of MEP and CMP partly independent of land use, with different emphases in the entire floodplain of a main river catchment area, a widespread contamination of soils is probable.

In addition, every larger particle will be reduced in size to microplastic and later nanoplastic after a certain time as a result of degradation processes in the environment (Chamas et al. 2020; Napper und Thompson 2019).

However, because this degradation is very slow and with modeled half-lives ranging from 250 years (HDPE bottle) to > 2500 years (PET bottle) in buried conditions, the plastic contamination could be present over a long period (Chamas et al. 2020). The long half-lives and slow degradation are contrary to the larger fraction of strongly weathered and therefore ATR-FTIR unidentified particles in this study. As the number of field studies considering plastics properties in soils (e.g., weathering status, surface degradation) is still very small, an evaluation of the modeled values from field samples is difficult (Andrady 2017; Xu et al. 2019). A faster degradation of particles through environmental factors, especially of the particles surfaces, which does not represent a half-life, therefore seems, in general, possible. Even if the absolute contents of CMP in this study appear small, they demonstrate that, despite the heterogeneous distribution, plastics (a) widely occur in floodplain soils, (b) occur at greater depths than previously assumed, and (c) have the potential to cause environmental degradation. Because floodplains are important ecosystems in the transition between terrestrial and fluvial systems, have an important role in food production and act as a connecting space between landscapes, further monitoring in a spatial context of plastic pollution is essential in the future.

3.2.4 Conclusion

The spatial-research approach enables statements about plastic occurrence and distribution in the three-dimensional system of the soilscapes. Using the example of floodplain soils, it could be demonstrated that plastic particles are heterogeneously distributed but still occur widespread in soils. Even if the comparison between recent studies is limited due to the different spatial conceptions, analytic methods and quantitative values used, we can conclude that the MEP and CMP concentration and particle features (e.g. shape, polymer type) are widely comparable to the findings in other studies. However, the spatial approach allows us to draw first conclusions about the processes which could be relevant for the spatial distribution discovered. From the lateral particle distribution, it can be concluded that a complex source pattern leads to the plastic pollution of floodplain soils. Together with the increase of maximum values with the flow length and the influence of floods as input path from the water bodies, an interaction between terrestrial and fluvial processes can be assumed. The heterogenous vertical MEP and CMP trends, with detections at greater depths than previously assumed, could indicate vertical in situ transfer. Additionally, the comparison with sedimentation rates shows that sedimentation processes alone could not be the major source of plastic pollution. In general, if comparatively large particles already cause widespread pollution in floodplain soils, the contamination through microplastics in soils could be immensely greater. Even if a sufficient data basis is missing so far, this would clearly challenge today’s management strategies for handling plastic contamination in soils. As complex sources seem to occur, further research should focus on the identification and quantification of potential sources of plastic contamination.

Additionally, the investigation of in situ processes (e.g., vertical transport, particularly for microplastics), risk assessments for plant uptake, and especially more data on spatial dependencies of plastic contamination can improve further management of plastic contamination in soils.

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3.3 Deposition and in-situ translocation of microplastics in floodplain soils

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Abstract

The microplastic (MP) contamination of oceans, freshwaters, and soils has become one of the major challenges within the Anthropocene. MP is transported in large quantities through river systems from land to sea and is deposited in river sediments and floodplains. As part of the river system, floodplains and their soils are known for their sink function with respect to sediments, nutrients, and pollutants. However, the questions remain: To what extend does this deposition occur in floodplain soils? Which spatial distribution of MP accumulations, resulting from possible environmental drivers, can be found? The present study analyzes the spatial distribution of large (L-MP, 2000–1000 µm) and medium (M-MP, 1000–500 µm) MP particles in floodplain soils of the Lahn River (Germany). Based on a geospatial sampling concept, the MP contents in floodplain soils are investigated down to a depth of 2 m through a combined method approach, including MP analyses, soil surveys, properties, and sediment dating. The analysis of the plastic particles was carried out by density separation, visual fluorescence identification, and ATR-FTIR analysis. In addition, grain-size analyses and 210Pb and 137Cs dating were performed to reconstruct the MP deposition conditions. The results prove a more frequent accumulation of MP in upper floodplain soils (0–50 cm) deposited by flood dynamics since the 1960s than in subsoils. The first MP detection to a depth of 2 m and below recent (>1960) sediment accumulation indicates in-situ vertical transfer of mobile MP particles through natural processes (e.g., preferential flow, bioturbation). Furthermore, the role of MP as a potential marker of the Anthropocene is assessed. This study advances our understanding of the deposition and relocation of MP at the aquatic-terrestrial interface.

Keywords

Plastics, Sedimentation, River, Soilscape, Density Separation, Sediment dating

3.3.1 Introduction

Global plastic pollution of marine, freshwater, and terrestrial ecosystems is a major challenge in the Anthropocene (Cole et al. 2011; Karbalaei et al. 2018; Zhang et al. 2020; De-la-Torre et al. 2021a). Plastics within the environment are often defined as man-made, polymeric or co-polymeric, and solid and insoluble materials that are produced (primary) or fragmented (secondary) to a defined particle size (Andrady 2017; Bancone et al. 2020; Hartmann et al. 2019). The particle size definition is not generally accepted but rather discussed within the scientific community. However, the following size classes and terms are frequently used: microplastics (MP), with a size between 1 and 5000 µm and in addition larger particles; mesoplastics (MEP, >5000 µm up to 25 mm); and smaller particles, nanoplastics (NP, <1 µm) (Andrady 2017; Hartmann et al. 2019). ISO/TR 21960:2020 defines macroplastics (>5 mm), large microplastics (5000–1000 µm), microplastics (1000–1 µm), and nanoplastics (<1 µm). The exponential growth of global plastic production since the 1950s (1950: 1.7 million tons (Mt)) resulted in an annual production of about 368 Mt. in 2019 and therefore a huge potential over 70 years for plastics entering the environment (Ellen MacArthur Foundation 2017; PlasticsEurope 2018, 2020). Plastics entering the environment are broken down over time by physical and chemical processes (Napper und Thompson 2019; Barnes et al. 2009; Chamas et al. 2020). Modeled half-life times for buried plastic particles can exceed 2500 years, showing a long residence time in the environment (Chamas et al. 2020). If, despite insufficient knowledge, we consider a global plastic cycle as comparable to a geological cycle, sooner or later all plastic residues end up in the oceans (Zalasiewicz et al. 2016).

Plastic pollution in the marine environment was the starting point of today's research on MP, beginning in the 1970s, and is one of the main focuses of the scientific community to date (Carpenter und Smith 1972; Hidalgo-Ruz et al. 2012; Wright et al. 2013). Regarding the question of possible sources of plastic accumulation in the oceans, it has been demonstrated that freshwater systems play an important role in the global plastic flow (Siegfried et al. 2017; Alimi et al. 2018; Lechthaler et al. 2020). For example, it was estimated that up to 91% of the global plastic waste entering the environment is transported by waterways (Lechthaler et al. 2020).

However, freshwater systems cannot be regarded as transport routes only. Going back to the idea of a global plastic cycle as pendant to geological cycles, temporary deposition of sediments in river systems is known (Stubbins et al. 2021). This deposition particularly concerns floodplains, which surround rivers in their morphological transfer zone. This area of river systems – with their soils build-up from fluvial deposits – is also known to be a temporary sink for sediments (Bridge 2003; Brierley und Fryirs 2007; Fryirs und Brierley 2013).

Floodplains are important ecosystems and natural habitats. They maintain important functions for water balance (flood retention, groundwater recharge) and connect a river and its catchment. They are also the drainage system of landscapes (Bridge 2003).

Floodplains join and follow the river through various landscapes, like geological bedrocks, and are known as important deposition and accumulation sites for fluvial sediments, nutrients, and pollutants (e.g., heavy metals) (Opp et al. 1993; Kalias et al. 2003; Houben 2012; Fryirs und Brierley 2013; Martin 2019). Furthermore, floodplains are a transition zone between fluvial and terrestrial environments, resulting in the formation of semiterrestrial floodplain soils. In addition, they have an important function for humans in several parts of the world in that they have suitable conditions for agricultural use and are often subject to intensive cultivation (Blettler et al. 2017; Scheurer und Bigalke 2018). The worldwide floodplain area consists only of 0.61% of the total terrestrial continental area (Nardi et al. 2019). In Germany, the floodplain areas of rivers with a catchment >1000 km2 account for around 4.4% of the national area (Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit 2009).

The number of studies on microplastics in floodplain soils is still very limited, with only three studies focusing on the quantification of MP. Scheurer and Bigalke (2018) showed, based on Swiss floodplain soils, that MPs are found in 90% of the investigated soils and that the number of MPs (0 to 55.5 mg kg^{-1}) is clearly related to the population density of the respective river catchment. Another study from 2020, using the example of the floodplains of the River Inde (North Rhine-Westphalia), observed that microplastic content increases with increasing flow length, particularly in sliding slopes of meandering bends that act as microplastic hotspots (Lechthaler et al. 2021). Furthermore, a first reconstruction of the flood- plain chronology based on MP was achieved within the study of Lechthaler et al. (2021). However, both studies focus on riparian soil areas and consider only depths of up to 5 cm (Scheurer und Bigalke 2018) or 110 cm (Lechthaler et al. 2021).

The previous study from Weber and Opp (2020) was the first to quantify mesoplastics (>5 mm, MEP) and coarse microplastics (>2 mm, CMP, overlap with large microplastics according ISO/TR 21960:2020) in floodplain soils in a more spatial, systematic manner than the previous "explorative" topsoil studies. Even if a further subdivision of the plastic size fractions is questionable in view of the large number of existing MP size definitions (Hartmann et al. 2019), the previously introduced CMP fraction corresponds to the differentiation between coarse and fine soils in soil science (Weber und Opp 2020). The concentrations found for those relatively large particles show average loads of 2.06 p kg^{-1} (±1.55 p kg^{-1}) for MEP and 1.88 p kg^{-1} (±1.49 p kg^{-1}) for CMP throughout the floodplain cross-section but are heterogeneously distributed in floodplain soils with regard to maximum contents, down to depths between 75 and 100 cm (Weber und Opp 2020). This first evidence of plastic particles in deeper soil layers has led to the assumption that vertical in-situ transfer – mainly through bioturbation because MEP and CMP particles can hardly be transported through pore space by their size – can take place in floodplain soils. Furthermore, the calculation and comparison of sedimentation rates indicate that sedimentation processes alone cannot be the major source of MEP and CMP contamination in floodplain subsoils (Weber und Opp 2020).

This is also illustrated by the findings of Kiss et al. (2021), which suggest various influencing factors of MP deposition and the complexity of related processes for river sediments within channels.

The present study explicitly focuses on the analysis of plastic particles extracted from the same soil samples used in the previous study of Weber and Opp (2020), but smaller particles to a lower limit of 500 µm (corresponding to large MP and MP in accordance with ISO/TR 21960:2020) were analyzed. The current state of research proves that plastics and MPs are present in floodplain soils and that these soils can be considered a potentially temporal sink for MP. However, input processes like the deposition by floods or direct anthropogenic sources (e.g., littering, agriculture), as well as the mobility of deposited MP, are still unclear. In addition, assumptions like the vertical in-situ transfer and plastic inputs from flooding and land use (Weber und Opp 2020) have to be verified for smaller MP particles. Given that plastics in soils are an increasing threat to terrestrial ecosystems, the open questions are of particular relevance. Previous studies suggest a wide range of impacts of MP on soil properties (physical and chemical), soil organisms, and plant growth (Huerta Lwanga et al. 2017; Souza Machado et al. 2018a; Rillig et al. 2017a; Hüffer et al. 2019; Zhang et al. 2019). Moreover, 95% of global food production is obtained directly or indirectly from soils (Food and Agriculture Organization of the United Nations (FAO) 2015). If soils are vulnerable to plastics, and if initial evidence shows that MP can also enter the food chain and the human body, the consequences for global food security and the ecological state of soils will be unacceptable for human societies in the Anthropocene (Lahive et al. 2019; Rillig et al. 2019; Selonen et al. 2020; Ragusa et al. 2021).

Based on the initial results of larger particles, this paper focuses on the quantification and spatial distribution of relatively large MP-particles within the size classes of large MP (L-MP, 2000–1000 µm) and medium MP (M-MP, 1000–500 µm) to examine and prove the assumptions from the previous study for smaller particles against the background of possible higher mobility in soils (Kooi und Koelmans 2019; Waldschläger und Schüttrumpf 2019a). The lower limit of 500 µm was set by the methodology used, and the middle limit of 1000 µm corresponds to a commonly used upper limit of microplastics in different studies (Hartmann et al. 2019; ISO/TR 21960:2020).

This paper therefore aims to improve the understanding of the deposition and potential in-situ transport of L-MP and M-MP in floodplains soils and through a combined method approach including MP analyses, soil properties, and sediment dating. Based on the former conclusions from Weber and Opp (2020) and the current status quo of research in fluvial systems, the following key issues are addressed:

(1) Which concentrations and spatial distribution of relatively large microplastics according L-MP and M-MP occur in floodplain soils of the Lahn River?

(2) Is it possible to trace lateral and vertical spatial distribution of both MP fractions back to specific environmental drivers against the background of an assumed higher mobility of smaller MP particles?

(3) Can vertical in-situ transfer processes and the sedimentation (fluvial deposition) of MP be proven through the combination with sediment dating?
(4) Can the conditions and processes of MP deposition in floodplain systems be reconstructed with the use of MP as a stratigraphic marker?

3.3.2 Materials and methods

3.3.2.1 Study area

A geospatial sampling approach was implemented within the floodplain area of the Lahn River (Hesse, Germany). The Lahn River, located in central Germany, has a total length of 245.6 km and a catchment area of 5924 km^2 (Regional Council Giessen 2015; Meschede und Warr 2019). Floodplain sediments and soils were formed by the deposition of flood-wave transported silts and loams, with typical higher organic matter content, during the late Holocene and latest Pleistocene above older Pleistocene gravel and sand deposits (Rittweger 2000; Bos und Urz 2003). The floodplain soils within the direct surrounding area of the Lahn River comprise a total area of 88.9 km^2 within the federal state of Hesse. Major soil types are Fluvisols (70.7 km^2), Gleyic Fluvisols (6.2 km^2), Fluvic Gleysols (2.7 km^2), and Stagnic Fluvisols (6.4 km^2) (Hessian Agency for Nature Conservation, Environment and Geology 2020). The investigated floodplain soils are partwise under agricultural usage (crop- or grassland), except for riparian strips and settlements. In general, the Lahn River catchment can be classified as rural, with only 8.4% of strong anthropogenic land use (urban, traffic, industry) and a population density of 266 inhabitants per km^2 (Regional Council Giessen 2015). Urban areas are restricted to four medium-sized cities along the river course (Martin 2012).

Like other regions in central Europe, the Lahn River valley is subject to frequent flood events, a high-flood event most recently occurring in 1984 (Gleim und Opp 2004). Following heavy-precipitation events, flood events dominate in the Lahn catchment area from November through March (Gleim und Opp 2004). Since the 1960s, for example, an average flood level of 504.3 cm (approx. 104.3 cm above bank full level) and flood discharges between 327 m^3/s (February 1994) and 223 m^3/s (January 2005) have been measured at the Marburg gauge (upper middle reach) (Gleim und Opp 2004; Hessian Agency for Nature Conservation, Environment and Geology 2021a). Floodplain areas that have not been dammed or newly created retention areas are flooded almost annually, while areas farther afield have been flooded, on average, every 5.5 years since 1960 (annual interval of the 10 highest discharges at the Marburg gauging station) (Hessian Agency for Nature Conservation, Environment and Geology 2021a). Therefore, an ongoing record of sediment deposition and local bank erosions through floods, even if spatially and temporally strongly varying, can also be observed in the present (Martin 2015, 2019), therefore including the potential delivery and deposition of microplastics from the fluvial system.

3.3.2.2 Geospatial sampling approach

In distinction to common “explorative” sampling approaches in microplastics research, the applied design is composed of a spatial systematic and representative sampling, which recognized different environmental processes and their natural drivers (Weihrauch 2019; Weber et al. 2020). A spatial representative floodplain cross-transect sampling and the consideration of full soil profiles down to a depth of 2 m in contrast to popular topsoil samplings was performed (Weber und Opp 2020). Representative floodplain cross-transects were selected by locating sites within regularly flooded areas, with no anthropogenic interruptions (e.g., dams) and at a distance from urban centers in different landscape settings of the Lahn Valley (Weber und Opp 2020). Because the soils in floodplain areas are the result of fluvial system dynamics (e.g., flood water, sedimentation, erosion) and anthropogenic impacts within a “human-natural entanglement” (Edgeworth 2011), which act on a local and a landscape level, this approach tries to integrate both spatial dimensions. This assumes that floodplain soils have to be understood as part of a landscape in which environmental processes take place and thus are part of a “soilscape” (Willgoose 2018). To record and study the environmental processes and drivers responsible for the distribution and spread of microplastic in floodplain soils, it is necessary to consider a larger part of the landscape. In the case of the study area, and with regard to (micro-)plastic contamination, various processes such as flooding, erosion, or land use are important because they could have an influence on the deposition, accumulation, and mobility of plastic particles in the soils itself. To understand these processes, not only on a soil profile itself but also in the spatial context of the flood- plain landscape and its soilscape, a geospatial approach was applied to identify suitable and representative sampling sites.

The evaluation of the lateral distribution of microplastics in floodplain soils can be conducted at two spatial scales: Level one follows a longitudinal gradient on the catchment scale (metric measure: river-km), and level two follows the floodplain cross-sections (transect sites) from proximal to distal floodplain areas (metric measure: distance from active river channel). After a geospatial selection process, including a previously conducted soil survey that was presented in Weber and Opp (2020), four transect sites within the floodplain landscape (level 1) were selected whereby each site is representative for a specific river section with similar properties in terms of soil formation, morphology, flood dynamics, and land use: site ELM represented upper reaches within Rhenish Slate Mountains, smaller floodplain areas with young and sandy floodplain soils and high surface dynamics; site ROT (upper middle reaches) and site STD (middle reaches) represented middle reaches with wide floodplain valleys, thick loam deposits, and flat floodplains with edge depressions; and site LIM represented the lower reaches after a narrow valley section with individual valley widenings, flood loam deposits, and flat floodplains (Figure 26, Figure A 8, Figure A 9, Figure 13) (Weber und Opp 2020).

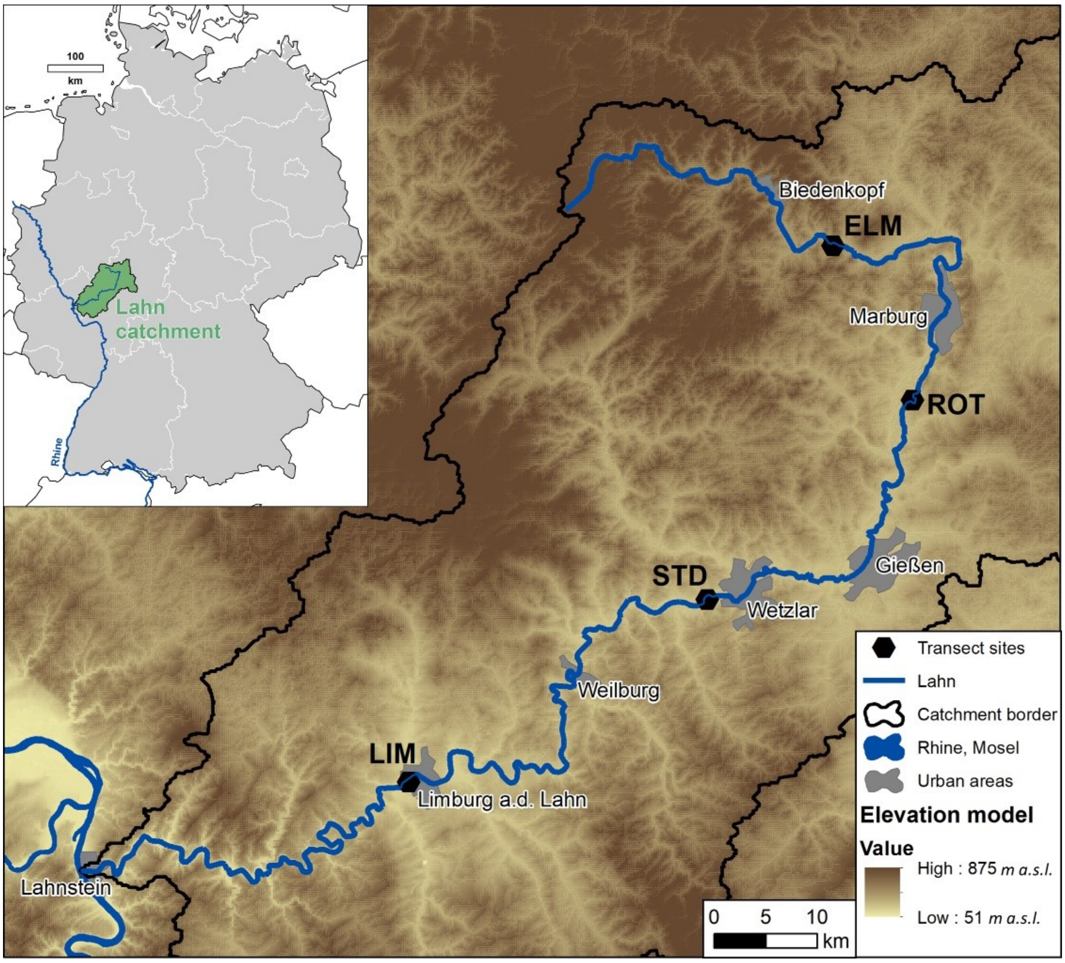


Figure 26: Top left: General map showing the location of the Lahn catchment in Germany. Right: Elevation map showing the course of the Lahn with urban centres and the selected transect sites. Data basis: NUTS 2021 (© EuroGeographics for the administrative boundaries), WISE Large rivers (© European Environmental Agency), Digital terrain model 200 (©GeoBasis-DE/BKG 2021). Detailed maps of transect sites and elevation profiles can be found in Figure A 8 and Figure A 9.

At each transect, two sampling plots (ELM, ROT) or four sampling plots (STD, LIM) including two soil profiles (drill cores) per plot were established between the river bank and the floodplain edge (level 2) (Figure 26, Figure A 8, Figure A 9). The sampling plots should thereby represent the floodplain cross-section with its typical but often diverse morphological forms (natural levee, flood channel, flats, back swamp). Even if surface altitude changes at each transect ranging within ±0.5 m, each transect site consists of interruptions by flood channels, small dirt roads, or ditches (Figure A 8, Figure A 9). The terrain between the sampling plots slopes on average by 0.5 m from the natural levee (higher) to the floodplain edge (lower and partly with back swamp) (Table A 3). Only at transect LIM, the outermost plot is already on the lower slope, which, however, is still in the flooding area. Therefore, the transect sites showing an aggrading near-bank zone and a convex floodplain develop with lower lying distal zones, where the gradient is interrupted by channels or anthropogenic interventions.

Two soil profiles with a distance of 10 m were drilled to a depth of 2 m via pile core driving (stainless steel, Ø 100 mm and 80 mm) and sampled according the following depth sections:

10 cm sections for 0–0.5 m, 25 cm sections for 0.5–1.5 m, and 50 cm sections for 1.5–2.0 m. Soil material from both cores was pooled, resulting in an average dry sample mass of 1150 g (111 samples) (Figure A 10). Pooled samples were transported in cornstarch bioplastic bags (Mater-Bi bags, Bio Futura B.V., Rotterdam, Netherlands). The comparatively large number of samples is because of previous studies, which showed very heterogeneous occurrences of microplastics in soils (Liu et al. 2018; Scheurer und Bigalke 2018; Corradini et al. 2019). Because no plastic tools were used, no blank control was performed in the field, even if minor contamination with clothing fibers cannot be ruled out.

Soil samples for dating were taken at the transect sites ELM (upper course, core ELM-D) and LIM (lower course, core LIM-D) behind the natural levee (each next to the points ELM-1 or LIM-1), under grassland (ELM-D), or natural riparian vegetation (copses, herbs) at LIM-D (Figure 13). For this purpose, a drill core (Ø 80 mm, 1 m depth) was drilled and then carefully excavated to obtain a drill core free of disturbances as far as possible. The core was subsequently divided into 2 cm sections, which were extracted in the field and transported in PE-bags. In this way, 42 samples from core ELM-D (0–84 cm soil depth) and 45 samples from core LIM-D (0–90 cm soil depth) were obtained.

Stratigraphy and pedogenesis of each soil profile were documented according the German soil classification (Ad-hoc AG Boden 2005), the FAO Guidelines for soil description (FAO 2006), and the WRB 2015 (IUSS Working Group 2015). Soil properties (horizon sequences) and soil type according to WRB are documented in Table A 1 (Appendix).

3.3.2.3 Sample preparation, soil analysis, and dating

Sample preparation followed Weber and Opp (2020), who analyzed plastic particles within the coarse soil fraction (>2 mm) from the same samples. Sample preprocessing was carried out without using plastic tools or materials (including cotton lab coats) by reducing the exposition time for each sample as much as possible to avoid air contaminations and a control of three cellulose filters (LLG-Labware, Meckenheim, Germany), which were openly displayed in the laboratory during preparation. No fibers could be detected visually using a stereomicroscope. Field fresh soil samples were transported in cornstarch bags, dried (45°C for 4 days), carefully mortared to solve soil macroaggregates, and afterwards dry-sieved. Sieving was conducted with stainless-steel sieves (Retsch, Haan, Germany) covered by stainless-steel plates according to the size classes of MEP (>5000 µm), CMP (>2000 µm), and MP (<2000 µm). To homogenize the sample and simultaneously obtain a representative subsample (max. 12.5% of total sample volume) for standard soil analyses, the sample was divided by means of a rotary sampler (Retsch, Haan, Germany). Each size fraction and subsample were afterwards weighed and stored in fresh cornstarch bags. Standard soil analyses included the determination of organic matter (OM) and texture analyses. The content of OM was measured by loss of ignition (DIN ISO 19684-3:2000–08). Soil texture was determined for each sample with the Integral Suspension Pressure Method (Durner et al. 2017) after samples had been prepared according to DIN ISO 11277:2002–08.

Soil samples for dating purposes were transported in PE-bags, weighed field-fresh, and then dried at 50°C in a drying chamber for 4 days. Afterwards, they were ground and sieved to 2 mm through stainless-steel sieves. The coarse soil (>2 mm) and the fine soil fractions (<2 mm) were dry-weighed. A subsample (approx. 27 g) was placed in 50 mL PE-containers and sent to the laboratory for further analyses. Soil moisture, coarse soil fraction, and soil density were calculated.

Samples for dating purposes were analyzed at the Gamma Dating Center, Department of Geosciences and Natural Resource Management, University of Copenhagen for measurements of the activity of ^{210}Pb and ^{137}Cs via gamma spectrometry. The measurements were carried out on a Canberra ultralow-background Ge-detector. ^{210}Pb was measured via its gamma-peak at 46.5 keV, ^{226}Ra via the granddaughter ^{214}Pb (peaks at 295 and 352 keV), and ^{137}Cs via its peak at 661 keV. The chronologies were calculated using a constant rate of supply (CRS) model in which the activity in the lower portion of the cores was calculated on the basis of a regression of the activity of unsupported ^{210}Pb versus cumulated mass depth (Appleby 2001; Andersen 2017).

3.3.2.4 Microplastic analysis

The presented analyses of microplastic particles within floodplain soils consisted of a three-step procedure: (1) separation, (2) staining, and (3) identification. Because soil is an environmental medium containing different materials or substances, the major components, namely, (a) mineral component; (b) organic component, which must be separated from the target; and (c) microplastics (Hurley und Nizzetto 2018; Möller et al. 2020; Ruggero et al. 2020; Thomas et al. 2020).

Separation of mineral components was performed by the commercially available “MicroPlastic Sediment Separator” (MPSS) (Hydro-Bios Apparatebau GmbH, Kiel-Altenholz, Germany). One special feature of the MPSS is its large size, which allows for large sample volumes per run but which also requires long separation times (here: 15 h). Within this study, it was therefore possible to analyze the whole sample volume, deducting the subsample for standard analyses, which ranges from 376.0 to 3478.3 g (mean: 1305.2 g) or from 250 to 2200 mL dry soil sieved <2 mm (Figure A 10). Based on the principle of density separation, organic sample components and the searched plastic can rise because of their similar material density within the separation unit, while mineral components remain at the bottom (Imhof et al. 2012). Recovery rates of the MPSS are estimated to be 100% for large MP (1–5 mm) and 95% for smaller MP (1000–40 µm) (Imhof et al. 2012). Potential plastic contaminants (e.g., airborne) were controlled by blank samples, which are empty runs (Stock et al. 2019). In a total of five blanks (during 41 MPSS runs with a maximum of three instruments), 5 potential plastic particles (fragments and a single filament with a length of 1254.5 µm) with a mean size of 112.98 µm were found. Because of their size (smaller than 300 µm), identification of their polymer type was not feasible with the available ATR-FTIR spectrometer.

The MPSS unit was filled with a previously sieved (300 µm) sodium chloride (NaCl) solution, which had been adjusted to a density of approximately 1.2 g ml^{-1}.

Solution density was double checked before and after the separation process via pipetting and weighing, as well as through an aerometer (1.900 bis 2.000 g cm3, Greiner-Glasinstrumente, Lemgo, Germany) (Fig. S4). With a revolving rotor, sample material was added, and the MPSS unit was closed (dividing chamber). The rotor was left running for a total of 60 min and the separation process for another 14 h. After a total separation time of exactly 15 h, the integrated ball value was closed, and the dividing chamber removed to rinse the separated material into glass beakers using filtered NaCl solution. The remaining sample material (complete sample set) was then separated into the following size classes using stainless-steel sieves (Ø 75 mm, Atechnik, Leinburg, Germany) and filtered (mesh size: 50 µm) deionized water: >1000 µm (L- MP) and >500 µm (M-MP). After sieving, residues were filtered on pleated cellulose filters (LLG-Labware, Meckenheim, Germany).

To separate the remaining sample of organic material and potential plastic particles in L-MP and M-MP fractions, a Nile Red staining procedure and visual fluorescence setup were applied (Maes et al. 2017; Konde et al. 2020). The following procedure enables a distinction between organic material and suspected microplastics in a faster and easier working step because decomposition was not feasible as a result of the content of large plant matter. Following the suggestions of Konde et al. (2020), a Nile Red solution with a concentration of 20 µg ml^{-1} Nile Red (Sigma-Aldrich, Taufkirchen, Germany) solved in an ethanol-acetone (1:1) mixture was dropped on each filter using a pipette and subsequently was sprayed on (using a spray bottle). The initial dropping prevents the loss of particles because of the subsequent spraying with uniform coverage of all particles on the filter. Filters were stained for 10 min at 50°C within a drying chamber before visual analysis (Konde et al. 2020). Stained filters were afterwards visually investigated under a stereomicroscope (SMZ 161 TL, Motic, Hong Kong) with a self-built fluorescence setup (Excitation: 465 nm LED; Emissions 530 nm color long pass filter: Thorlabs, Bergkirchen, Germany) (Konde et al. 2020). Filters were observed systematically to observe the entire filter surface under fluorescent and white light (Figure 10, Figure A 11). Each fluorescent particle and other potential plastic particles (matching the criteria according to Norén, 2007) were collected and stored in microplates (Brand, Wertheim, Germany). Potential plastic particles were classified according to visual surface characteristics (particle type, surface form and surface degradation according Hidalgo-Ruz et al., 2012), photographed (Moticam 2, Motic, Hong Kong), and measured the largest diameter (Motic Images Plus 3.0, Motic, Hong Kong).

To verify the plastic origin, because staining methods are not free from impairments (Maes et al. 2017), and to identify the polymer type, each suspected plastic particle was analyzed with a Tensor 37 FTIR spectrometer (Bruker Optics, Ettlingen, Germany) combined with a Platinum-ATR-unit (Bruker Optics, Ettlingen, Germany).

In some cases, adherent soil or organic material was removed with stainless-steel tweezers. The Platinum-ATR-unit was cleaned with 2-propanol ($CH_3CHOHCH_3$) between each measurement. Measurements were performed with 20 background scans followed by 20 sample scans per sample. Spectral resolution was set to 4 cm^{-1} in a wavenumber range from 4000 cm^{-1} to 400 cm^{-1} (Primpke et al. 2017; Primpke et al. 2018).

3.3.2.5 Limitations

Despite the continuous development of analytical methods for microplastics in soils, no standardized method has been established to date (Bläsing und Amelung 2018; Möller et al. 2020). The present work focuses on the combination and adaptation of methodological approaches already presented. First, in the case of density separation within the MPSS, the recovery rates were reported to be >95% for particles down to 40 µm in size by the developers (Imhof et al. 2012). However, the construction and size of the device involves considerable time and expense, which is only profitable when larger sample volumes are used (Coppock et al., 2017). In contrast to other concentrated salt solutions (e.g., $ZnCl_2$), the flotation medium that was used (NaCl) is cost-effective and environmentally friendly (Coppock et al. 2017). A limitation arises from the fact that only plastic particles with a density of <1.2 g ml^{-1} can be separated. Common polymer types such as polyethylene terephthalate (PET) or polyvinyl chloride (PVC) may not be separated. Second, although the Nile Red staining procedure shows recovery rates up to 96.6% from spiked marine sediments in combination with density separation, this method is not free from impairments (Maes et al. 2017). In contrast to other methods such as the oxidation of organic matter (e.g., by acid digestion), Nile Red staining offers a completely particle-preserving approach. However, depending on the surface of organic material, but especially on calcium-containing shells (e.g., isolated freshwater mussels in alluvial sediments), Nile Red can also bind these non-plastic organics and thus affect the visual distinction between plastics and non-plastics (Konde et al. 2020). From 225 selected particles during the Nile Red staining, 46 particles were too small or degraded for ATR-FTIR analysis (<300 µm, adherent to organic components); and of 179 spectroscopically measured particles, 21 particles (11.73%) were classified as natural (non-plastic) material. Therefore, Nile Red staining had a false positive rate of approximate 12.0%.

Finally, 158 particles were identified as MP. This limitation of staining natural organics should be lifted by (a) systematic examination of the sample under fluorescent and white light, and (b) a subsequent identification of the particles using analytical methods such as ATR-FTIR to prevent overestimation. Because the application of an FTIR spectrometer with ATR unit (like Tensor 37, Bruker Optics, Ettlingen, Germany) is carried out by hand only, particles smaller than 500 µm or <300 µm should not be investigated because they are difficult to handle and often provide insufficient contact area with the ATR crystal. Within this study, we were able to achieve a satisfactory (r^2 >0.7) match for 11 particles below 500 µm, but had still to exclude 46 particles (Figure A 12).

Furthermore, in the case of heavily degraded and weathered particles, there may be no match with different spectral databases because the quality of the spectra is insufficient (Primpke et al. 2018).

Finally, potential contaminations during field and laboratory work must be considered limitations, despite various measures to prevent them (e.g., avoiding plastic tools, blank controls, liquid filtration). The above mean concentration of contaminants in blank samples is 1 particle per sample, which means that the results partwise overlap with the laboratory error. However, it was also found that the contaminants with a size between 53.3 µm and 159.4 µm were significantly below the particle size considered here (smallest identified particle with a size of 219.35 µm). Therefore, we conclude that contamination, although not definitely excludable, appears negligible for the plastic particles considered with regard to their size range.

3.3.2.6 Data and statistical analysis

Data processing of FTIR spectra, including atmospheric compensation and baseline correction (concave rubber band method), was performed in OPUS 7.0 (Bruker Optics, Ettlingen, Germany) and Spectragryph (Version 1.2.14; Menges, 2020; Oberstdorf, Germany). Spectra identification and polymer type assignment was carried out according to a previously defined scheme (Figure A 12). Because the available OPUS database (OPUS 7.0 internal database) contained insufficient entries of plastic products (only industrial polymers) and no entries of natural materials, the following procedure was performed with each spectrum: Particles with an identification hit quality higher than 700 within OPUS 7.0 (OPUS band-based standard algorithm) were counted as identified polymer type or group. In the case of particles with an identification hit quality between 700 and 300, the absorption bands were manually checked for polymer identification according to the criteria of Jung et al. (2018). Spectra of particles with a hit quality less than 300, as a limit for satisfactory identification (Primpke et al. 2017; Primpke et al. 2018; Lorenzo-Navarro et al. 2018), were compared with spectra databases for natural materials provided by Spectragryph (Kimmel_Center: Collection of 363 FTIR absorbance of natural and biogenic material of archaeological interest; provided by S. Weiner from Kimmel Center for Archaeological Science, Weizmann Institute of Science, Israel). In the case of no match, the spectra were finally matched with the database of "Open Specy" (Cowger et al. 2020). With the help of this database a satisfactory match (spectral correlation r^2 >0.7) with plastic or natural material was always achieved. In case of a match with natural material, potential plastic particles were counted as natural material and excluded from further analyses. Finally, the amount of MP was calculated from 158 clearly identified particles. The contents are given in particles per kg (dry soil weight) mp kg^{-1} or in sub-concentrations per size class as L-MP kg^{-1} for large microplastics (1000–5000 µm) or M-MP kg^{-1} for medium microplastics (<1000 µm).

Basic statistical operations were performed in Microsoft Excel 2013 (Microsoft; Redmond, WA, USA), in R (R Core Team 2020), and in RStudio (Version 3.4.1; RStudio Inc.; Boston, MA, USA).

Data visualization, tests for normal distribution (Shapiro-Wilk), linear regression analyses, Pearson or Spearman correlation analyses, and variance analyses (ANOVA) were conducted with the standard R-packages and "graphics," "stats," "vioplot," "ggplot2," "ggridges", and "scatterplot3d." We interpreted statistical analysis results as significant with a p-value < 0.05.

3.3.3 Results and discussion

3.3.3.1 Microplastics and their characteristics in floodplain soils

In total, 79 of 111 soil samples contained plastics (71.2%). One hundred and fifty-eight particles could clearly be identified as plastic, found at depths down to 2 m. The identified particles result in average plastic concentrations of 2.75 MP kg^{-1} (number of particles in particle size class per soil dry weight), composed from 1.32 L-MP kg^{-1} and 1.43 M-MP kg^{-1} (Figure 27a). With the exception of the plastic-free samples (28.8%), the values vary between 0.36 up to 30.46 MP kg^{-1}. In comparison to other studies, which also analyzed smaller MP particles, the concentrations found here are clearly below those in agricultural topsoil. For example, the average of 70.0 ± 12.91 MP kg^{-1} (5.0–0.02 mm plastics) reported by Liu et al. (2018) and the amounts of 0.6–10.4 MP g^{-1} (<2.0 mm plastics) found by Corradini et al. (2019) are clearly above the levels found here. Furthermore, the plastic average abundance of 18,760 MP kg^{-1} (10.0–0.5 mm plastic) reported by Zhang and Liu et al. (2018) exceeds the contents determined in this study several times.

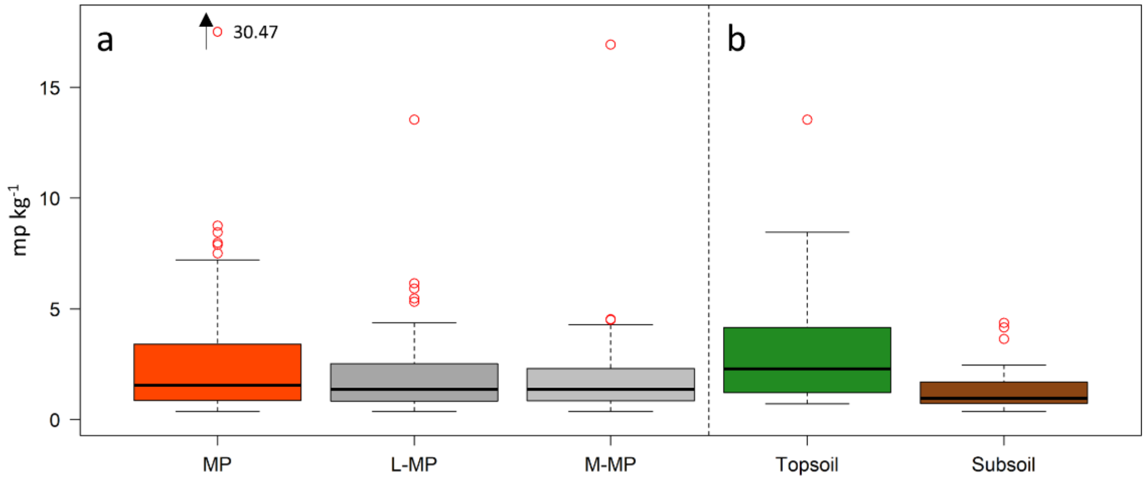


Figure 27: Overview of microplastic concentrations in floodplain soils of the Lahn River. (a) Concentrations of total microplastics (2000–291.4 µm, MP, n = 158 particles), large microplastics (2000–1000 µm, L-MP, n = 89 particles), and medium microplastics (1000–291.4 µm, M-MP, n = 69 particles) given in particles (mp) per kg (soil dry-weight). Arrow indicating outlier outside the range. (b) Concentrations of total microplastics (2000–500 µm, MP, n = 158 particles) within topsoils (related soil A-horizon, depth: 5 to max. 30 cm) and subsoils given in particles (p) per kg soil dry weight.

A sufficient comparison with the first study on microplastics in floodplain topsoils, reported for Swiss nature reserves by Scheurer and Bigalke (2018), is not feasible because of the different unit (mg kg^{-1}).

In the case of the investigation of bank profiles and topsoils of the Inde River (North Rhine-Westphalia) by Lechthaler et al. (2021), their corrected average concentrations with 47.9 MP kg^{-1} (depth profiles) and 25.4 MP kg^{-1} (surface samples) for microplastics with a size between 500 and 5000 µm also exceed those reported here.

Same as the results for larger plastic particles (MEP, CMP) (Weber und Opp 2020) and similar to the work of Lechthaler et al. (2021), the contents in topsoil (0–30 cm) are clearly above those in subsoil (30–200 cm) (Figure 27b). Average values of 3.33 MP kg^{-1} in topsoils and 1.34 MP kg^{-1} in subsoils are significantly different (p-value = 0.0002).

The size of the identified particles detected in the 500 µm and 1000 µm sieve ranges from 219 µm to 8321 µm, with an average of 1171 µm (n = 158). 10.1% of all ATR-FTIR-identified particles were smaller than lower sieve mesh size of 500 µm, but measurable (Figure 28). The majority of particles had a size between the minimum value and 2000 µm and was found in the upper 50 cm of soil column, including fragments, films, and some filaments. Of the identified particles, 24.1% had a size larger than the coarse microplastic and mesoplastic border and are mesoplastics, despite the previous sieving procedure. Because the longest diagonal of the particles was consistently measured, the width of these particles can be less than 2000 µm. This is also clear from the fact that only filaments (measurement of filament length) occur in the size range above 5000 µm.

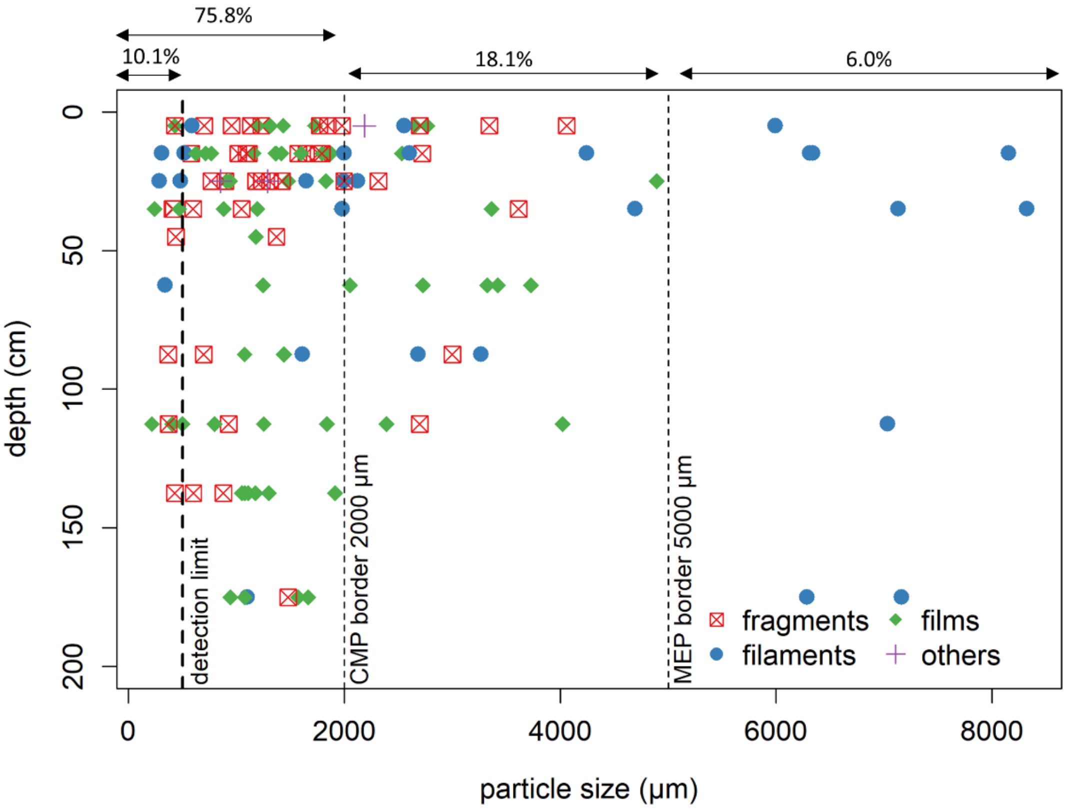


Figure 28: Depth distribution of plastic particles (n = 158) differentiated by size and shape, including the common size borders for ATR detection (500 µm), coarse microplastics (CMP, >2000 µm), and mesoplastics (MEP, 5000–8000 µm).

Regarding the particle morphology, major particle types are films (42.3%), fragments (31.5%), and filaments (24.2%) with usually irregular or degraded shapes, except in the case of filaments, which show regular surfaces (Figure 29, Figure A 13). This result clearly corresponds to the findings within the Inde River catchment (Lechthaler et al. 2021). More than half of all particles detected show a weathered (59.7%) or incipient alteration (11.4%) surface according to visual criteria, whereas fresh surfaces occur in 22.8% of all particles (Figure 29d).

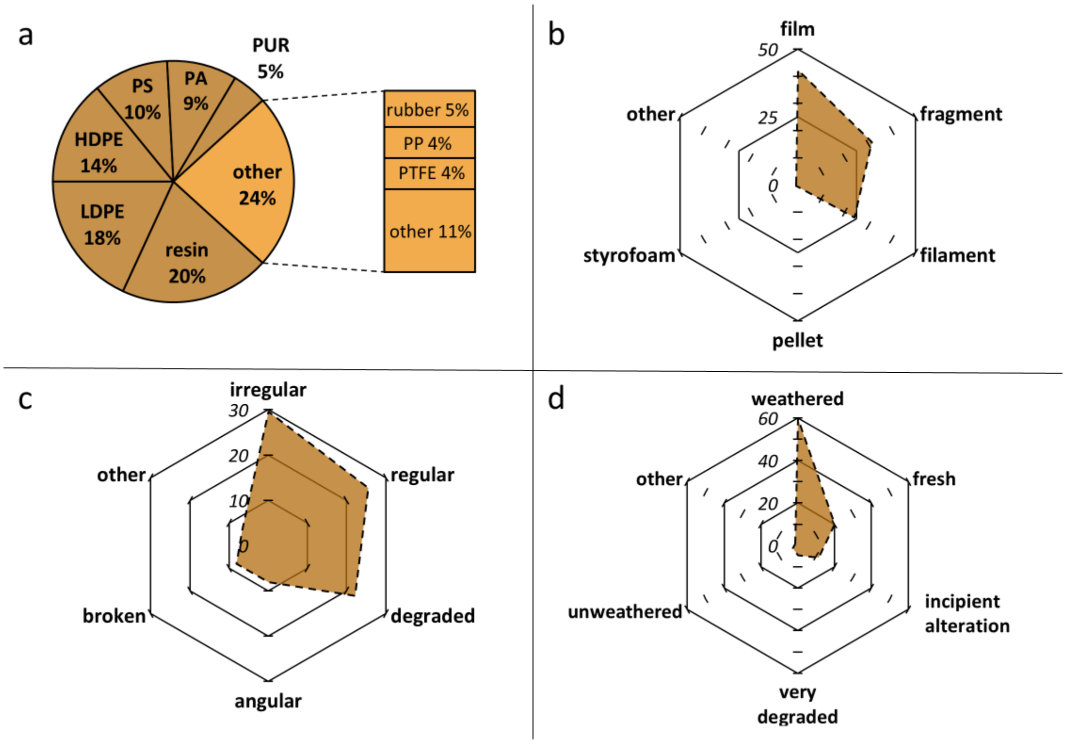


Figure 29: Microplastic particle characteristics (n = 158). (a) Identified polymer types through ATR-FTIR analyses (class "other" includes polymers such as PET, CSM, ABS). (b) Percentage share of particle shapes. (c) Percentage share of surface forms. (d) Percentage share of degradation state.

Typical polymer types like low-density polyethylene (LDPE) or high-density polyethylene (HDPE), polystyrene (PS, unexpanded), and polyamides (PA) could be identified by ATR-FTIR analysis. The results correspond to the most frequently produced and used plastics in Europe (PlasticsEurope 2018). One surprising finding was the high proportion (20.1%) of resins (synthetic or polymer resins, grouped as resins) in contrast to other current studies on microplastic in soils (Liu et al. 2018; Piehl et al. 2018; Scheurer und Bigalke 2018; Zhang und Liu 2018; Corradini et al. 2019; Lechthaler et al. 2021). The particles classified as "resins" could be reliably identified only by the OpenSpecy database. The resin entries contained in the database are from Primpke et al. (2018) and include epoxides, polyurethane acrylic, phenoxy, and polyamide resins, which explains the frequent assignment in OPUS 7.0 to PA (with low hit quality). In principle having resins as the largest group of plastic types could be plausible because these are used in many applications (e.g., as paintings or coatings) on plastic objects. However, it is not possible to infer the exact chemical substance from the result of the class "resin" obtained by OpenSpecy, for which a manual spectrum interpretation would be necessary.

3.3.3.2 Lateral microplastic distribution

Figure 30a shows the range of total MP concentrations at each transect from the upstream (ELM, river km: 202) to the downstream site (LIM, river km: 57). Average values are significant different between site ELM and ROT, as well as ROT and STD. Median values including plastic-free samples are 0.75 MP kg^{-1} (ELM), 0.20 MP kg^{-1} (ROT), 0.76 MP kg^{-1} (STD), and 0.40 MP kg^{-1} (LIM). The simple assumption of an increasing accumulation of microplastics in floodplains with increasing flow length of the river, caused by an increasing number of potential plastic sources and available water quantity and sediments, cannot be upheld unequivocally (Scheurer und Bigalke 2018; Xiong et al. 2018; Liu et al. 2019). Moreover, local phenomena (e.g., floodplain surface morphology, vegetation or anthropogenic impacts like impoundment), instead of a superordinate accumulation, probably cause a heterogeneous distribution.

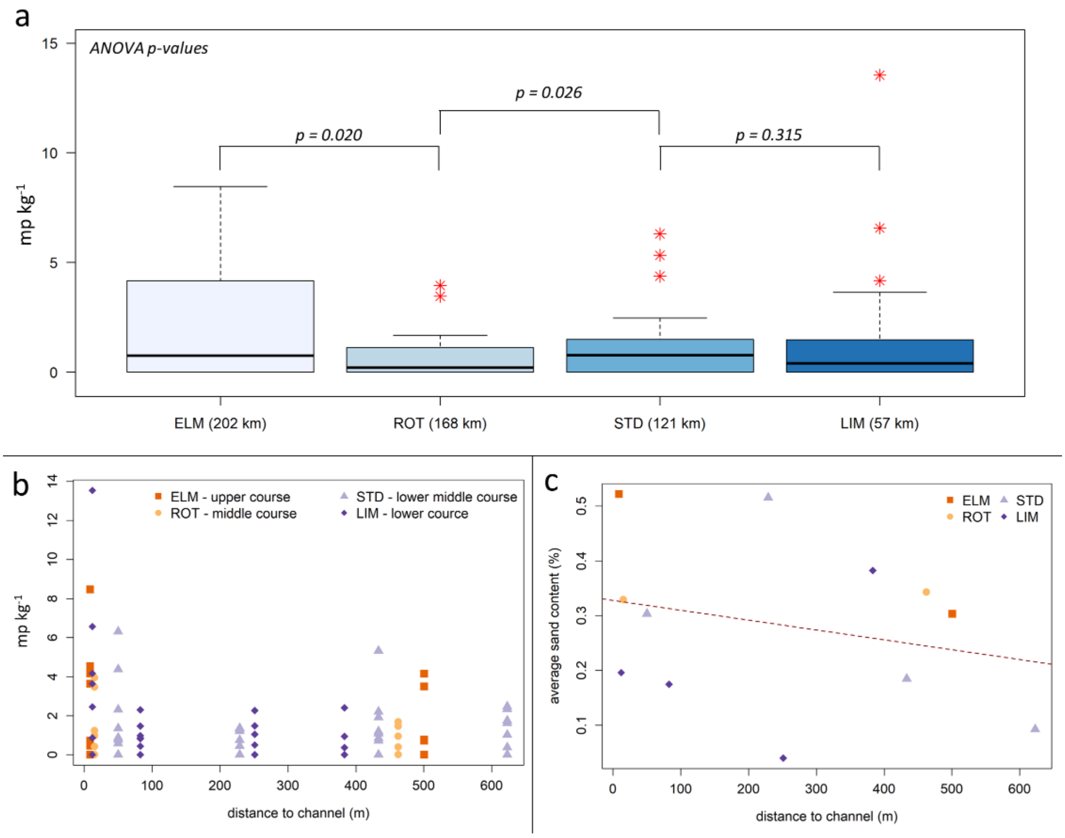


Figure 30: Lateral microplastic distribution on the catchment scale by sampling site (total number of samples = 111; ELM and ROT with only two sampling points per cross-section). (a) Total MP concentrations (mp kg^{-1}); red asterisks represent outliers. (b) Total MP concentrations (mp kg−1) versus distance to channel (m) at each sampling point. (c) Average sand content (%) down to 50 cm depth versus distance to channel (m) of the four sampling sites (n = 12).

Regarding the MP distribution along transects, maximum concentrations occur next to the river bank and within a short distance from the river (Figure 30b). Furthermore, the plastic concentration reaches a plateau around the mean value of 2.14 MP kg^{-1}, with a slight increase at a distance of 400 to 500 m from the river bank.

With reference to the grain size differentiation in floodplain areas, from coarse-grained (sandy) sediment depositions in the near-channel area to fine-grained (clayey) depositions in the floodplain margins, caused by the decreasing flow velocity during floods, one could assume that also higher plastic contents occur in the margins, since the lowest flow velocities prevail there (Bridge 2003; Brierley und Fryirs 2007). However, the highest plastic contents do not occur in the marginal zone but near the river (Figure 30b). Figure 30c illustrates the average sand concentration within the upper 50 cm soil at each sampling point. With the exception of the ROT transect, the sand content of all transects decreases with distance from the river. Outliers in the STD and LIM transects are due to the location of the points in a flow channel (STD-2, younger sandy flow channel deposits) and the deposition of colluvic material through slope erosion at the floodplain edge of the LIM transect (LIM-4). The highest MP contents are reached where the sand contents at transect level are also highest (near water bodies like river banks). Even though the sedimentation and erosion properties of plastic particles differ from those of the sediment (Waldschläger und Schüttrumpf 2019b), the question arises as to how this spatial distribution pattern is formed. In the area close to the watercourse (proximal floodplain), where increased deposition of sands take place, flow velocities should be significantly higher during floods as in the floodplain edge area (distal floodplain), where the reduced velocities (caused by higher terrain roughness) result in the de- position of finer sediments (clay and silt fraction) (Bridge 2003; Fryirs und Brierley 2013). The deposition of plastic particles also requires a reduced flow velocity because of their low density and other properties such as shape or degradation (Tibbetts et al. 2018; van Melkebeke et al. 2020). An explanation could be that more plastic particles are deposited in areas with increased accumulation of younger sediments (more frequent flood activity and higher sediment accumulation near the channel). Land use and associated surface roughness (vegetation) as causes for higher concentrations near the channel can also not be excluded (Klein et al. 2015; Tibbetts et al. 2018).

In general, the differences in MP concentrations between land use classes and associated vegetation (natural riparian vegetation, cropland, grassland) are significant between natural riparian vegetation and cropland or grassland (p-value: <0.01) but insignificant between grassland and cropland (p-value: 0.95) (Figure 31a). The riparian class with a median of 2.45 MP kg^{-1} is therefore clearly above the concentrations of cropland (median 0.37 MP kg^{-1}) and grassland (median 0.48 MP kg^{-1}), which can be attributed to the increased concentrations in the area near the river banks (especially site LIM-1). Comparable to the results for larger plastic particles (MEP, CMP) (Weber und Opp 2020), an accumulation of higher microplastic concentrations in the investigated particle size range of down to 500 µm does not seem to occur in the area of intensive agricultural use (cropland).

Although agriculture cannot be dismissed as a potential source of microplastics (e.g., from sources such as sewage sludge, compost, fertilizers, hay bale nets) (Corradini et al. 2019; Braun et al. 2021), the spatial position within the floodplain and the surface roughness caused by vegetation and land use (e.g., woods and dense herbs at natural riparian zones) appear to be more important factors to explain the lateral distribution of L-MP and M-MP particles.

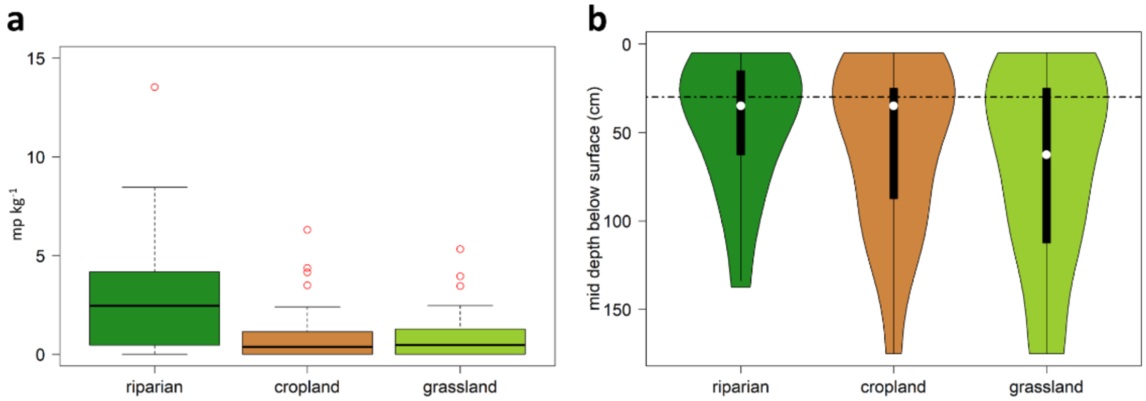


Figure 31: Microplastic distribution under different land use classes. (a) Total microplastic concentration (mp kg^{-1}) by land use class (riparian = 17 samples, cropland = 34 samples, grassland = 60 samples). (b) Depth distribution (vioplot: boxplot with kernel density, white dot: median, black bar: interquartile range) of plastic concentrations (mean sample depth in cm) with medium tillage depth (plough tillage, for recent and relict soil horizons) by dotted line.

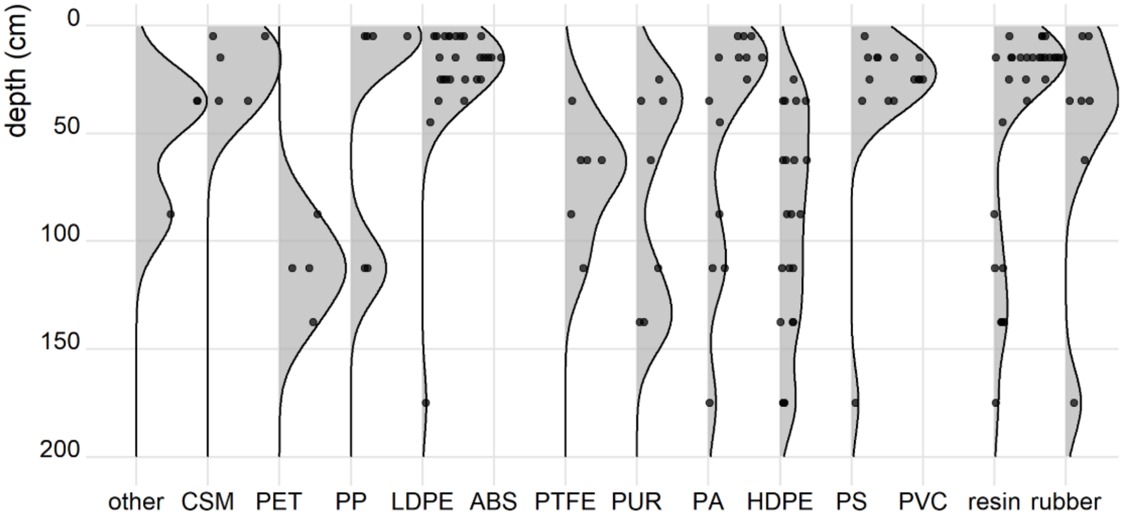
3.3.3.3 Vertical microplastic dynamics

With the exception of the study by Lechthaler et al. (2021), microplastics have never been searched for at soil depths up to 2 m. If the depth of the floodplain soils is differentiated according to soil horizons, the higher contents are clearly located in the topsoil horizons (A horizons) with average values of 3.33 MP kg^{-1} higher than in the subsoil horizons (e.g., B horizons) with 1.34 MP kg^{-1} (Figure 27b, Table A 1). Independent of the soil stratigraphy, the upper 50 cm (corresponding to 5 samples from one drill core) of the floodplain soils contain 67.65% of the identifiable plastic, whereas the depth range 50 to 200 cm (also 5 samples from one drill core) contains only 32.35% (Figure 28). With the exception of filaments, only particles with a size <2000 µm were found in depths greater than 125 cm. The median particle size within the upper 50 cm is 1421.5 µm with major particle types of fragments, films, and filaments, whereas within the lower 150 cm the median particle size is slightly smaller with 1301.0 µm (films and fragments, less filaments). This finding indicates, that smaller particles could be more mobile within the soil column reaching greater depths through possible displacement pathways (e.g., pore space, preferential flow pathways) (Weber und Opp 2020).

Comparing the depth distribution in different land use types (Figure 31b), concentrations are similar, even if in the natural riparian area depths >150 cm are only reached in a few single cases. Median depth distribution is 35 cm for riparian and cropland and 62.5 cm for grassland. The vertical distribution at the sampling site level is independent of this. The greatest depths (150–200 cm) are reached at ROT (proximal floodplain) and STD (proximal and distal floodplain) sites.

The two deepest depths (125–150 cm) are at sites LIM (proximal floodplain) and ROT (proximal floodplain). Particles therefore reach depths of up to 2 m, regardless of the distance to the watercourse, the soil type, or land use. Significant correlations, neither superordinate nor site-specific between depth distribution and soil parameters (e.g., grain size, bulk density, OM, root distribution), could not be found (examples given Figure A 14). This and the occurrence of plastic-free samples, by unidentified particles but also by no particles found, indicate a clearly heterogeneous depth distribution starting at 50 cm depth, whereas a more homogeneous distribution occurred in the upper soil areas (0–50 cm). Similar findings in a different environmental setting have already been found for sandy sediment deposits on beaches (Brazilian coast), confirming the assumption that in the case of a heterogeneous depth distribution, larger sample volumes, and a larger number of samples are necessary (Turra et al. 2014; Martinelli Filho und Monteiro 2019).

Heterogeneity also applies to the vertical distribution of polymer types and associated age of earliest possible occurrence (EPO age). Vertical structuring of floodplain soils is most commonly related to depositional history of sediments, which is related to sedimentation rates (Bridge 2003). Floodplain chronology can be assessed by different methods, as well as by plastics themselves: Because the global plastic production started its exponential growth in the 1950s, plastics within floodplain soils could act as a new marker of floodplain chronology (Lechthaler et al. 2021). For each identified polymer type, the EPO age can be added, based on the production starting year or year of patent registration (Weber und Opp 2020; Lechthaler et al. 2021). Based on the EPO age, each polymer of this study can be used as a specific marker for the time between 1910 and 1990. As indicated in Figure 32, it becomes clear that the empirical depth distribution of different polymer types is not equal over the depth. Seventyone percent of identified polymers including resins, LDPE, PS, and PA show a peak within the upper 50 cm of floodplain soils. Only HDPE, the third most frequent polymer, shows an equal distribution over depth. Assuming that polymers that have been released into the environment for a long time (e.g., rubber, resin, PVC with EPO ages <1912) are found more frequently at deeper layers than "younger" polymers (EPO age >1950), this should be reflected in the vertical distribution (Figure 32). In fact, this is only achieved for very young polymers such as chlorosulfonated polyethylene (CSM, EPO age: 1990s). All other polymers do not show a clear superordinate separation but also a heterogeneous distribution over the depth. However, it must be considered that, based on the applied method, polymers with a density >1.2 g cm^3 are strongly underrepresented. Therefore, polymer types with a density >1.2 g cm^3 can only be determined semi-quantitatively. Nevertheless, because this is a systematic error, comparability of the depths remains possible for all considered polymers.



	other	CSM	PET	PP	LDPE	ABS	PTFE	PUR	PA	HDPE	PS	PVC	resin	rubber
Count[a]	*3*	*6*	*4*	*7*	*28*	*2*	*6*	*7*	*15*	*23*	*15*	*2*	*32*	*8*
Age[b]		1990	1973	1954	1952	1948	1941	1937	1935	1935	1931	1912	1910	1820
upper soil 0-50 cm	1.1%	2.1%	0.0%	4.2%	27.4%	1.1%	1.1%	3.2%	10.5%	5.3%	14.7%	1.1%	24.2%	4.2%
subsoil 50-200 cm	2.3%	0.0%	7.0%	4.7%	2.3%	2.3%	7.0%	9.3%	7.0%	37.2%	0.0%	0.0%	16.3%	4.7%

[a] Count of particles from the total number of 158 identified particles

[b] Age of earliest occurence (production / patent/ adopted from information in https://www.bpf.co.uk/Plastipedia/Plastics_History/Default.aspx

Figure 32: Depth distribution (density plot with joint density estimation, data points represent polymer count and are randomly shifted) of different identified polymer types and occurrence of different polymer types (sorted by age: production start or patent submission) in upper and lower soil areas. Polymer type abbreviations are explained in Table A2.

Nevertheless, bearing the given limitations in mind, a vertical separation into two parts can be observed: (a) The upper floodplain soil section (approx. 0–50 cm) with a clear MP accumulation, the occurrence of mixed polymer type composition (old and young), but also the exclusive occurrence of very young polymers (CSM); and on the other hand (b) the lower soil section (approx. 50–200 cm) with partwise MP occurrence, individual hotspots and increased occurrence of older polymer types.

3.3.3.4 Reconstruction of microplastic deposition and translocation

Information on lateral and vertical MP distribution within floodplains soils in combination with derived EPO age and other soil parameters allows a first assessment of the deposition conditions of microplastics in floodplains based on a geospatial sampling approach. Summarizing the spatial distribution, it can be stated that an increased MP concentration occurs in the area of the proximal floodplain (i.e., the upper 50 cm of the floodplain soil; Figure 32). Areal regression shows a clear decrease in MP content with increasing depth and a decrease with distance from the watercourse (distal floodplain), although individual hotspots occur near the surface.

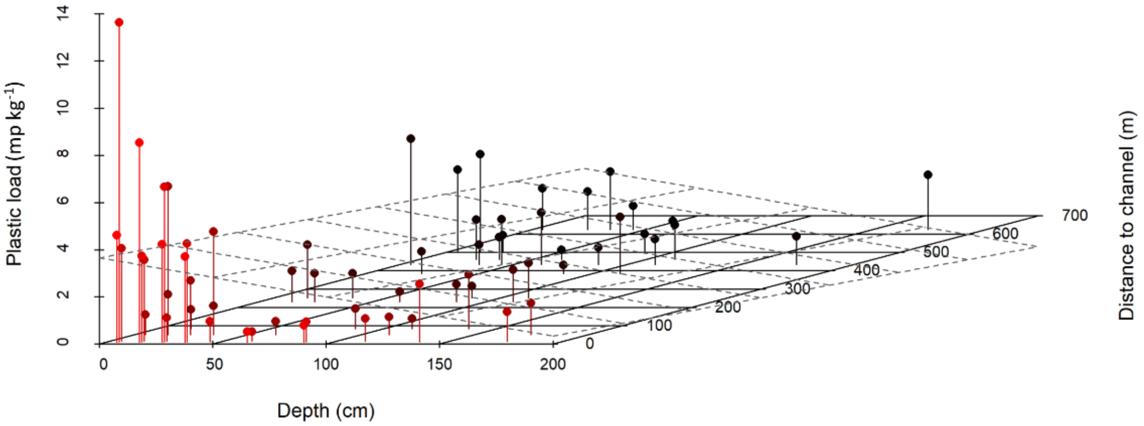


Figure 33: Spatial representation of total microplastic loads (MP kg^{-1}) by depth (cm) and distance from the channel (m). Grey area (dotted lines): Regression area of combined concentrations. Colour scale of pins ranging from red (proximal floodplain) to black (distal floodplain) based on distance to channel (m).

The areal regression (Figure 33) indicates a dependence of MP loads on the metric factors (a) depth in the soil profile and (b) distance to the water-course. Because no dependence on other soil or anthropogenic parameters (e.g., bulk density, land use, proximity to transport routes) could be proven, the MP input seems to be mainly attributable to floods as a transport medium because they reach proximal areas more frequently than distal ones. To examine this relationship, the question arises concerning the exact age of the sediments, especially the enrichment layer (0–50 cm). From both dating cores (ELM-D: upper course, LIM-D: lower course), located at the proximity of the channel, it was possible to achieve sufficient results through the ^{210}Pb and ^{137}Cs dating. In case of the radionuclide ^{210}Pb, both cores show a steady concentration increase the closer to the soil surface (Figure A 15). ELM- D shows an average ^{210}Pb concentration of 40.76 Bq kg^{-1} (0–90 cm) with a maximum concentration of 62.36 Bq kg^{-1} in the section 0–2 cm and an in- crease within the upper 20 cm of sampling core. Comparable concentrations are also found in the LIM-D core with an average ^{210}Pb concentration of 53.33 Bq kg^{-1} (0–90 cm) and maximum concentration of 82.93 Bq kg^{-1} in the section 4–6 cm. The analyses of ^{137}Cs concentrations enable the identification of concentration increases or peaks related to the atomic bomb tests of the 1950s to 1960s (increase or peak in 1963) and the entry due to the Chernobyl nuclear disaster in 1986 (peak) (Andersen, 2017). A significant increase in ^{137}Cs concentrations can be observed for core ELM-D from 55 cm depth (first peak: 47 cm with 9.11 Bq kg^{-1}, second peak: 17 cm with 22.50 Bq kg^{-1}) and for core LIM- D from 51 cm depth (first increase: 43 cm with 14.23 Bq kg^{-1}, peak: 31 cm with 24.91 Bq kg^{-1}) (Figure 34a). Based on the dating results, it can be concluded that near channel floodplain sediments were deposited within the 1960s at depths between 40 and 50 cm (Fig. 9b). Calculated sedimentation rates related to the period between 1986 and 2020 (34 years) show an average sedimentation rate of 0.5 cm/year for the upper reaches of the Lahn River (ELM-D) and 0.91 cm/year for the lower reaches (LIM-D), significantly higher than the catchment area rates (Lang und Nolte 1999; Rittweger 2000; Martin 2015; Weber und Opp 2020).

Finally, it can be concluded that the sediment age reaching the 1960s at a depth of 50 cm corresponds clearly with the beginning increase of MP concentrations for near-channel zones (Figure 34c). This finding is limited to the proximal floodplain zones because an additional dating of distal sediments was not possible in this study.

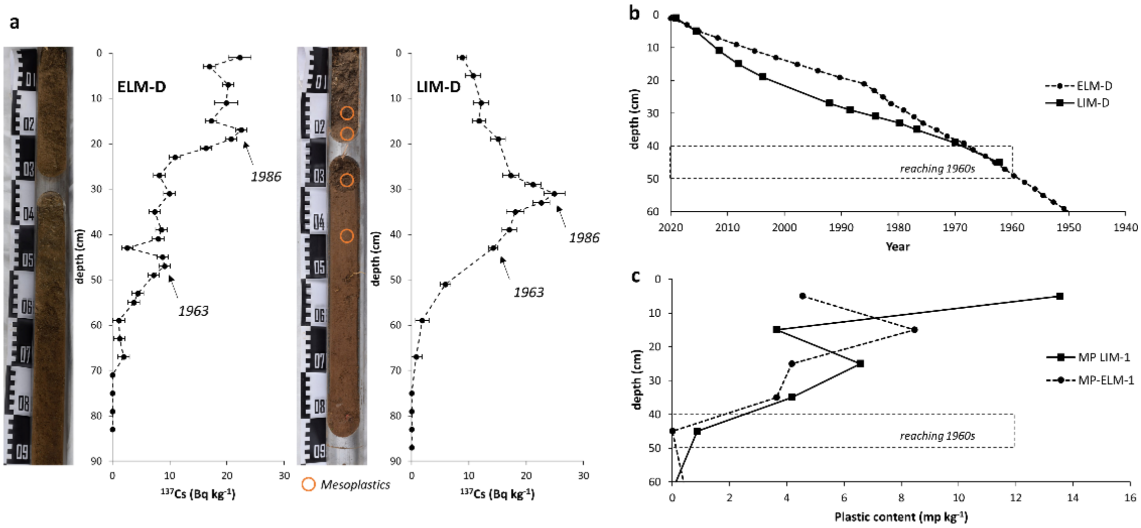


Figure 34: Sediment dating results. (a) ^{137}Cs (Bq kg^{-1}) concentrations for dating cores ELM-D and LIM-D with mesoplastics occurrence within core LIM-D (further information on soil density and ^{210}PB content is given in Fig. S10). (b) Calculated sediment ages (years) related to sediment depth (cm) for dating cores ELM-D and LIM-D. (c) Plastic content (MP kg^{-1}) related to sampling depth for sampling sites ELM-1 and LIM-1 (upper 60 cm, plastic content below ranging from ELM-1: 0.72 MP kg^{-1}, LIM-1: 0.85 to 2.45 MP kg^{-1}) corresponding to dating cores.

Combining the findings of lateral and vertical MP distribution with the dating results, it becomes even clearer that MPs are deposited in floodplain soils through sedimentation, with the increase in global production in the 1950s (exponential growth) (Andrady 2017; PlasticsEurope 2018, 2020). Because plastics were only used on a small scale before the 1950s, based on the dating results, the underlying plastic particles (>50 cm) cannot have reached these depths by natural deposition but only by in-situ transport (e.g., preferential flow, bioturbation) (van Schaik et al. 2014; Rillig et al. 2017b; Yu et al. 2019).

Finally, it can be concluded that the MP deposition and translocation in floodplain soils can be qualitatively analyzed by our integrated approach. MP particles can reach the floodplain area through different input pathways, whereas the flood water delivery seems to play a major role in the case of smaller particles than MEP and CMP. Accumulation of MP within young sediments (since 1960s) at near channel sections (proximal floodplain) indicates floods as a key environmental driver of MP deposition. Proximal floodplain areas are reached regularly by floods and showing an intensively sediment deposition in contrast to lower lying distal zones (Huggett. Richard 2007; Martin 2012). Sediment deposition at proximal floodplain zones can be observed (Figure A 8, Figure A 9). The lower and more heterogeneous occurrences of plastic in the remaining part of the floodplain also indicate transport by floodwater because only flood water reaches the floodplain at times over a wide area (Bridge 2003).

Beside this plastic accumulation in upper soil areas, vertical relocation processes must occur within the soil (Weber und Opp 2020). Only in-situ relocations can explain the MP occurrences down to depths of 150 to 200 cm (sediments older than increase in global plastic production). Although displacement through the pore space of the soil is conceivable, the grain size analyzed in this study show the widespread presence of loams (average contents: 19.64% clay, 48.03% silt, 32.22% sand) with a medium pore volume, and a displacement of comparatively large particles can take place only through macropores (van Schaik et al. 2014). Further possible processes that could be involved in a relocation and that are limited by the size of the particles (average of 1171.04 µm) can be flow paths (preferential) or disturbances of the soil structure (corridors, bioturbation) (Rillig et al. 2017b; Hüffer et al. 2019; Yu et al. 2019; Hartmann et al. 2020).

In conclusion, MP (a) accumulates in floodplain soils on the one hand and (b) is probably translocated on the other. There is also a distinction between a more immobile MP fraction and more mobile MP fraction (particles < 2000 µm), which can reach the deeper soil layers.

3.3.4 Conclusions

The spatial evidence of MP in floodplain soils and thus within the semi-terrestrial system (aquatic-terrestrial interface) and its sediments illustrates that MP have become part of the sedimentary transport and thus simultaneously of the geological cycle within the Anthropocene.

It has become clear that smaller plastic particles in the L-MP and M-MP size class occur widely dispersed in floodplain soils, as larger MEP and CMP particles, but reach significantly deeper layers down to 2 m. This first evidence of MP particles in such deep soil layers in combination with the clear accumulation in young sediments (deposited after 1960) strongly indicates for the first-time relocation of MPs <2 mm in soils. A size-dependent mobilization of MP particles can be assumed, as preferential flow paths, bioturbation or macropores offer possible pathways to move plastic particles into the depths of the soil column. Furthermore, the decreasing vertical gradient of MP loads starting with maximum contents in upper soil layers in proximal floodplain sites and lower levels in distant floodplain zones suggests that fluvial transport and deposition of plastic particles by floods are the key environmental drivers of plastic deposition in floodplain soils. Larger amounts of plastic are found in areas (a) that are flooded more frequently, (b) where larger amounts of sediment are deposited (riparian corridor with natural riparian vegetation), and (c) where the vegetation has a greater roughness (retention properties).

The temporal dimension and clear accumulation that corresponds to the increase in global plastic production confirm that plastic can, in principle, act as a stratigraphic marker of sediments in the Anthropocene, as suggested before (Price et al. 2011; Zalasiewicz et al. 2016; De-la-Torre et al. 2021a). However, the pure occurrence of plastic cannot represent a specific marker because vertical displacement processes to depths of 2 m (mobile fraction < 2000 µm) and for larger particles (>2000 µm) already down to shallower depths of 1 m (Weber und Opp 2020) are possible.

Even if the consequences of plastic contamination in soils and sediments for different ecosystems are still under investigation and discussion, the widespread occurrence and accumulation of plastic alone should give cause for reflection. Plastic as a purely anthropogenic material without a natural equivalent and long residence times (Zalasiewicz et al. 2016; Chamas et al. 2020) has no place in the environment. Humans influence the environment, and thus the future of the Earth, in manifold ways. Plastics should be understood as part of this influence and, against this backdrop, should be researched with a much stronger spatial focus. For further research on plastics, MP in floodplains, and in the semiterrestrial system in general, we recommend the following priorities:

1. Spatial quantification: in the context of a global plastic cycle, the representative spatial quantification of plastic and MP amounts in soils and sediments must be expanded. More data is needed to better understand and model plastic fluxes in the environment. Furthermore, temporal variations in hydrological situations could affect MP amounts at the same points over time and should therefore be investigated in future work.
2. Environmental drivers: processes like the mobility and displacement (lateral and vertical) of MP in soils and sediments should be analyzed in more detail. This analysis can be done in laboratory experiments (e.g., pot experiments) and in the field (e.g., pore characteristics, tracer experiments with plastic themselves or common tracers). The aim should be to understand the site-dependent key processes for MP mobility and to assess the resulting risks for the environment.
3. Stratigraphic relevance: plastics and microplastics could play an important role in accessing the stratigraphic records and changes within the Anthropocene. The fate of plastics, not only as a stratigraphic marker in floodplains, but also within different soils (especially anthropogenic soils), should be further investigated. In particular, the mobility of MP particles in soils could limit the use of MP as a marker, whereas larger plastic particles with lower mobility (MEP) could be used. Combinations with or extensions of available dating methods should be verified.

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3.4 Spatial connections between microplastics and heavy metal pollution within floodplain soils

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Abstract

Soils contain an increasing number of different pollutants, which are often released into the environment by human activity. Among the “new” potential pollutants are plastics and microplastics. “Recognized” pollutants such as heavy metals, of geogenic and anthropogenic origin, now meet purely anthropogenic contaminants such as plastic particles. Those can meet especially in floodplain landscapes and floodplain soils, because of their function as a temporary sink for sediments, nutrients, and pollutants. Based on a geospatial sampling approach, we analyzed the soil properties and heavy metal contents (ICP-MS) in soil material and macroplastic particles, and calculated total plastic concentrations (Ptot) from preliminary studies. Those data were used to investigate spatial connections between both groups of pollutants. Our results from the example of the Lahn River catchment show a low-to-moderate contamination of the floodplain soils with heavy metals and a wide distribution of plastic contents up to a depth of two meters. Furthermore, we were able to document heavy metal contents in macroplastic particles. Spatial and statistical correlations between both pollutants were found. Those correlations are mainly expressed by a comparable variability in concentrations across the catchment and in a common accumulation in topsoil and upper soil or sediment layers (0–50 cm). The results indicate comparable deposition conditions of both pollutants in the floodplain system.

Keywords

Plastic pollution, Metals, Metalloids, River systems, Freshwater pollution

3.4.1 Introduction

Nature is exposed to a variety of human influences. Part of these influences is the input of foreign substances and or pollutants into a wide variety of ecosystems worldwide. Similar to all other ecosystems, soils are particularly affected by such human impacts. Soils form the basis of human life, with 95% of global food being produced directly or indirectly on soils (Food and Agriculture Organization of the United Nations (FAO) 2015). In addition, soils are important ecological systems, integrated into all global material cycles (e.g., C-cycle), water filters (groundwater treatment), and much more (Blume et al. 2016; Willgoose 2018). The intensive use of soils worldwide makes them vulnerable towards human utilization and the input of pollutants (Alloway 2013).

Soils are intensively researched concerning the enrichment, mobility, and fate of heavy metals and metalloids. These naturally occurring metals and metal compounds – in the case of heavy metals, defined as metals with a density >5.0 g cm^3 – show geogenic background levels in all soils, as they are released into the environment through rock weathering (Alloway 2013). However, human activity during the industrial revolution (e.g., construction and transport), mining for ores, and the resource use of modern society have led to heavy metals contamination through anthropogenic inputs (Alloway 2013; Dudka und Adriano 1997; Gałuszka et al. 2014). However, through intensive research, the ecotoxicological consequences of heavy metals are well studied, which has led to national legislation in many countries, as well as monitoring of contaminated sites and measures to reduce or improve this soil pollution (Blume et al. 2016; Alloway 2013).

Conversely, a new foreign substance and potential pollutant has been detected in a wide variety of ecosystems for a few years now. Plastics, and in particular microplastics with a size below <5 mm, occurring in the environment as particles consisting of man-made polymers, now pose a new environmental challenge (Andrady 2017; Barnes et al. 2009; Karbalaei et al. 2018; Souza Machado et al. 2018a). In addition to the worldwide detection of microplastics in all ecosystems (Barnes et al. 2009), it is now possible to detect microplastics in compost (Braun et al. 2021), garden (Huerta Lwanga et al. 2017), agricultural (Corradini et al. 2019; Liu et al. 2018; Zhang und Liu 2018; Zhang et al. 2019; Piehl et al. 2018), and floodplain soils (Scheurer und Bigalke 2018; Lechthaler et al. 2021; Weber und Opp 2020). Furthermore, it has also been shown that plastic can be transported in soils (Hüffer et al. 2019; Rillig et al. 2017b), and can have an impact on soil structure (aggregates) (Zhang und Liu 2018), plants, and organisms (Yu et al. 2019; Rillig et al. 2017a; Rillig et al. 2019). Even if it has not yet been conclusively clarified whether there is an extensive risk to soils, soil organisms, or humans (uptake into the food chain), plastic is fundamentally a foreign substance in soils and, thus, corresponds to a contamination whose pollution status is still discussed (Xu et al. 2019; He et al. 2021b; Hurley und Nizzetto 2018).

The simultaneous occurrence of metals and plastic in soils raises the question of whether there are connections and interactions between these two groups of pollutants. In the case of heavy metals and plastic particles, studies from marine and aquatic environments demonstrated that interactions between heavy metals and microplastics take place in an aqueous environment (Holmes et al. 2012). Thereby, it was shown that, in marine environments, microplastics can desorb (e.g., Cd, Zn) and adsorb (e.g., Cu, Pb) heavy metals (Munier und Bendell 2018). The sorption of heavy metals was demonstrated in laboratory experiments for Cu and Zn to polystyrene (PS) and polyvinyl chloride (PVC) fragments in seawater (Brennecke et al. 2016). Plastics can, therefore, be seen as a transport vehicle of metals in aquatic environments (Holmes et al. 2012). In addition to the adsorption of heavy metals from the surrounding medium, further studies indicate the release of heavy metals into the environment through particle degradation (Wang et al. 2017; Imhof et al. 2016). Significantly, metals and heavy metals can enter into polymer products and, thus, into microplastic particles through additives. In this context, the number of potential additives is extremely diverse. Examples are flame retardants (Al and Zn), heat stabilizers (mostly Cd, Pb, Ba, and Sn in PVC), slip agents (Zn), inorganic pigments (Cr, Co, and Pb), or fillers (clay minerals and metal powders) (Hahladakis et al. 2018). Although the main focus has been on the interrelationships between heavy metals and plastic particles in aquatic environments, since 2019, a limited number of studies have also been conducted on these interrelationships in soils (Figure 35).

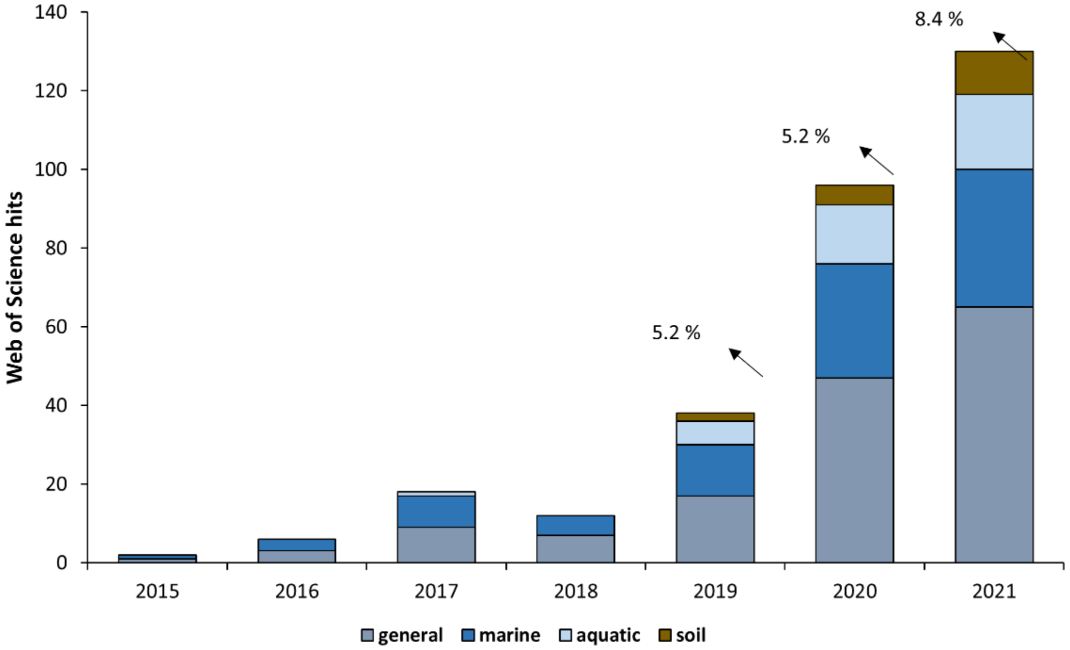

Figure 35: Web of Science (Clarivate) hits for different search term combinations (microplastic + heavy metal + “term”) (date: 27 November 2021).

For soils in which heavy metals and plastic particles are embedded in a mineral- organic matrix, partly with water (pore water), ad- and desorption processes comparable to those in aquatic environments have been obtained so far. Verla et al. (2019) reviewed the attachment of heavy metals to microplastics via adsorption considering the influence of polymer type and shape of the plastic particle (Verla et al. 2019).

The assumption is that metal ions can adsorb on microplastic surfaces and that the adsorption rate increases over time due to the presence of biofilms and a larger surface area resulting from degradation of the plastic particles (Verla et al. 2019). Other studies suggest an adsorption or desorption of heavy metals depending on the specific metal and the concentration of both pollutants in the soil (Li et al. 2020b). In addition, the influence of the presence of microplastics on heavy metals has been investigated: The presence of microplastics seems to reduce the exchangeable, carbonate-bound, and Fe-Mn-oxide-bound fraction of the metals, while it increases the organic-bound fraction (Yu et al. 2021). Furthermore, the bioavailability of Cu, Cr, and Ci seems to be affected by the presence of microplastics, whose presence also affects critical factors (e.g., DOC and pH) of the chemical behavior of heavy metals in soils (Yu et al. 2020). From the research to date, it can be concluded that relationships and interactions exist between heavy metals and microplastics in soils, as well as in the aquatic environment. However, the question arises as to whether these findings also apply to other types of soils and what role spatial factors play in the connection?

One suitable category of environmental space and landscape to study those interactions is floodplains and their soils. Both substances are present within floodplain soils, due to the sink function of floodplains (Lechthaler et al. 2021; Weber und Opp 2020; Blettler et al. 2017). Rivers and their floodplains interact with each other through flood water dynamics, material flows, and their context as a part of a semi-terrestrial ecosystem (Bridge 2003). Sediments and sediment-bound substances from the entire catchment of a river system can temporally be deposited in floodplains, which are, therefore, an important part of global material flows (Bridge 2003; Siegfried et al. 2017). Similar dynamics can also be assumed for plastic particles within the environment (Siegfried et al. 2017; Lechthaler et al. 2020; Liu et al. 2019; Xiong et al. 2018). Assuming that this is the main source (besides direct sources, e.g., agriculture) of pollutants in floodplain soils, both pollutants can be studied under comparable input conditions in floodplain soils. Previous research has documented levels of mass-based microplastics concentrations from 0 to 55.5 mg kg^{-1} for Swiss floodplain soils (Scheurer und Bigalke 2018), or particle-based concentrations ranging from 0 to 186.3 p kg^{-1} in different floodplain soils of the Lahn and Inde River (Germany) (Lechthaler et al. 2021; Weber und Opp 2020; Weber et al. 2021c). Furthermore, a wide-ranging, heterogeneous spatial distribution down to depths of two meters and associated in-situ vertical displacement has been demonstrated (Lechthaler et al. 2020; Weber und Opp 2020). Morphological factors, land use, and flood dynamics (sedimentation dynamics) appear to influence the spatial distribution of microplastics in floodplain soils (Lechthaler et al. 2020; Weber und Opp 2020).

Despite this knowledge, many questions about the spatial distribution of microplastics in soils in general, and especially in floodplain soils, remain unanswered, which is not least due to the few studies with a representative spatial context (Weber et al. 2020). Considering the few studies conducted so far on the relationships and interactions between heavy metals and microplastics in soils, even more questions remain about interrelationships, processes, and potential environmental risks.

This study aims to combine geospatial research with data from a case study floodplain on meso- and microplastic levels published in the work of Weber and Opp (2020) and Weber et al. (2021) to identify possible spatial and chemical connections between both pollutants in floodplain soils. This overall objective will be achieved through the following objectives:

1. Provide a spatial representative overview of the spatial distribution of heavy metal and plastic concentrations in floodplain soils.
2. Identify where spatial relationships between the two pollutants occur and which natural environmental drivers could be responsible for these relationships.
3. Perform a coherent pollution assessment based on the interrelationships of heavy metals and plastics and provide an outlook for further research within this young field of research.

3.4.2 Materials and Methods

3.4.2.1 Study Area and Geospatial Sampling

Field work and sampling was conducted within the floodplains of the Lahn River located in central Germany. Profound details about sampling sites and geospatial sampling approach were made available in Weber and Opp (2020) and Weber et al. (2021). The Lahn drains an area of approx. 5924 km^2 with a river length of 245.6 km and an approximate floodplain area of 88.9 km^2 in the Federal State of Hesse, Germany (Regional Council Giessen 2015). The floodplain soils are mostly formed by organic-rich silt and loam, which was deposited by frequent historical and recent floods in the floodplain area. As with other floodplain landscapes, especially in central Europe, the Lahn catchment is affected by historical mining, subsequent industry, and general human use (smaller urban spaces and infrastructure: 7.0% of total land use) (Regional Council Giessen 2015; Martin 2019). Previous studies within the Lahn catchment area show that heavy metals (Cu, Pb, and Zn) are frequently deposited in floodplain soils as consequence of historical mining and related industry (Martin 2012, 2015). The current land use of the catchment area (housing, infrastructure, and agriculture) favors the release of plastics and microplastics into the Lahn River, resulting in historical and recent depositions of (micro-)plastics within the Lahn floodplain. Based on these circumstances, the Lahn floodplain offers the opportunity to investigate the interrelationships between both the deposition of (micro-)plastics and the enrichment of metal(oid)s in floodplain soils.

The geospatial sampling approach was applied at four floodplain cross-section transects, representative of different floodplain soilscapes (floodplain soils and floodplain landscapes) of the Lahn River (Weber et al. 2021c). Each transect site is located within regularly flooded areas (yearly flooding to 5.5 years) and shows no anthropogenic interruptions (Weber et al., 2021). At each transect, two (upper catchment) or four (lower catchment) sampling plots containing two soil profiles (distance: 5 m) were drilled via pile core driving (100 mm and 80 mm core diameter; maximum depth: 2 m) and sampled according the following depth sections: 10 cm sections (for upper 0.5 m), 25 cm sections (for 0.5–1.5 m), and 50 cm sections (for 1.5–2.0 m) (Weber et al. 2021c).

Sampling plots represent the floodplain cross-section with its diverse morphological forms, showing surface altitude changes of 0.5 m with interruptions from flood channels and a general slope from higher natural levees to the lower floodplain edge with the partwise occurrence of back swamps (further information on floodplain morphology can be found in Weber et al., 2021).

Root density was estimated in the field according to the German guidelines of soil mapping (Ad-hoc AG Boden 2005). Stratigraphy and pedogenesis of each soil profile were documented according to the German soil classification (Ad-hoc AG Boden 2005) and the FAO Guidelines for soil description (FAO 2006), as well as the WRB 2015 (IUSS Working Group 2015).

3.4.2.2 Laboratory Analysis

Soil samples were transported within corn starch bags (Mater-Bi bags, Bio Futura B.V., Rotterdam, Netherlands) and dried at 45 ◦C in a drying chamber for a maximum of four days. Subsequently, the samples were carefully mortared and dry sieved according to size classes >5 mm, >2 mm, and <2 mm through stainless-steel sieves (Retsch, Haan, Germany). Afterwards, sample material <2 mm was homogenized and divided by means of a rotary sampler (Retsch, Haan, Germany) to obtain representative sub-samples.

We measured the organic matter content (OM; via loss on ignition at 550°C; DIN 19684–3:2000–08) and pH (with 0.01 M $CaCl_2$; m:V = 1:2.5) within the subsample material. Additionally, we determined soil texture with the Integral Suspension Pressure Method (Durner et al. 2017) after the samples had been prepared according to DIN ISO 11277:2002–08. The carbonate content of each sample was determined after reaction with a few drops of 3.23 M hydrochloric acid (HCl) according to Ad-hoc AG Boden (2005).

3.4.2.2.1 Metal Analysis

An analysis of metal concentration was performed for (1) soil samples and (2) macroplastic and coarse microplastic particles obtained from microplastic analysis (see chapter 3.4.2.2.2). For soil samples (1), analysis of the pseudototal concentrations of the metals (Al and Fe), heavy metals (V, Cr, Co, Ni, Cu, Sn, Cd and Pb), and the metalloid As was performed after the digestion of 1 g prepared subsample with 20 ml aqua regia (12.1 M HCl and 14.4 M HNO_3; ratio 1:3; DIN ISO 11466:2006-12). Metal content was quantified with an inductively coupled plasma–mass spectrometry (ICP–MS; XSERIES 2; Thermo Fisher Scientific, Bremen, Germany). The ICP–MS system was calibrated with a certified multi-element standard solution (ROTI®STAR; Carl Roth GmbH, Karlsruhe, Germany). Each digest of a soil sample was measured three times and averaged. The resulting mean metal concentrations were converted into units (mg kg^{-1}). Relative standard deviation (RSD) was quantified for all single measurements after threefold measurements to account for data reproduction and the effects of heterogeneous matrixes (Voica et al. 2012). Data with an RSD 20 % were excluded from further evaluation (Thomas 2001).

Detection limits were calculated by multiplying the mean standard deviation of 10 repeated blank measurements by a factor of 3, but no measurement results were below the respective detection limit.

To analyze the metal(oid) concentrations of macro- and coarse microplastic particles, 32 particles (from 9 soil samples) were analyzed (Table A 4). All plastic samples had a weight of >10 mg. The plastic particles were crushed using stainless steel tongs, except for one sample, which had to be ground using a CryoMill (CryoMill, Retsch, Haan, Germany) due to an extraordinary hardness. Subsequently, the comminuted particles were digested with 6 mL purified HNO_3 (65%) at 260°C and 120 bar for 20 min within acid-cleaned Teflon tubes (Turbowave; MLS-MWS, Leutkirch, Germany). The acid digestion protocol dissolves nearly all adsorbed and additive metals in the dissolved phase (Catrouillet et al. 2021).

Concentrations of the metals Al and Fe, the heavy metals V, Cr, Co, Ni, Cu, Sn, Cd, and Pb, as well as the metalloids As, Sb, and Se within digests were quantified with ICP-MS (Triple-Quadrupol ICP-MS 8800; Agilent, Santa Clara, CA, USA). Since no reference samples for plastics were available, certified water samples (SPS-W1, SPS- W2: Spectrapure Standards AS, Oslo/Norway; TMDA_64.3: CCRMP Canadian Certified Reference Materials Project, Ottawa (Ontario)/Canada) were used. The deviation of the recovery was consistently <10 %. Metal concentrations were reported in ppm.

3.4.2.2.2 Microplastic Analysis

Details of microplastic analyses, special sample preparation, contamination prevention, and methodological limitations are documented in Weber and Opp (2020) and Weber et al. (2021). In general, mesoplastics (MEP, >5 mm) and coarse microplastics (CMP, >2 mm) were visually identified from sieving fractions using a stainless-steel bowl with an imprinted grid (1 1 cm grid size) and inspected under stereomicroscope (SMZ 161 TL, Motic, Hong Kong) (Weber und Opp 2020). Large microplastics (L-MP, >1 mm) and medium microplastics (M-MP, >0.3 mm) were analyzed after density separation (NaCl solution, density adjusted to 1.2 g ml^{-1}) performed within the MicroPlastic Sediment Separator (MPSS) (Hydro-Bios Apparatebau GmbH, Kiel-Altenholz, Germany). After density separation, sieving, and filtration (cellulose filters; LLG-Labware, Meckenheim, Germany) of floating sample material, a Nile Red staining procedure (20 µg ml^{-1}Nile Red solution, Sigma-Aldrich, Taufkirchen, Germany) was applied (Konde et al. 2020; Maes et al. 2017). Stained filters were afterwards visually detected under a stereomicroscope (SMZ 161 TL, Motic, Hong Kong). Final identification of each potential plastic particle within the MEP, CMP, L-MP, and M-MP size class was performed by a Tensor 37 FTIR spectrometer (Bruker Optics, Ettlingen, Germany) combined with a Platinum-ATR- unit (Bruker Optics, Ettlingen, Germany). Data processing of FTIR spectra was performed in OPUS 7.0 (Bruker Optics, Ettlingen, Germany) and Spectragryph (Version 1.2.14; Menges, 2020; Oberstdorf, Germany). Final spectra identification and polymer type assignment was carried out according to Weber et al. (2021).

3.4.2.3 Statistics and Data Evaluation

Basic statistical operations were performed in Microsoft Excel 2013 (Microsoft; Redmond, WA, USA), in R (R Core Team, 2020), and in RStudio (Version 3.4.1; RStudio Inc.; Boston, MA, USA). Statistical tests were applied to examine relationships and differences between the collected datasets based on regression and correlation analyses, as well as to identify significant differences between concentrations and sampling locations or depths. Data visualization, tests for normal distribution (Shapiro–Wilk), linear regression analyses, Spearman correlation analyses, and variance analyses (ANOVA) were conducted with the standard R-packages as well as “graphics”, “stats”, “vioplot”, “ggplot2”, “ggridges”, and “scatterplot3d”. Significances were tested on different levels. We interpreted the results of statistical analysis to be significant when reaching a p-value <0.05. Basic geoinformatics evaluations were carried out in ArcMap (Version 10.3, Esri Deutschland GmbH, Kranzberg, Germany).

For the spatial and absolute comparison of plastic and heavy metal contents in floodplain soils, the total amount of plastic (Ptot) was calculated (Equation (6)) and documented as unit particles per kg soil dry mass (p kg^{-1}).

$$P_{tot} = \sum MEP + CMP + LMP + MMP \tag{6}$$

In order to provide an effective risk assessment – and ascertain the pollution characteristics – of heavy metals, as well as conducting a spatial comparison with plastic contamination, we calculated different pollution indices according to Kowalska et al. (2018). Each of the applied indices shows an effective assessment of contamination and the spatial contamination differences (Kowalska et al. 2018). To measure the potential impact of anthropogenic heavy metal pollution, we calculated the “Enrichment factor” (EF) (Equation (1), according chapter 2.2.3.6),

$$EF = \frac{\left[\frac{HM}{LV}\right] sample}{\left[\frac{HM}{LV}\right] GB} \tag{1}$$

where HM is the concentration of individual heavy metals and LV is the reference concentration of Fe. Geochemical background (GB) concentrations for the calculation of EF and PLI, as well as comparative values, were calculated based on the average values for Hesse floodplain soils provided in Friedrich and Lügger (2011). A total of 341 samples (64 floodplain silt substrates and 277 floodplain sand substrates) were averaged.

Additionally, the “Pollution Load Index” (PLI) (Equation (3), according chapter 2.2.3.6), based on the “Single Pollution Index” (PI) (Equation (2), according chapter 2.2.3.6) for each heavy metal, was calculated,

$$PI = \frac{HM}{GB} \tag{2}$$

$$PLI = \sqrt[n]{PI_1 \times PI_2 \times PI_3 \times PI_n} \tag{3}$$

where PI is the single pollution index of each heavy metal calculated as PI = HM.

To assess the potential toxicity a of heavy metal contamination, the “Contamination Security Index” (CSI) (Equation (4), according chapter 2.2.3.6) was calculated

$$CSI = \sum_{n=1}^{n} w\left(\left(\frac{HM}{ERL}\right)^{\frac{1}{2}} + \left(\frac{HM}{ERM}\right)^{2}\right) \tag{4}$$

with W (the weight of each heavy metal) computed according to Pejman et al. (2015), and HM (the individual concentration of each heavy metal), ERM (median value of the effect range), and ERL (lowest value of the effect range) calculated according to Long et al. (1995). Finally, the “Potential Ecological Risk Index” (RI) (Equation (5), according chapter 2.2.3.6) was calculated according to Hakanson (1980) to assess potential ecological risks of heavy metal concentrations in floodplain soils

$$RI = \sum_{i=1}^{n} E_r^i \tag{5}$$

with n (the number of heavy metals) and Er (the single index of the ecological risk factor) calculated by Ei = Ti x PI with Ti (toxic response coefficient) and PI (the Single Pollution Index).Heavy metal concentrations were also compared to legal standards for soils (German national legislation) (Bund-/Länderarbeitsgemeinschaft Bodenschutz (LABO) 2003; Bundesregierung 1998).

3.4.2.4 Limitations

The presented work combines and adapts different methodological approaches from microplastic research and soil sciences. With regard to the well-recognized and – so far – intensively studied heavy metals, the methods used are subject to standardized applications. Heavy metal analysis from soil samples was controlled by standards guided by the geogenic background values of Hessian floodplain soils [61]. Measurement of heavy metals in plastic particles was controlled by certified water samples. In both cases, the detection limits of the ICP-MS measurement were not reached.

With regard to (micro-)plastic analyses, limitations and insecurities were intensively discussed within the work of Weber and Opp (2020) and Weber et al. (2021).

Based on the (micro-)plastic analysis conducted, only plastic particles with a density <1.2 g ml^{-1} in a size range between 0.5 and >5 mm were separated. The density separation unit used in this study showed recovery rates of up to 95% (Konde et al. 2020), whereas the Nile Red staining exhibited recovery rates of up to 96.6 for marine sediments (Maes et al. 2017). To prevent overestimation of plastic concentrations, samples were systematically examined and all collected particles subsequently analyzed via ATR-FTIR (Weber et al. 2021c). Therefore, there may only have been an underestimation of the plastic concentrations, as plastics with a density >1.2 g ml^{-1} (e.g., PET) could only be recorded semi-quantitatively. Moreover, numerous studies have shown an increase in plastic content with decreasing particle size (Weber und Opp 2020). Here, however, the particle size limit was clearly 500 µm.

Finally, there are also uncertainties in the assessment of plastic concentrations in soils. Unlike other pollutants, there are no legal limits. The comparison with other studies is often limited due to differences between methodologies, and the consequences and impacts of (micro-)plastic on soils are still under investigation.

3.4.3 Results

3.4.3.1 Floodplain Soil Properties

According to the FAO (2006) grain size classification, the studied floodplain soils of the Lahn River catchment consist mainly of floodplain silt loams with average composition of silt (48.03%) > sand (32.33%) > clay (19.64%). We found that the sand content decreases from the upper reaches (site ELM) to the lower reaches (site LIM), whereby it increases from an average depth of 100–150 cm to >60 cm in some cases, depending on the position within the floodplain (embankment or former flow channels) (Figures S1–S4). Maximum clay contents (>25%) are only reached within single clay layers (e.g., floodplain edge depression) (Figure 36c). The organic matter content ranges between 1.59 and 21.07% with a total average of 5.49%. Topsoils (0–30 cm) show significantly higher organic matter content (average: 7.35%) in contrast to subsoils (average: 4.66%). Absolute maximum values (>20.0%) occur within single organic clay-rich layers (clay mud). On average, the amount of organic material decreases with depth (in line with root density) (Figure 36a). The floodplain soils studied can, therefore, be classified as silty, organic-rich fluvial deposits, which is typical for fluvial deposits (Bridge 2003; Rittweger 2000). Within the fluvial deposits, deposited during the Holocene, Fluvisols and Gleysols have developed (Weber et al. 2021c). From the preliminary study, it can also be deduced that for sediments close to the river (river bank and proximal floodplain), the upper 40–50 cm of the floodplain sediments are very young (deposition since the 1960s) (Weber et al. 2021c). The soil properties differ mainly in terms of land use, groundwater levels (hydromorphic conditions), and portions of coarse soil fragments (gravel).

Horizon sequences contain Ah or Ap (Abp) above combinations of B, Bl, Bgl, Bgr, or Br horizons. Within the Fluvisols and Gleysols, the soil pH ranges between 5.11 (moderately acid) and 6.94 (neutral) with a total average of 6.12 (very weak acid) (Figure 36b). Regarding the dependence of heavy metal mobilization on the pH value, only the mobilization limit value of Cd (at 6.5) falls below this level (Figure 36b) (Blume et al. 2016).

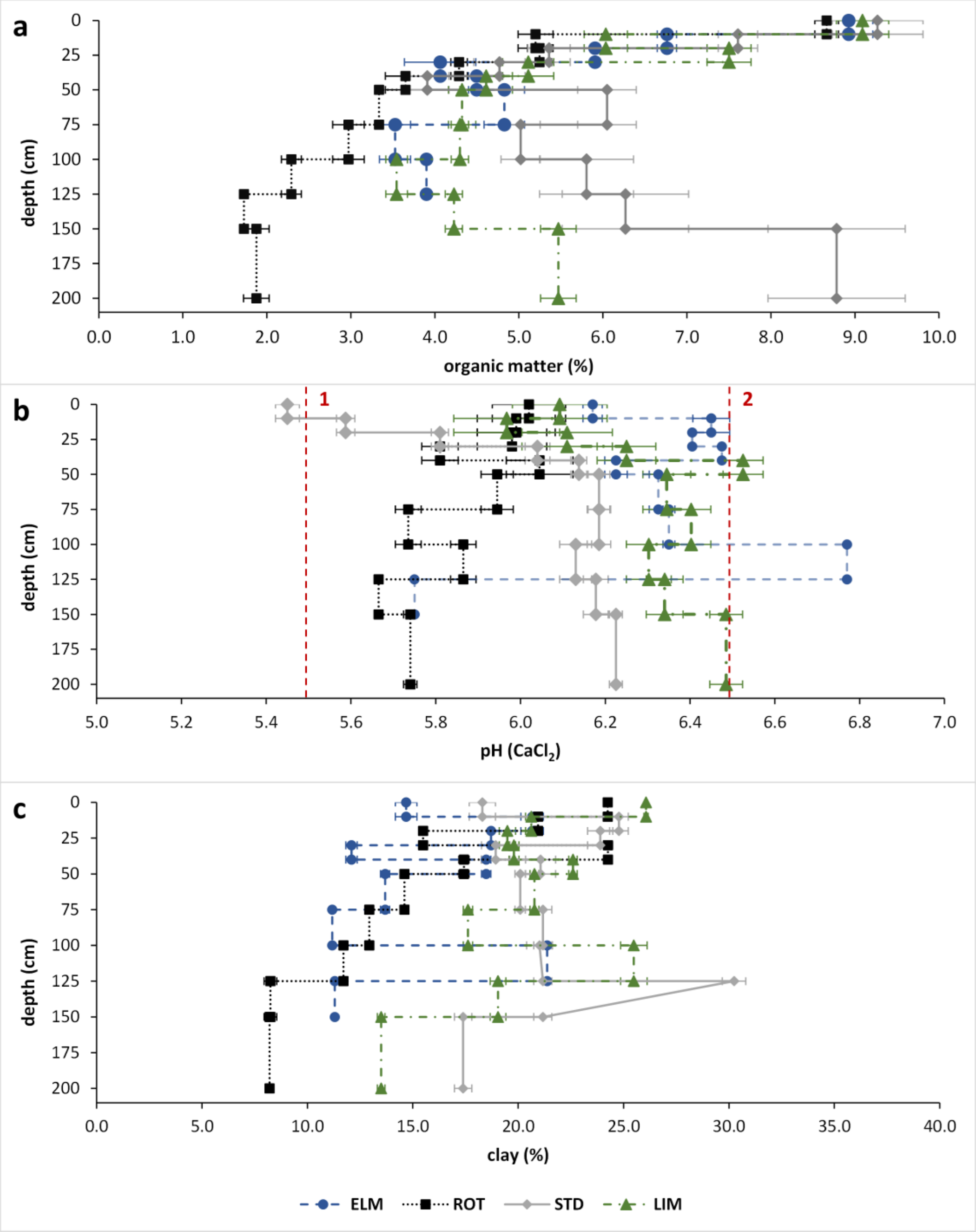

Figure 36: Floodplain soil properties for sampling areas. (a): Organic matter content (%) according to LOI analyses (maximum outliers excluded); (b): pH (-) values with mobilization limit values (1: Cd; 2: Zn, Ni, Co, As; according to Blume et al., 2004); (c): clay content (%).

In summary, floodplain soil properties have the potential for an accumulation of heavy metals and (micro-)plastics. Whereas, on the one hand, the comparatively small amounts of clay and fine silt indicate reduced heavy metal adsorption (clay minerals), the proportion of organic matter and the only slightly acidic pH value show tendencies for low heavy metal mobility and adsorption of organic constituents (Alloway 2013).

3.4.3.2 Spatial Relationships between Plastic and Metal Concentrations

3.4.3.2.1 Total Plastic Concentration

Total plastic concentrations (Ptot, calculation presented in chapter 3.4.2.3) range from 0 to 21.12 p kg^{-1} with an overall average concentration of 1.66 p kg^{-1}. Detailed descriptions of plastic particles' characteristics, polymer types, and additional information can be found in Weber and Opp (2020) for MEP (mesoplastic, >5 mm) and CMP (coarse microplastic, >2 mm) as well as in Weber et al. (2021) for LMP (large microplastic, >1 mm) and MMP (medium microplastic, >0.5 mm) size classes.

Considering the Ptot concentrations at the catchment level, it is clear that the mean values per sampling site of 2.65 p kg^{-1} in the upper reaches (site ELM) decrease in the middle reaches (site ROT: 1.01 p kg^{-1}, site STD: 1.33 p kg^{-1}) and increase again up to 1.96 p kg^{-1} in the lower reaches (site LIM) (Figure 37). The mean differences in Ptot concentrations between the sampling sites are significant (ANOVA $p < 0.01$). Despite this finding, the maximum Ptot concentrations increase with increasing flow length. At the sampling site level, the highest average Ptot concentrations are always reached near channel sites (proximal floodplain) and decrease with increasing distance to the river (distal floodplain), except for point STD-3 (inactive flow channel) (Table 7). The site LIM with the sampling point LIM-1 (river bank) shows the absolute maximum average Ptot concentration (5.26 p kg^{-1}) of all investigated floodplain soils. The vertical distribution is clearly divided into two sections: Higher concentrations of Ptot always occur in surface soils (Ah or Ap horizons) or in the upper 40–50 cm of the soils. Below this depth, the contents decrease clearly and zero values occur more frequently (Figure 38). As also documented in one of the former studies, the main amount of Ptot and the highest concentrations are thus present in the young upper soil layers of the fluvial floodplain sediment (Weber et al., 2021). Comparing the summed Ptot contents with those of other studies in floodplain soils, it is apparent that the general level of plastic pollution within the Lahn River catchment seems to be lower than in other studied catchments (Scheurer und Bigalke 2018; Lechthaler et al. 2021; Blettler et al. 2017) or than the often studied agricultural topsoils (Huerta Lwanga et al. 2017; Liu et al. 2018; Zhang und Liu 2018; Zhang et al. 2019; Piehl et al. 2018; Corradini et al. 2019). Nevertheless, the wide spatial distribution indicates a general accumulation of plastic particles in floodplain soils, as is already known for other pollutants such as heavy metals (Fryirs und Brierley 2013).

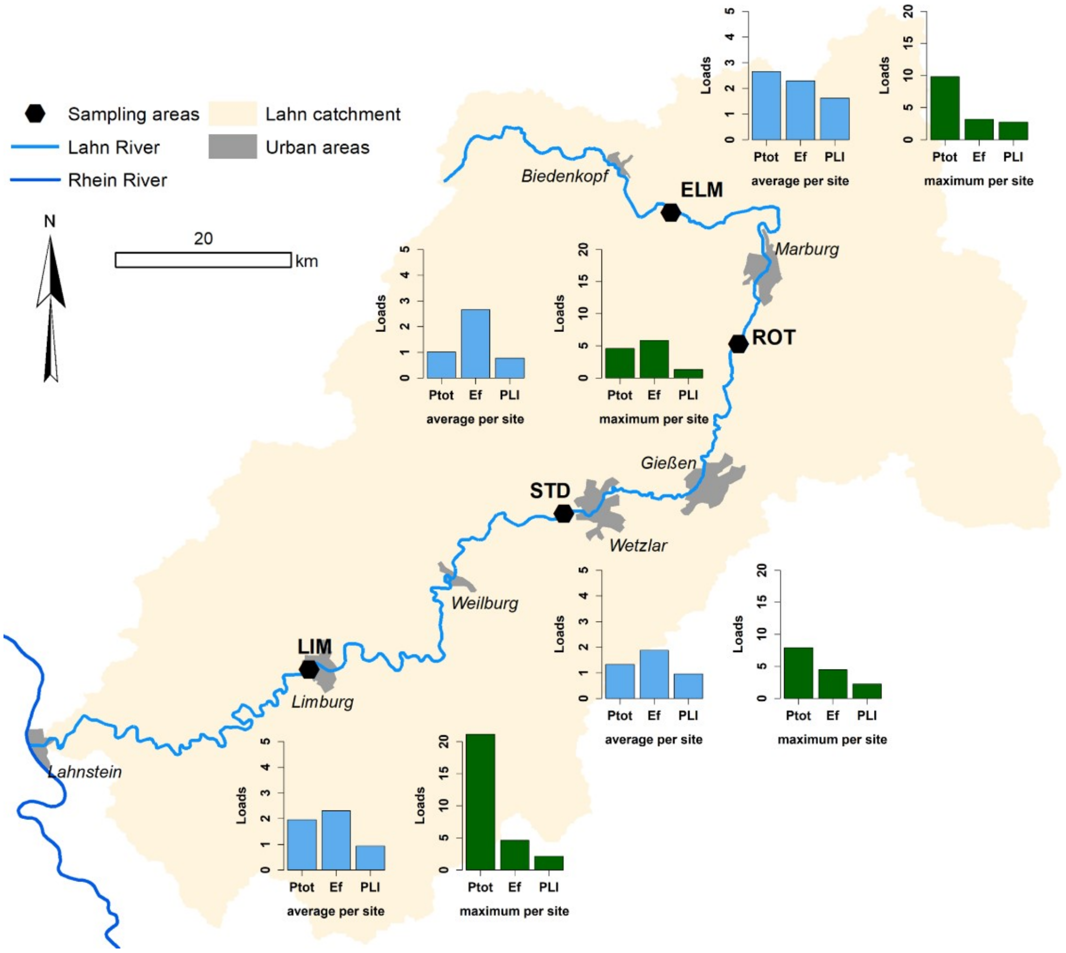

Figure 37: Overview of plastic and heavy metal loads in the Lahn catchment. Ptot: total plastic concentrations (p kg^{-1}), calculated as the mean value from all samples of a transect; Ef: enrichment factor; PLI: pollution load index (both calculated as the mean value from all metals analyzed in soil samples of a transect).

3.4.3.2.2 Heavy metal concentrations

The presence of heavy metals in soils, and especially floodplain soils, due to the delivery and sedimentation of eroded soil material from the entire catchment is widely recognized. The analyzed heavy metals as well as the metalloid As were detected in all samples, regardless of site position or sampling depth. In general, the following metals are present, in decreasing order based on their average values: Zn (51.39 mg kg^{-1}) > Ni (29.05 mg kg^{-1}) > Cr (28.00 mg kg^{-1}) > Pb (22.20 mg kg^{-1}) > Cu (15.56 mg kg^{-1}) > V (15.40 mg kg^{-1}) > Co (10.18 mg kg^{-1}) > As (6.24 mg kg^{-1}) > Cd (0.25 mg kg^{-1}) (Figure A 20). Those concentrations are comparable to the concentrations of Cu, Pb, and Zn in previous studies conducted by Martin (2012; 2015; 2019). The spatial differences in the contents of the individual metals are very heterogeneous (Table 7). Compared to mean global concentrations in topsoil (Kabata-Pendias 2011), the maximum values of Cr, Ni, Cu, As, Cd, and Pb as well as the top 25% of the concentrations (third quartile) from Ni, As, Cd, and Pb exceed the comparison values (Table 7). All maximum values as well as the mean values of Cr, Co, Ni, Cu, and Cd also exceed the geogenic background levels (Friedrich und Lügger 2011).

The legal precautionary levels for loamy soil, according to the German Federal Soil Protection Ordinance (BBodSchV, 1998), are only exceeded by eight samples for Cr, Ni, Cu, and Cd (Table 7) (Bundesregierung 1998).

Whereas the Enrichment factor (Ef) and the Contamination security index (CSI) indicate a moderate enrichment of heavy metals with low-to-moderate severity of contamination, the Pollution load index (PLI) and the Ecological risk index (RI) show a deterioration of soil quality as well as a strong ecological risk for 38.1% and 33.9%, respectively, of all samples (Table 7).

Regarding the spatial distribution of heavy metal contamination on the catchment scale and based on the indices that are calculated with geogenic background contents (Ef and PLI), the average and maximum loads show only minor differences with the course of the river (Figure 37). Sampling sites or points with clear outliers do not appear. Against this background, it is possible to assume that the Lahn floodplains are contaminated with heavy metals across the catchment area, with these being of partly geogenic and partly anthropogenic origin.

At the sampling site level, for both the location within the floodplain cross transect and the vertical distribution, a division comparable to the spatial distribution of the Ptot content is detectable. The highest average as well as maximum values of all calculated indices are always reached at the near channel sites (proximal floodplain), except site STD (Table 7). Regarding the vertical distribution, a clear decrease in the indices' values, most clearly for Ef and RI, and for proximal as well as distal floodplain locations, can be observed for the upper 50 cm of floodplain soils (Figure 38). In addition, the values of CSI and PLI show a decrease over depth, but this is less explicit than the other calculated pollution indices. Even if there are outliers in deeper soil layers depending on the location, the content of heavy metals decreases significantly ($p = 0.01$) for all pollution indices in the lower (>50 cm) soil layers.

Table 7: Overview of average plastic and heavy metal loads with calculated pollution indices.

Sampling site	**Soil profile**	**Ptot (p/kg)**[a]	**Heavy metal concentrations (mg/kg)**										**Pollution indices**			
			V	Cr	Co	Ni	Cu	Zn	As	Cd	Pb		Ef[b]	PLI[c]	CSI[d]	RI[e]
ELM	ELM-1	4.00	18.40	38.01	14.40	49.41	33.23	105.25	7.93	0.51	44.63		2.72	1.74	1.18	325.5
	ELM-2	1.31	23.12	37.36	14.74	41.81	21.71	61.66	9.74	0.23	21.72		1.81	1.32	0.95	187.4
ROT	ROT-1	1.49	10.43	19.27	6.97	20.49	13.50	50.24	4.81	0.25	20.05		3.45	0.95	0.67	262.5
	ROT-2	0.54	11.60	20.12	7.69	19.87	8.88	29.73	4.48	0.12	12.64		1.86	0.68	0.59	92.6
STD	STD-1	2.04	16.70	29.75	11.15	29.40	14.72	44.32	6.01	0.20	15.74		1.80	0.90	0.74	134.0
	STD-2	0.51	14.94	26.42	9.27	27.94	14.05	43.53	6.18	0.16	16.40		1.70	0.89	0.71	129.6
	STD-3	1.83	18.05	33.26	10.65	31.44	17.66	58.37	7.20	0.35	25.44		2.28	1.17	0.81	216.7
	STD-4	0.96	16.83	31.65	9.70	29.42	14.71	44.92	6.70	0.17	20.79		1.74	1.00	0.77	127.3
LIM	LIM-1	5.26	14.15	28.73	13.43	35.10	17.71	72.81	6.36	0.48	31.89		3.18	1.39	0.93	325.0
	LIM-2	0.91	14.49	26.67	10.35	27.68	13.90	51.09	5.66	0.30	25.37		2.32	1.05	0.18	186.7
	LIM-3	0.64	15.55	27.82	9.39	25.44	13.73	40.72	6.15	0.18	22.07		1.79	0.91	0.17	124.1
	LIM-4	0.81	11.48	19.26	5.92	15.77	6.80	24.92	4.21	0.10	13.46		1.77	0.52	0.54	64.1
SHW[f]			-	60.0	-	29.0	38.9	-	0.7	0.4	27.0	Specific limit values[g]	>5.0	>1.0	1.0-2.0	180-360
GBH[h]			38.3	25.0	8.8	24.0	13.3	58.5	8.0	0.1	27.0	Interpretation of limit value	moderate enrichment	deteriorate-ion of soil quality	low to moderate severity	Strong ecological risk
LPL[i]			-	60.0	-	50.0	40.0	150.0	-	1.0	70.0					
Samples (n) exceed LPL or limit value (total n = 118)				*2*		*9*	*3*	*0*		*1*	*0*		*1*	*45*	*1*	*40*

[a] Average total plastic load (particle per kg soil dry weight), [b] Enrichment factor, [c] Pollution load index, [d] Contamination security index, [e] Ecological risk index, [f] Average content surface horizons worldwide (Kabata-Pendias, 2011), [g] Specific limit values for pollution indices (Kowalska et al., 2018), [h] Geochemical background in Hessian floodplain soils (Friedrich and Lügger, 2011), [i] Legal precautionary level for loamy soil according to German Federal Soil Protection Ordinance - BBodSchV (1998)

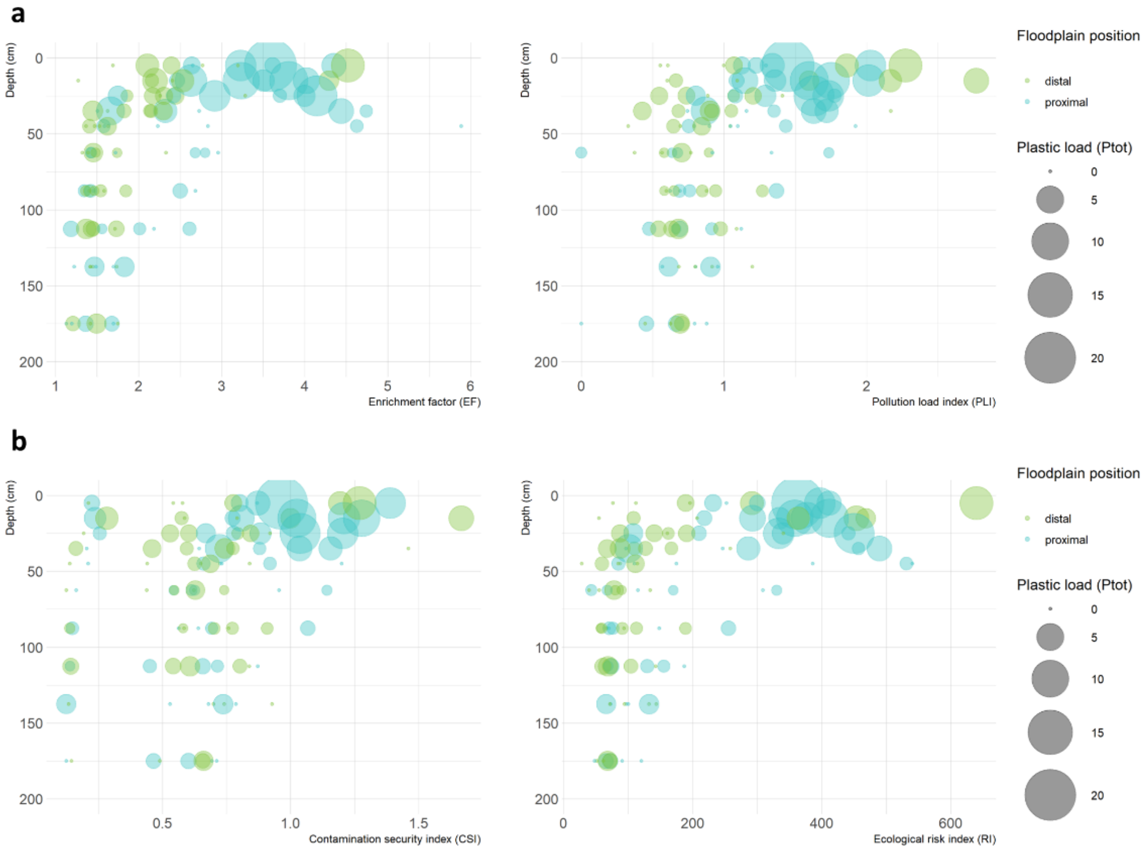

Figure 38: Depth distribution of plastic and heavy metal concentrations in floodplain soils. (a): With mean pollution load indices (Ef and PLI) based on geochemical background values; (b): With mean pollution load indices based on risk assessments (CSI and RI). Colour separation according to proximal or distal location in the floodplain. Sizes of the dots depend on the plastic concentration (Ptot) standardized to the maximum content.

3.4.3.2.3 Correlations between Plastics and Heavy Metals

A general spatial connection based on the spatial distribution patterns of plastics and heavy metals was found in the studied floodplain soils. Both contaminants show a comparable distribution on the catchment level, with higher contents in the upper reaches (site ELM), decreasing contents in the middle reaches (site ROT and STD), and a renewed increase in the lower reaches (site LIM), especially in their maximum values (Figure 37). Spatial correlations also occur in the depth distribution. Both the levels of heavy metals, expressed by pollution indices, and the levels of total plastic concentrations differ in the upper and lower soil layers. An accumulation of both contaminants can, therefore, be observed in the upper 40–50 cm of the floodplain soil, for both the proximal and the distal floodplain sites (Figure 38).

The spatial correlations found provide an opportunity to also examine the possible correlations statistically. Spearman rank correlation coefficients (RSP) of Ptot data with individual heavy metals show significant ($p = 0.05$) weak ($r_{SP} < 0.3$) positive correlations with the concentrations of Cr, Co, Ni, Cu, Zn, Cd, and Pb for the entire soil profiles (Table 8).

With regard to the examined division of the accumulation into upper 50 cm and lower soil areas, the corresponding division of the dataset shows more significant (added V and Fe) and stronger (weak to clear, r_{SP} >0.5) correlations in the upper soil layers and no significant correlations in the lower soil layers. The same can be observed for correlations with the pollution indices, where significant weak correlations exist in the upper soil layers. No significant correlations can be observed for the relationship between Ptot and soil properties, except for organic matter content (r_{SP} 0.31–0.36) and root density (r_{SP} 0.30–0.33). Therefore, it can be assumed that in the upper soil layers, the heavy metal contents increase (positive correlations) with increasing plastic content and likewise with increasing content of organic material. This can be an indication of chemical relationships, such as comparable adsorption conditions (organic-bound) or an indication of identical deposition conditions (flood water delivery).

Table 8: Spearman correlation of total plastic load (Ptot) with metals, pollution indices and soil properties for different soil depths.

row	**column**	**entire soil profile**		**upper soil (0-50 cm)**		**subsoil (50-200 cm)**	
		cor	**p**	**cor**	**p**	**cor**	**p**
Ptot[a]	V	0.18	0.06	**0.26**	**0.04**	-0.04	0.79
	Cr	**0.36**	**0.00**	**0.51**	**0.00**	0.04	0.80
	Fe	0.16	0.10	**0.33**	**0.01**	-0.04	0.78
	Co	**0.24**	**0.01**	**0.39**	**0.00**	-0.01	0.93
	Ni	**0.25**	**0.01**	**0.47**	**0.00**	-0.08	0.59
	Cu	**0.32**	**0.00**	**0.47**	**0.00**	-0.11	0.42
	Zn	**0.37**	**0.00**	**0.53**	**0.00**	-0.11	0.46
	As	0.15	0.11	0.25	0.06	-0.14	0.31
	Cd	**0.39**	**0.00**	**0.57**	**0.00**	-0.12	0.39
	Pb	**0.34**	**0.00**	**0.41**	**0.00**	-0.12	0.39
	Ef[b]	**0.35**	**0.00**	**0.38**	**0.00**	-0.04	0.78
	PLI[c]	**0.35**	**0.00**	**0.48**	**0.00**	-0.06	0.66
	CSI[d]	**0.33**	**0.00**	**0.49**	**0.00**	-0.03	0.84
	RI[e]	**0.34**	**0.00**	**0.43**	**0.00**	-0.10	0.46
	clay	-0.01	0.92	-0.09	0.49	-0.07	0.64
	silt	0.14	0.13	0.17	0.21	-0.02	0.89
	sand	-0.10	0.30	-0.09	0.50	0.04	0.79
	pH	-0.05	0.63	-0.02	0.91	0.06	0.68
	OM[f]	**0.31**	**0.00**	**0.36**	**0.00**	-0.01	0.96
	bulk density	-0.05	0.61	-0.17	0.19	0.13	0.35
	root density	**0.33**	**0.00**	**0.30**	**0.02**	-0.03	0.85

Significant correlations ($p < 0.05$) in bold text. [a] Total plastic load (p kg^{-1}), [b] Enrichment factor, [c] Pollution load index, [d] contamination security index, [e] Ecological risk index, [f] Organic matter (%)

Within the context of possible chemical relationships, weak-to-strong, but always positive, inter-element correlations were found for individual heavy metals (Figure 39a), indicating a combined metal pollution from similar long-term sources (Manta et al. 2002). Correlations between heavy metal contamination (pollution indices) and environmental drivers of heavy metal behavior (fine soil fraction, sand fraction, organic matter content, and pH) could not be found. Only PLI correlates strongly positively with organic matter content and RI and Ef correlate very weakly negatively with pH (Figure 39b).

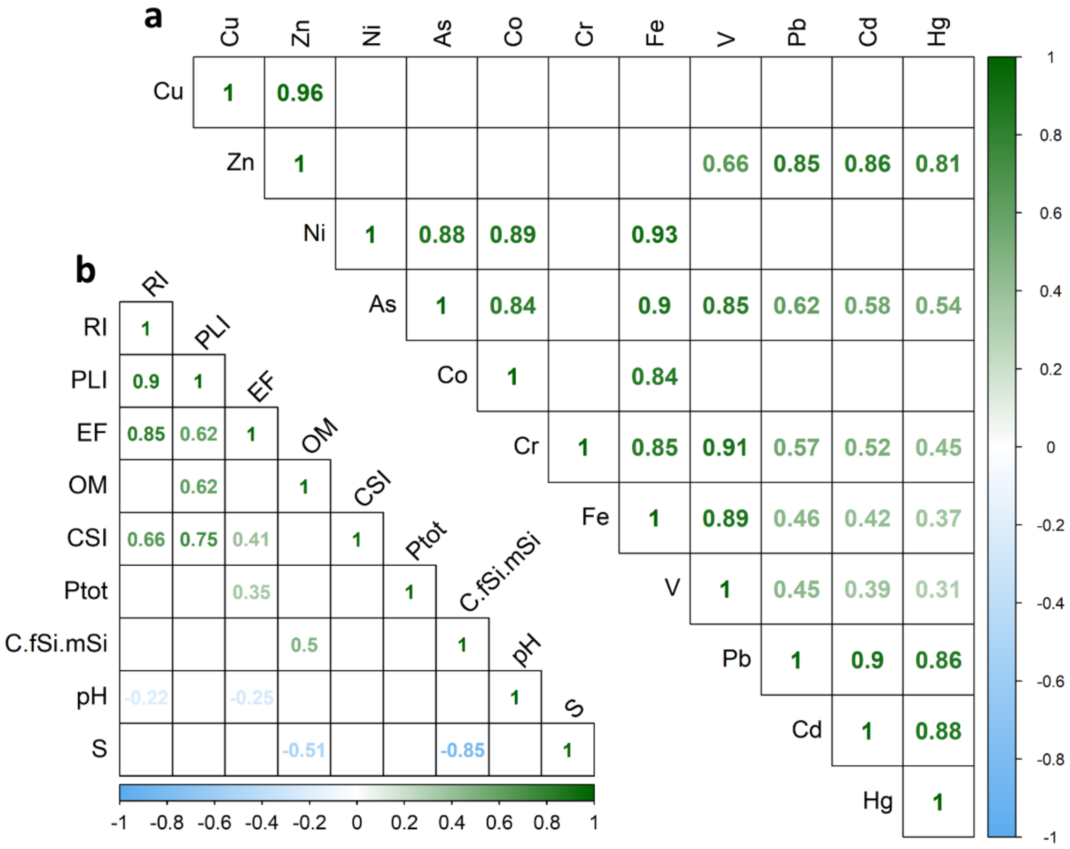

Figure 39: Spearman correlation matrix in first principal component order (n = 110, insignificant values with p <0.05 excluded). (a): Heavy metals and metalloids; (b): Pollution indices and floodplain soil properties (RI: ecological risk index; PLI: pollution load index; EF: enrichment factor; OM: organic matter content (%); CSI: contamination security index; Ptot: total plastic concentration (p kg^{-1}); C.fSi.mSi: sum of fine soil fraction containing clay as well as fine and middle silt (%); S: sand content (%).

3.4.3.3 Heavy Metals in Macroplastics and Coarse Microplastics

The macroplastics and coarse microplastic particles used for analyses of heavy metal content comprise fragments, films, and plates with sizes >2 mm from nine soil samples with mainly white or transparent colors and an average particle mass of 42.13 mg plastic per soil sample (Table A 4). The analyzed plastic particles comprise low-density polyethylene (PE-LD), polypropylene (PP), chlorosulfonated polyethylene (CSM), polyamide (PA), and poly(methyl methacrylate) (PMMA) (Table A 4). The heavy metal concentrations quantified for these particles can include both adsorbed metals and metals added to the plastic as additives (Catrouillet et al. 2021).

With regard to the average concentrations, the order of metal concentrations is as follows: Zn (94.63 ppm) > Cr (67.56 ppm) > Pb (34.23 ppm) > Cu (28.13 ppm) > Ni (23.52 ppm) > V (20.28 ppm) > Sb (18.43 ppm) > Sn (10.21 ppm) > Cd (8.43 ppm) > Co (3.82 ppm) > As (2.55 ppm) > Se (1.30 ppm) (Figure 40). The highest sums (>300 ppm) of heavy metal concentrations were found in samples STD-4-1 (PP, film), ROT-1-2 (PE-LD, massive fragment), and STD-1-2 (CSM, fragment and film). The maximum values (outliers in Figure 40) can also be traced back element-specifically to these three samples. Since comparative and reference values (by law) for the evaluation of the metal contents are missing, the focus here can only be on the presentation of the concentrations and the connection with the sample matrix.

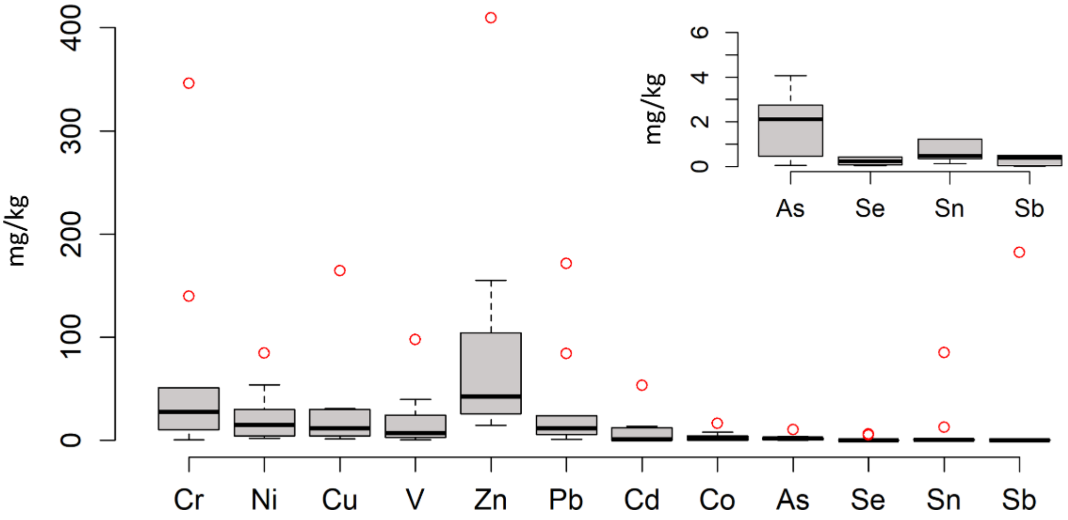

Figure 40: Heavy metal loads extracted from macroplastic particles (n = 10).

From the entire dataset, total plastic loads, pollution indices, and soil properties can be used for comparison with the sum of heavy metals from the particles (Figure 41). Whereas the comparison with PLI and Ef shows no clear trend, the comparison with Ptot suggests a decrease in the sum of heavy metals with increasing Ptot content (Figure 41a). The same decrease is observable in comparison to pH values (Figure 41b). In contrast, heavy metal content appears to decrease with decreasing OM or clay content. Due to the limited number of samples (n = 10) and the heterogeneous data distribution, correlation analyses lead to insignificant results.

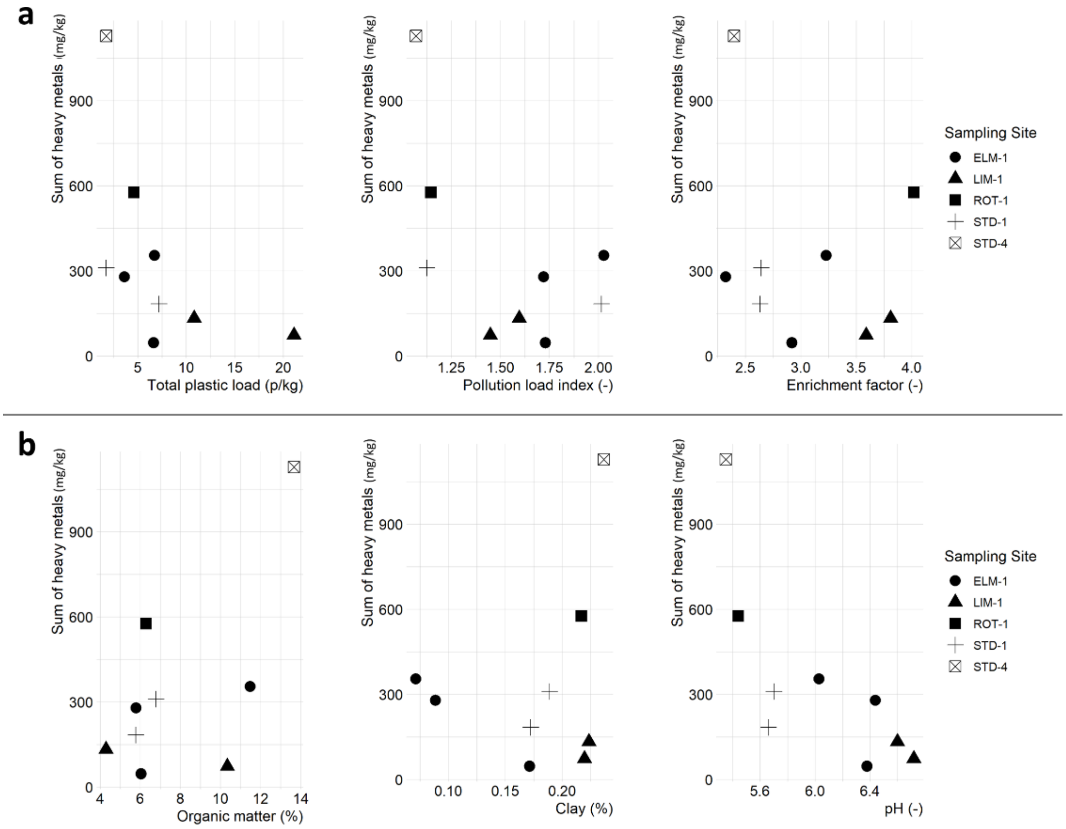

Figure 41: Comparison of sum of heavy metals (ppm) extracted from macroplastic particles with (a) total plastic concentrations and pollution indices (PLI and EF) of the respective soil sample and (b) floodplain soil properties of the respective soil sample per sampling site.

3.4.4 Discussion

3.4.4.1 Spatial Correlations

Macroplastics and microplastics, as well as heavy metals, are present in floodplain soils of the entire Lahn River catchment. Furthermore, based on the conducted geospatial sampling approach, the results indicate spatial relationships between both contaminants. Various studies have determined the presence of partwise increased metal concentrations in the floodplain soils, pore water, and water, as well as suspended particulate matter of the Lahn River (Hahn et al. 2021; Hahn et al. 2016). In general, heavy metal loads and their spatial distribution are comparable to the results of previous studies conducted in the Lahn River catchment (Martin 2012, 2019). In the case of the metals Cu, Pb, and Zn evaluated by Martin (2008, 2012) for near-channel positions, the concentration ranges correspond to the data presented here for those three metals (Martin 2012). The increase in concentrations described in these studies for the course of the river could not be traced here, neither for proximal sites (near-channel) nor for the entire transects.

Regarding the total plastic concentrations, a regional comparison was not possible due to the lack of case studies to date. In comparison to microplastic concentrations in soils, documented for topsoils under agricultural usage, the contents found here are comparatively low (Liu et al. 2018; Zhang und Liu 2018; Piehl et al. 2018; Corradini et al. 2019). For example, Liu et al. (2018) reported average concentrations of 70.0 p kg^{-1} (>0.02 mm plastics) and Corradini et al. (2019) documented a range of 0.6–10.4 p g^{-1}. The microplastic concentrations reported for Swiss floodplain topsoils (average: 5 mg kg^{-1}) are hard to compare with our results due to the different units applied (Scheurer und Bigalke 2018). The average concentrations of microplastics documented for the Inde River catchment (North Rhine-Westphalia, Germany), ranging from 25.4 p kg^{-1} up to 47.9 p kg^{-1}, are comparable to the results of Weber et al. (2021) and show that the mean contents in the floodplains of the Lahn are significantly lower and only maximum contents reach the mean range in the Inde river (Lechthaler et al. 2021). However, it is important to note that due to the different sampling and analysis methods, only limited comparability can be ensured here. This also applies to the investigated (micro-)plastic size classes, as many studies, unlike ours, also examine particles <300 µm, which can explain the increased concentrations.

In contrast to the problems for the comparison of plastic concentrations, the spatial distribution of plastic concentrations in floodplain soils is comparable to the studies of Scheurer and Bigalke (2018) and Lechthaler et al. (2021). Both studies documented an increase in plastic concentrations with stream length or, rather, a correlation between plastic concentrations and population density within the catchments. With reference to this lateral distribution over the catchment, the Ptot concentrations also show an increase along the length of the river, with the exception that higher contents (mean and maximum) were already present in the upper reaches (Figure 37). No direct impact of the urban centers along the Lahn River (the cities of Marburg, Gießen, Wetzlar, and Limburg) was found. However, a general increase in Ptot levels may suggest an increased occurrence of potential sources along the river. The same applies to heavy metal contents, even if these show a higher variability at the catchment level, probably caused by the different environmental sources (e.g., geogenic activity, mining) (Dudka und Adriano 1997).

In addition to the correlations in variability at the lateral catchment level, spatial correlations occur primarily at the vertical level (depth distribution in the floodplain soils). The clear separation with higher contents in the upper soil layers (0–50 cm) and significant correlations between Ptot and metal contents illustrate these spatial relationships. Following the indications from previous research, indicating flood water delivery as the main source of plastic particles in floodplain soils, this shared source and the comparable transport behavior could also explain the spatial connections (Lechthaler et al. 2021; Weber et al. 2021c).

3.4.4.2 Pollution Sources and Interactions

Assuming the same sources and deposition conditions for both contaminants in flood- plain soils, the question arises as to whether this only applies to the river and floodplain area, or also to the wider catchment area, and whether and how these contaminants interact. In contrast to plastics, heavy metals are a natural component of river and floodplain sediments, expressed by the natural and thus geogenic background contents (Bridge 2003; Kabata-Pendias 2011). In case of the Lahn River catchment, the regional geology, which includes rocks of the Rhenish Slate Mountains (Devonian and Carboniferous), Triassic sandstones, and Tertiary volcanic rocks, provides a high spatial variation of geogenic metal contents (Friedrich und Lügger 2011; Meschede und Warr 2019). Both contaminants, metals and plastic, have the characteristic that they can be introduced anywhere within the catchment area. In contrast to heavy metals, which have been entering the environment for a long time mainly through human use, whether through mining or industry, the situation is different for plastics (Zalasiewicz et al. 2016).

Plastics, as polymers, were first developed by humans in the last 100 to 120 years, whereby global plastic production first began in the 1950s (Andrady 2017; Zalasiewicz et al. 2016). Thus, plastic particles, regardless of their input pathway, have only been able to enter the environment and, thus, river systems and floodplains for about 70 years. The steady and exponential growth of global plastic production makes it likely that large quantities of plastic have only recently been released into the environment (PlasticsEurope 2018). The short time span in which plastic can enter the environment is also expressed in the accumulation of plastic particles in the upper floodplain soil layers and has already been discussed by Weber et al. (2021). Since the findings demonstrate that this accumulation also partially applies to heavy metals, it may suggest that the current sources of metals and plastics could be identical. With respect to the environmental and landscape properties of the Lahn River catchment sources, such as urban areas (and especially urban wastewater) (Tibbetts et al. 2018), traffic (e.g., tire abrasion: plastic; brake abrasion: heavy metals) (Manta et al. 2002) or agriculture (Yu et al. 2020; Yu et al. 2021) are able to release both groups of contaminants into the environment and the fluvial system of the Lahn River.

In addition to the environmental sources described above, heavy metals can also originate from the plastic particles themselves (Hahladakis et al. 2018; Catrouillet et al. 2021). The results show that all metals analyzed were present in the investigated macroplastic and coarse microplastic particles. Previous research in the aquatic as well as in the terrestrial environment has shown both phenomena – the adsorption of metals from the surrounding environmental medium and the release of additive metals (Holmes et al. 2012; Imhof et al. 2016; Yu et al. 2021; Catrouillet et al. 2021). Despite the unmanageable number of additives in plastic production, some of the notable concentrations from the results could perhaps originate from such additives. The comparatively high contents of Zn can be attributed to inorganic flame retardants or slip agents, for example (Hahladakis et al. 2018).

In addition, the highest total contents of metal load within plastic particles was detectable within two CSM (chlorosulfonated polyethylene) particles, a polymer type that obtains its special properties through vulcanization with metal oxides (e.g., lead(II) oxide or zinc oxide) (Happ et al. 2000). A statement about the adsorption on plastic particles is not possible due to the given methodological limitations based on digestion method. The presence of heavy metals in the surrounding soil matrix from which the plastic particles were isolated would make adsorption processes possible. Previous studies have shown that adsorption is metal- specific, concentration-dependent, and promoted by degraded particle surfaces (Verla et al. 2019; Yu et al. 2020). The accumulation of plastic held in the upper soil layers in combination with mostly degraded or highly weathered plastic particles would thus promote adsorption of the metals, but also promote their release through degradation of the particles (Verla et al. 2019). Significant correlations between Ptot and organic matter in the upper soil layer (r_{sp} 0.32) and between the pollution load index and the organic matter content (r_{sp} 0.62) could furthermore indicate the influence of the presence of plastic, resulting in an increase within the organic-bound metal fraction (Yu et al. 2020).

3.4.4.3 Risk Assessment

The main difference between plastic particles and heavy metals in terms of their environmental risk is that comparatively little is known about the actual risk posed by plastic contamination. In general, it should be clear that plastics, in contrast to metals, do not have any benefit or use within the environment, as they are anthropogenic foreign objects in soils, sediments, or water. Metals, on the other hand, are partly essential (e.g., Fe, Co, Cu, Ni) for all organisms (Alloway 2013). However, excessive concentrations in combination with toxic metals (e.g., As, Cd) lead to a wide variety of potential risks for ecosystems, organisms, soil functions, and ultimately human health (Alloway 2013). Common practices for risk assessments of heavy metal pollution in soils are based on different exposure pathways, exposure times, and potential doses as well as on national legislation values considering those factors (Alloway 2013; Bund-/Länderarbeitsgemeinschaft Bodenschutz (LABO) 2003; Bundesregierung 1998). The early state of plastic research, especially in soils, has so far not resulted in limit values or other legislation on maximum levels of plastic in soils (Bundesregierung 1998; Kabata-Pendias 2011). Likewise, long-term monitoring of heavy metals in soils often provides geochemical background values for comparison (Kabata-Pendias 2011). These cannot be determined in the case of plastic contamination, as the geogenic background content of plastic in soils must be zero due to its purely anthropogenic origin.

Against this background, the results of the present study show that in floodplain soils, a low-to-moderate risk can be expected solely by heavy metal enrichment. Legal precautionary levels are exceeded only very singularly by contents of Cr, Cu, Ni, and Cd, whereby no spatial hot spots can be identified (Table 7). The calculated pollution indices demonstrate a low-to-moderate enrichment or severity (Ef, CSI), but a general deterioration of soil quality (PLI) and a strong ecological risk (RI).

Even if the calculated indices are limited by the introduced comparative values, the data basis (341 samples) of the regional background values in floodplain soils can be assessed as comparatively good.

Furthermore, floodplain soil properties indicate a rather low mobility, since both the high contents of organic material and the widespread hydromorphic conditions (groundwater influence) promote the binding of the metals to humus complexes as well as to Fe-Mn oxides (Blume et al. 2016). As the floodplains are mostly used for agriculture, these risks exist for the soil–crop impact pathways, but also for the soil–groundwater pathway due to heavy metal enrichment up to a depth of 2 m (Bund-/Länderarbeitsgemeinschaft Bodenschutz (LABO) 2003; Bundesregierung 1998). However, as the levels are low in contrast to the excessive contamination found in the direct surroundings of industrial plants and military sites, or in anthropogenic and urban soils in general, the basic environmental risk from metals alone can be assessed to be low (Alloway 2013; Kowalska et al. 2018).

Remembering the restrictions on assessing the risk of plastic contamination, it can only be argued that the widespread presence of plastic particles in floodplain soils down to a depth of two meters and the accumulation in upper soil layers form the potential for possible risks. The variety of possible risks was discussed in a wide range of reviews (Andrady 2017; Xu et al. 2019; Kowalska et al. 2018). However, for the area of floodplain soils, the following contamination pathways should be pointed out in particular: As in the case of heavy metals, microplastics, especially those of small particle size, can be taken up by plants and organisms, which can ultimately lead to their uptake into the human food chain (Rillig et al. 2017b; Rillig et al. 2019; Ragusa et al. 2021). Evidence of microplastics in human excrement or even in placentas suggests that consequential risks from plastic itself (foreign bodies) or additives are possible (Ragusa et al. 2021). Furthermore, floodplains are important ecosystems and, in some cases, important agricultural areas due to their fertile soils. Therefore, all risks that affect soil fertility or soil functions (e.g., influence on soil aggregates, C-dynamics) should not be neglected, even if they cannot yet be conclusively assessed (Xu et al. 2019; He et al. 2018b; Hurley und Nizzetto 2018). Finally, floodplains assume important functions as flood retention areas but also as filters for groundwater, and they play an important role in global water cycles. The indication of a mobile microplastic fraction in floodplain soils (Weber et al. 2021c) and the general mobility of heavy metals in soils (Calmano et al. 1993) can, therefore, also pose a risk for groundwater and, thus, for drinking water. If both contaminants are now combined in a joint risk assessment, it can be stated that both pollutants alone can represent environmental risks, especially in soils, along different pathways. As already indicated by other studies, both contaminants seem to lead to combined effects through mutual influence (adsorption and desorption processes) or the influence on critical environmental drivers that control the degree of contamination (e.g., OM, DOC, and pH as factors for the chemical behavior of metals) (Verla et al. 2019; Yu et al. 2020). The spatial correlation of both pollutants in floodplain soils with the same sources, transport, and deposition conditions, as shown by the results presented here, could further enhance such a tandem interaction of the pollutants.

Although Martin (2012) observed a decrease in heavy metal concentrations at riverine sites of the Lahn, the enrichment of upper soil layers could also lead to further endangerment in the future. Under climate change, an increase in heavy rainfall events followed by more severe floods is predicted for Central Europe (Masson-Delmotte 2018). Stronger floods with increased side or bank erosion could lead to the remobilization of both contaminants, as well as further transport and effects in other ecosystems.

3.4.5 Conclusions

Based on our geospatial research approach and with regard to the study objectives, we were able to demonstrate the presence and spatial distribution of heavy metals and plastic particles in floodplain soils. Furthermore, we were able to detect spatial correlations between both contaminants in the studied floodplain soilscapes. Those spatial correlations can be expressed by a comparable variability in concentrations across the catchment and in an accumulation in upper soils (0–50 cm). Furthermore, macro- and coarse microplastic particles were also found to contain heavy metals of adsorbed or additive origins. The spatial correlations are indicative of similar pathways of release, transport, and deposition of both contaminants in floodplain depositional systems. In terms of the evaluation and assessment of the spatial relationships found, however, there is a lack of comparative data. Therefore, more quantitative studies considering plastic concentrations in soils and floodplain systems should be conducted using comparable and standardized methods.

In particular, improvements can be made in the analysis of heavy metals or plastic particles from the environment. In contrast to the method used here with a nearly complete digestion of the particles, different digestion protocols should be used in the future. These offer the advantage that, depending on the strength of the digest used, a distinction between adsorbed and additive metals in plastic particles and, if necessary, different adsorption rates can be documented in order to establish a better correlation with metal contents in the surrounding soil matrix. More research is needed to understand the chemical and physical relationships between plastic particles and heavy metals, as well as to assess the environmental impacts and hazard potential of plastics and microplastics. As with “recognized” pollutants, only a scientific basis can provide a foundation for the introduction of limit values based on laws and management strategies.

Finally, we encourage further and deeper research at this interface between terrestrial and aquatic ecosystems, whose soil landscape is subject to dynamic processes. In particular, with regard to the presence and spatial relationships of plastics and heavy metals, these could also be present for other pollutants (e.g., organic pollutants). Further research should, therefore, initially focus on the following points:

- Quantitative spatial assessment of plastic and heavy metal contaminations in different floodplains and river systems.
- Consideration of heavy metals in different chemical bonds and analysis of adsorbed and additive metals in order to draw conclusions about the sources and interactions.
- Examination of contaminants in both soil water (pore water) and groundwater in order to better understand their mobility and possible associated risks.

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3.5 Meso- and microplastic distribution and spatial connections to metals of interest contaminations in highly cultivated and urbanised floodplain soilscapes – a case study from the Nidda River (Germany)

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Abstract

Floodplain soilscapes act as temporary sinks in the environment and are nowadays affected by multiple contaminant accumulations and exposures, including metals of interest and plastics. Despite increasing knowledge of the occurrence and behaviour of plastics at the interface between aquatic and terrestrial systems, there are still major uncertainties about the spatial distribution of plastics, their sources and deposition, as well as spatial relationships with other contaminants. Our recent case study addresses these questions, using the example of a river system ranging from rural to urban areas. Based on a geospatial sampling approach we obtained data about soil properties, heavy metal contents via ICP-MS analyses, and particle-based (171 µm – 52 mm) plastic contents, analysed using sodium chloride density separation, visual fluorescence identification and ATR-FTIR analysis. We found plastic contents of 0.00–35.82 p kg^{-1} and heavy metal enrichment (Enrichment factor 1.1–5.9). Levels of both contaminations occur in the lower range of known concentrations within floodplain soils and show a different spatial distribution along the river course and in the floodplain cross-section. Furthermore, we found that plastic enrichment occurs in the uppermost soil layers, while heavy metal enrichment is located at greater depths, indicating different sources and deposition periods. Finally, direct short to long-term anthropogenic impacts, like floodplain restoration or tillage may affect plastic enrichments, raising questions for future floodplain management regarding contamination assessments.

Keywords

Plastic; Heavy metal pollution, Wetland, Soil, Fluvial, Density Separation

3.5.1 Introduction

After an initial half-decade of investigating plastic contamination in terrestrial environments, and with increasing progress in the development of suitable analytical methods, it has become clear that our soils contain far more plastics than perhaps previously assumed (Qi et al., 2020; Zhang et al., 2020). After plastics were detected in soils of different soilscapes, from highly cultivated to semi-natural soilscapes (Qi et al., 2020; Koutnik et al. 2021), whether microplastics can be found in soils, appears no longer to be the major question. Rather, the question now is about where, and to what extent, high concentrations of plastics can be found, what spatial differences exist and what the reasons are for different susceptibility levels of soils to plastics?

When talking about plastics in soilscapes, there are various definitions and size classifications resulting from the different research disciplines dealing with plastic contaminations in the environment (Hartmann et al., 2019). Plastics in the environment can be defined as solid and insoluble, polymeric or co-polymeric, human-made particles that are produced (primary form) or fragmented by biogeochemical and physical processes (secondary form) to a certain size range (Bancone et al., 2020; Andrady, 2017). Microplastics (MP) are currently defined according to ISO/TR 21960:2020 as particles with a size between 1 µm and 1000 µm (International Organisation for Standardisation, 2020). Additionally, particle size-based distinctions can be made between nanoplastics (<1 µm), large microplastics (1–5 mm), coarse microplastics (2–5 mm), meso- (>5 mm) and macroplastics (>25 mm) (Hartmann et al., 2019, Weber and Opp, 2020). Furthermore, plastics as environmental contaminants can be distinguished from other contaminants, like metals of interest (potentially environmentally harmful metals), through their recent occurrence and the absence of geogenic background levels (Zalasiewicz et al., 2016).

Potential impacts from plastics in general, but especially MP particles on soils, comprise influences on soil structure, material balance, the release of pollutants or the uptake of plastics into the food chain (Wang et al., 2020). An assessment of possible environmental impacts of plastics requires knowledge about the spatial occurrence of plastics in soils, which is still largely lacking. Furthermore, dissolution of additives from plastics (e.g., metals of interest and plasticisers) which are partly persistent and toxic, or an accumulation of pollutants on plastics, could be observed in marine and terrestrial environments (Catrouillet et al., 2021; Hahladakis et al., 2018). Studies from marine and aquatic environments, as well as laboratory experiments, demonstrated that microplastics adsorb (e.g., Cu, Pb) or desorb (e.g., Cd, Zn) metals of interest (Munier and Bendell, 2018). For soil environments the adsorption of metals of interest, depending on polymer type and particle shape, was detected (Verla et al., 2019). Finally, the presence of MP in soils can influence the heavy metal behaviour, like a reduction of the exchangeable, carbonate-bound and Fe-Mn-oxide bound fraction, while increasing the organic-bound fraction of the metals (Yu et al., 2021). Therefore, we wanted to investigate spatial relationships of plastics and metals of interest within floodplain soilscapes.

Floodplains and their soils today are primarily characterised by a "human-natural entanglement" (Edgeworth, 2011), resulting in deposited legacy sediments, and are in a conflict of use through the diverse natural services and anthropogenic beneficial activities (e.g., flood retention versus construction or agricultural land). Due to their spatial location in an aquatic-terrestrial interface, floodplain soils are exposed to unique influences, and have been subject to the constant impact of natural and anthropogenic pollutants (e.g., lead, copper, PAHs) (Dudka and Adriano, 1997). For example, floodplain soils can act as an accumulation site for metals of interest, which are released in the catchment area in addition to geogenic contents by historical mining, industry or traffic (Lair et al., 2009).

Floodplains cover only 0.5–1% of Earths land area, but river networks contain a significant portion of global plastic demand (Nardi et al., 2019). As the semi-terrestrial part of fluvial transport corridors in the global plastic cycle, and with a dominant transport direction from land to sea, floodplains could have an important role as temporary transfer and deposition areas of plastics (Siegfried et al., 2017; Lechthaler et al., 2020; Kiss et al., 2021). Plastics can enter floodplain areas, and therefore floodplain soilscapes, through direct point or local inputs (e.g., littering, sewage sludge application on fields) (Corradini et al., 2019; Piehl et al., 2018) or diffuse, more spacious inputs like surface runoff (from slopes) (Rehm et al., 2021) or flood water delivery (Christensen et al., 2020; Weber and Opp, 2020). Incorporated plastics can accumulate in the youngest and uppermost floodplain soil layers due to sedimentation since the 1960s, or agricultural utilisation, but also reaches deeper soil layers through in-situ displacement (Weber and Opp, 2020; Cao et al., 2021). Plastic abundance in floodplain soils seems to have a clear drop with the soil depth (Cao et al., 2021; Weber et al., 2021), but a heterogenous lateral distribution. Christensen et al. (2020) found in some parts higher plastic loads in the floodplain than in the stream channel, which may relate to remobilisation of deposited plastics, and exports during floods at the river channel (Hurley et al., 2018; He et al., 2021). The lateral distribution has been linked to population density in the catchment (Scheurer and Bigalke, 2018), land use (direct input agriculture) (Cao et al., 2021) and vegetation (trapping) (Weber and Opp, 2020) as well as floods (sediment deposition) (Lechthaler et al. 2021, Christensen et al., 2020). Different levels of particle-based plastic loads have been documented in floodplain soils: in the Lahn River catchment (Hesse, Germany) Weber and Opp (2020) documented loads of 0.62–5.37 p kg^{-1} for mesoplastics (> 5 mm) and 0.31–8.59 p kg^{-1} for coarse microplastics (2–5 mm), while Weber et al. (2021) report loads of 0.36–30.46 p kg^{-1} with a size of 219.0–8,321.0 µm (NaCl separation), where the mean size was 1171 µm and only a few particles occur with a size >2000 µm. A further study from Germany, investigating the Inde River (North Rhine Westphalia) documented average loads between 47.9 p kg^{-1} (depth profiles) and 25.4 p kg^{-1} (topsoils) for microplastics with a size between 500 and 5000 µm (canola oil extraction) (Lechthaler et al., 2021).

Christensen et al. (2020) found 23–330 p kg^{-1} in proximal floodplain topsoils (0–4 cm) of three rivers in Virginia (US) with average sizes of 290–1160 µm (NaCl separation), and Cao et al. (2021) report concentrations of 4.94–252.70 p kg^{-1} (5.0–0.1 mm, NaCl separation) down to 80 cm in intensively utilised agricultural soils of the lower Yangtze River floodplain (CHN).

Floodplain soils provide important ecosystem services like the retention of flood waters, filtration and groundwater formation, and not least as a fertile site for food production. In the meantime, it is becoming increasingly apparent that a wide variety of soil functions, and thus ecosystem services, could be affected by plastic particles in soils (Selonen et al., 2020; Wang et al. 2020). Therefore, knowledge about the spatial distribution, the identification of hotspots in soilscapes, and the natural and anthropogenic processes responsible for them, are indispensable for future risk assessments.

Furthermore, from a scientific perspective, the abundance of plastics in river sediments, both in and outside the stream channel, could also allow the study of recent sedimentary deposition processes based on plastic dating (Lechthaler et al., 2021; Turner et al., 2019). Thus, the temporal component of plastic deposition will be investigated based on polymer specific ages of possible earliest occurrence according Weber and Lechthaler (2021).

Against the background of current research on MP in floodplain soils, and the still open questions on the origin, spatial distribution, and interrelationships with other pollutants, this case study was conducted in a study area that is subject to a wide range of human impacts. The floodplains of the Nidda River and its catchment area can be considered very representative of Central European river basins due to the gradient from the rural upper reaches over agricultural heartland to the highly urbanised lower reaches. Furthermore, the associated land use, possible point and diffuse plastic sources and the conflicts arising around the floodplain and watercourse management, are also comparable to many intensively utilised floodplain areas. As the sink function of floodplains and depositional dynamics are already well studied for so-far recognized contaminants like metals of interest, a combined consideration of recognized metals and the new contaminant plastics, will be performed.

Regarding the predominant catchment and soilscape properties, we aim to investigate the following aspects and related issues at the aquatic-terrestrial interface:

1. Occurrence of plastics in floodplain soils with regard to spatial and temporal contexts, proving the hypothesis that the river course has a minor role in contrast to other factors (e.g., distance to the river), in spatial plastic distribution.
2. Relationships between plastics concentration and fluvial depositions, based on grain size and stratigraphy, proving the hypothesis that plastics enter floodplain soilscapes primarily through fluvial deposition.
3. Spatial relationships between metals of interest and plastics against the background of contamination patterns, proving the hypothesis of spatially distinct contamination patterns due to different contamination periods.

3.5.2 Methods

3.5.2.1 Study area

The Nidda River, with a length of 89 km, and its catchment with a total area of 1,942 km², are located in the Wetterau basin as part of the Hessian Depression in central Germany (Figure 42) (Lang and Nolte, 1999). In combination with a typical Central European climate and very fertile soils due to the loess accumulation, the Wetterau is an important cultural landscape, which has been inhabited and cultivated almost continuously since the early Neolithic period (Kühn et al., 2017; Jockenhövel, 1990). This long-lasting cultivation and deforestation also influence the soilscapes of the catchment area. While the upper reaches and upland positions are dominated by Cambisols developed in periglacial solifluction layers (basalt), the remaining catchment area is dominated by soils developed on loess (Luvisols, Regosols, relictic Chernozems, Stagnosols) (Kühn et al., 2017).

The floodplains of the Nidda River first appear after leaving the Vogelsberg (headwaters) and progressively expand with the river course; they consist mainly of Fluvisols (fine-grained Holocene flood loam and colluvial deposits) and partly of Gleysols and Stagnosols (Table 9). Floodplains, except for the direct riparian zones, are often cultivated as crop land, meadows and pastures. Large parts of the floodplains are part of a landscape conservation area for the protection of wet meadows and near-natural floodplain areas. However, the amount of land used for residential development and infrastructure facilities is also increasing, reaching a high level in the Frankfurt metropolitan area, and restricts near-natural or just cultivated floodplain areas severely.

The Nidda River itself, as a spatial connection through the basin landscape, can be classified as a medium-sized stream system with six major tributaries (Figure 42). Located in the cultural landscape, the stream is influenced by intense industrial and agricultural activities, including six industrial and municipal wastewater treatment plants in its course, and river engineering for flood protection (Brettschneider et al., 2019; Schweizer et al., 2018) (Figure 42). Today's land use along the Nidda River changes from a rather rural environment in the upper reaches (population density: 72 people km², settlement and traffic area: 10.6 %) to a heavily cultivated agricultural heartland in the middle reaches (population density: 282 people km², settlement and traffic area: 16.1 %), to the highly urbanised lower reaches in the Frankfurt metropolitan region (population density: 3077 people km², settlement and traffic area: 58.6 %) (Hessian State Statistical Office, 2021).

Table 9: Sampling site features with soil and soilscape properties.

Transect sites	**Catchment properties**			**Sampling points**	**Floodplain properties**			**Soil properties**			**Soilscape descritpion**[d]
	Catchment zone	River km[a]	Flood area (m)[a]		Morphological unit	Land use	Channel distance (m)	Soil type (WRB[b])	Horizont frequence[c]	Soil textures[c]	
NID	upper middle reaches	62.5	520.5	NID-1	backswamp	grassland	447.9	Fluvic **Gleysol** (Clayic)	Ahl-Bl-Br	SiCL and SiC	Very fine-grained fluvial soils under strong groundwater influence and enrichment of limnic layers (peat)
				NID-2	riparian plane	grassland	35.5	Endogleyic **Fluvisol** (Siltic, Clayic, Limnic)	Ah-B-Bl-Blr-Br-Lhr	SiL and SiC	
MOK	middle reaches	55.0	861.2	MOK-1	backswamp	grassland	859.7	Fluvic **Gleysol** (Siltic, Limnic)	Ahl-Blr-Br-Lhr	SiC and C	Fine-grained fluvial soils under groundwater and stagnig surface water influence and partial enrichment of limnic layers
				MOK-2	plane	grassland	467.0	Endogleyic, Endostagnic **Fluvisol** (Siltic, Limnic)	Ahg-Bgl-Bgr-Br-Lr	SiC and C	
				MOK-3	riparian	grassland	28.4	Epigleyic **Fluvisol** (Siltic)	Ah-B-Bl-Blr-Br	SiL	
OKA	upper lower reaches	35.5	777.5	OKA-1	backswamp	grassland	532.2	Endogleyic, Endostagnic **Fluvisol** (Siltic)	Ah-Bgl-Blr-Br	SiCL and SiC	Fine-grained fluvial soils under groundwater and stagnig surface water influence with partial anthropogenic influence (artefacts)
				OKA-2	plane	cropland	315.2	**Fluvisol** (Antric, Siltic)	Ap-B-Bgu-Bl-Blr	SiCL and SiL	
				OKA-3	riparian	cropland	23.0	**Fluvisol** (Antric, Siltic)	Ap-B-Bl-Br	SiL and SiC	
FRA	lower reach	2.0	427.0	FRA-2	plane	grassland	203.4	Endogleyic **Fluvisol** (Silitc)	Ah-Apb-B-Bl-Brl-Br	SiL and SL	Fine-grained fluvial soils partial under groundwater influence and strong anthropogenic urban influence
				FRA-1	plane	grassland	21.4	Fluvisol (Silitc)	Ah-B-Bl-Blr-Br	SiL	

[a] according to WRRL-Viewer Hesse (2021); [b] World Reference Base for Soil Resources (2015); [c] according to Guidelines for soil description (FAO, 2006); [d] according to the soil profiles presented here and preliminary survey of the wider sampling site environment

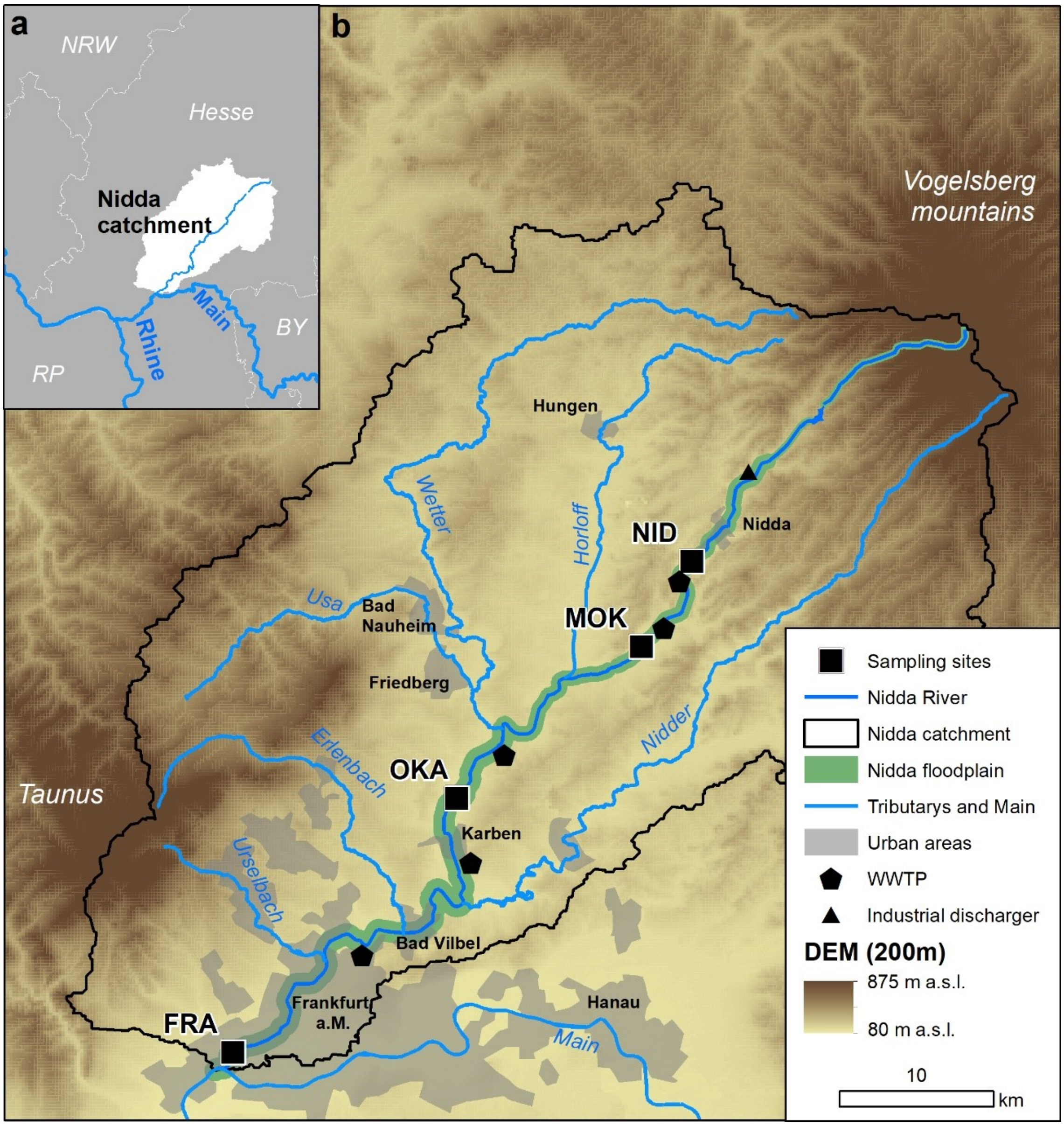

Figure 42: a: General map showing the location of the Nidda catchment in Germany. b: Nidda catchment with tributaries, transect locations and urban areas with location of wastewater treatment plants (WWTP) and industrial dischargers along the Nidda River. Data source: NUTS 2021 (© EuroGeographics for the administrative boundaries), WISE Large rivers (© European Environmental Agency), Digital terrain model 1 (© Hessian Administration for Soil Management and Geoinformation) and urban areas (© OpenStreetMap contributors 2021. Distributed under the Open Data Commons Open Database License (ODbL) v1.0.). Detailed maps of transect sites and elevation profiles can be found in Figure A 21.

Flood events under the hundred-year flood level (<HQ100) occur frequently between December and February in flood retention areas along the river course, with a total area of 44.8 km² (Regional Council Darmstadt, 2015). Flood protection measures, such as dams, widening of the cross-section, or flood retention basins in the catchment area, have been constructed since the 1920s and have been continuously expanded (Regional Council Darmstadt, 2015).

Nevertheless, ten high flood events with a discharge > 25.7 m³ s^{-1} for the gauge Nieder-Florstadt (ID: 24830050, between sampling sites OKA and FRA) occurred between 1967 and 2011, showing an average discharge of 28.2 m³ s^{-1} (max: 37.6 m³ s^{-1} in 1981), average discharge rate of 53.4 l (s $km^2)^{-1}$ and an average water level of 308 cm (max: 343 cm in 1981) (Regional Council Darmstadt, 2015). The average discharge during flood events exceeds the long-term middle discharge (MQ) of 3.0 m³ s^{-1} by 9.4 times.

Due to the natural environmental conditions, as well as the utilisation and anthropogenic influences, the Nidda River is part of a very characteristic catchment system, and comparable to many medium-sized rivers in central Europe. Intensive agricultural use, a high proportion of residential development and infrastructure, urban agglomeration in the lower reaches and diverse wastewater discharges, results in multiple possible point and diffuse (micro-)plastic sources, increasing along the river course.

3.5.2.2 Soil sampling

The selection of sampling sites was carried out with the aim of implementing a geospatial approach (Weber et al., 2020) and identifying sites representative of the floodplain landscape and its different soilscapes as already introduced by Weihrauch (2019), as well as Weber and Opp (2020). The selection was carried out with the help of a preliminary evaluation of geodata (aerial photos, geological map, soil map, morphology) and the following conditions: each sampling site a) must be representative of a stretch of watercourse with typical soil formations and landscape characteristics (Weihrauch, 2019), b) must be located in the designated floodplain (10–100 year flood events), c) should not be located in close proximity to potential MP point sources (e.g., garbage dump, sewage plant), and d) should be free of interruptions (infrastructure, dams) in the floodplain cross-section (Weber and Opp, 2020). Furthermore, each site should consist of a clear structure of floodplain morphology including levee, inactive flood channels and backswamp (Weber and Opp, 2020)

In contrast to other catchments, the anthropogenic utilisation and land use in the Nidda catchment was the major restriction for the identification of suitable sampling sites. Except for the headwaters, where no floodplain can be found due to narrow valley morphology, there are still four areas in the middle and lower reaches of the Nidda that show a floodplain width of 400–900 meters (on one side) and have not been dammed excessively. In these areas, which are part of the protected landscape area “Floodplain Association Wetterau,” four transect locations were selected after a preliminary soil survey, in order to represent the floodplain cross-section (Figure 42). Each transect location can be reached by annual floods, and would be flooded by 50–200 cm (sites NID and MOK) or 1–100 cm (sites OKA and FRA) during a hundred-year flood (Regional Council Darmstadt, 2015). Furthermore, the transect locations are partly affected by river and floodplain renaturation measures.

Land use comparison based on satellite images from 1933 and 2020 show that arable land changed to grassland at the distal floodplain of site OKA, and floodplain renaturation is taking place at sites NID, MOK and FRA (Figure A 22, Figure A 23).

Finally, soil sampling was conducted during summer 2019 and 2020 at the river transect locations, using pile core driving with stainless-steel cores (diameters of 100 mm and 80 mm) down to a depth of 2 m. At each site, two (NID, FRA) or three (MOK, OKA) points were sampled, each localised in the proximal or distal floodplain area, with an additional third point in the central floodplain at sites MOK and OKA as the floodplains are wider there. Sampling points were numbered as 1 (distal), 2 (central) and 3 (proximal) at sites MOK and OKA, 1 (distal) and 2 (proximal) at site NID and 1 (proximal) and 2 (distal) at site FRA.

At each sampling point of the transect, two complete cores at a distance of 5 m from each other, were extracted, resulting in 20 cores (Table 9). Soil stratigraphy and pedogenesis were documented according to the FAO Guidelines for soil description (FAO, 2006), and classified according to WRB 2015 (IUSS Working Group, 2015) and German soil classification (Ad-hoc AG Boden, 2005). Samples were collected from the two cores with stainless-steel spatulas and pooled in the field according to fixed depth levels (10 cm sections in 0–0.5 m, 25 cm sections in 0.5–1.5 m and 50 cm section from 1.5–2.0 m), resulting in 10 composite samples per sampling point (total: 100 samples, 385.5–3,704.6 g dry fine earth per sample), and stored bioplastic bags, made from corn starch (biological origin) and biodegradable (Mater-Bi bags, BioFutura B.V., Rotterdam, Netherlands).

Additionally, plastics fragments on topsoil surfaces were sampled if a conspicuous amount of plastics could be found around the drill points (Piehl et al., 2018). Visible plastic fragments were collected in a 20 m^2 area around the drill points, by two people walking straight lines in parallel (four-eyes-principle), according to Piehl et al. (2018). Surface sampling area was prepared by means of a tape measure and measuring rods, while a rectangle with the extension of 4x5 m was measured and marked around the centre (drill point). This additional procedure was conducted at the OKA sampling site (points OKA-2 and OKA-3).

3.5.2.3 Laboratory analysis

Field fresh soil samples were immediately dried at 45°C within opened bioplastic bags for four days in a closed drying chamber. Subsequently the sample material was carefully mortared (ceramic mortar) to break down soil macro-aggregates, and dry-sieved through stainless-steel sieves (Retsch, Haan, Germany), covered with a stainless-steel plate, to the size fractions >5 mm (mesoplastics), >2 mm (coarse microplastics and rock fragments) and <2 mm (large microplastics and fine-earth fraction). The fine-earth fraction was afterwards homogenised in a stainless-steel bowl and divided via a rotary sampler (Retsch, Haan, Germany), to obtain representative sub-samples for soil parameter and metal analysis. Each fraction was stored in corn starch bags.

3.5.2.3.1 Soil parameter and metal analysis

The moisture content of representative sub-samples (<2 mm, average mass: 99.6 g) was determined by drying (105°C), and the content of organic matter (OM) was determined via loss of ignition at 550°C (DIN 19684–3:2000–08) and both were recorded as percentage by weight (wt%). Additionally, the pH was measured with a pH 91 electrode (WTW, Weilheim, Germany) in a 0.01 M $CaCl_2$ solution (m:V 1:2.5). Carbonate content was determined after reaction with a few drops of 3.23 M hydrochloric acid (HCl) according to Ad-hoc AG Boden (2005) and soil texture was analysed via the Integral Suspension Pressure Method (Durner et al., 2017) after the samples had been prepared according to DIN ISO 11277:2002–08. Soil textures were reported according to Guidelines for soil description (FAO, 2006) and individual shares of clay, silt and sand, in percentage by weight (wt%).

Pseudo-total concentrations of the metal Fe, the metalloid As and the metals of interest V, Cr, Co, Ni, Cu, Zn, Cd, Hg, Pb were determined from digests of 1 g prepared subsample with 20 ml aqua regia (12.1 M HCl and 14.4 M HNO_3; ratio 1:3; DIN ISO 11466:2006-12). Metal concentrations were quantified using inductively coupled plasma–mass spectrometry (ICP–MS; XSERIES 2; Thermo Fisher Scientific, Bremen, Germany) and system calibration with a certified multi-element standard solution (ROTI®STAR; Carl Roth GmbH, Karlsruhe, Germany). Each digest was measured three times and averaged, resulting in converted results given in mg kg^{-1}. Relative standard deviation (RSD) after threefold measurements, and detection limits resulting from the multiplication of the mean standard deviation of 10 repeated blank measurements by factor 3, were used for correction (Voica et al., 2012; Thomas, 2001).

3.5.2.3.2 Plastics and microplastics analysis

Plastics and microplastics analyses were carried out according to the method and application first published by Weber & Opp (2020) and Weber et al. (2021). Visual identification with naked eye, or the help of a magnifying glass, was conducted for macro- and mesoplastics (>5 mm) and with the help of a stereomicroscope (SMZ 161 TL, Motic, Hong Kong) for coarse microplastics (>2 mm) after dry-sieving. Potential plastic particles were cleaned (deionised water) (Jung et al., 2018), dried (45°C), photographed and stored in rim jars made of glass with PE-caps for polymer identification.

The total fine-earth fraction (<2 mm) with a sample mass between 94.0 and 3552.1 g (mean: 1295.3 g) and a related average volume of 1053 ml (250–2750 ml), was used to separate out microplastic particles (Figure S4). For this purpose, a density separation with the "MicroPlastic Sediment Separator" (MPSS) (Hydro-Bios Apparatebau GmbH, Kiel-Altenholz, Germany) under the application of a saturated and >300 µm filtered NaCl-solution (density adjusted to 1.2 g/cm³ and controlled by balance and aerometer) was performed. Density control, before and after separation, shows a range between 1.195 to 1.218 g cm³ with an average of 1.203 g cm³, at an average solution temperature of 19.47°C (Figure A 24). The sample solution was stirred for 60 minutes and then allowed to settle for 19 hours.

At the end of the separation time, the integrated ball valve was closed, and separated material was rinsed into glass beakers using filtered NaCl solution. Afterwards, the remaining sample material, consisting of organic material and potential plastic particles, was separated into the following size classes using stainless-steel sieves (Ø 75 mm, Atechnik, Leinburg, Germany), and filtered (>50 µm) deionised water: >1,000 µm, >500 µm and >300 µm. After sieving, the sieve residues were filtered via vacuum-filtration on cellulose filters (Ø 47 mm, LLG-Labware, Meckenheim, Germany), and then transferred to glass petri dishes (Ø 90 mm or 200 mm) by rinsing with deionised water and drying at 50°C for two days, according to Prume et al. (2021).

To differentiate between organic material and potential plastic particles, a Nile Red staining procedure (20 µg mL^{-1} Nile Red ethanol-acetone (1:1) solution, Sigma-Adlrich, Taufkirchen, Germany) was applied (Maes et al., 2017; Konde et al., 2020). Nile red solution was applied with the help of a pipette and spray bottle and stained for 10 minutes at 50°C in a drying chamber (Konde et al., 2020). Stained petri dishes were afterwards visually inspected systematically under a stereomicroscope (SMZ 161 TL, Motic, Hong Kong), with fluorescence setup (Excitation: 465 nm LED; Emissions 530 nm colour long pass filter: Thorlabs, Bergkirchen, Germany) and transmitted light (Prume et al., 2021). This approach allows the visual identification of plastic particles, but is disrupted by the fluorescence of natural organic components in the red fluorescence range (e.g., chitin shell ants, freshwater mussel fragments), so the exclusion of organic particles must be based on surface structure (e.g., cell structures) or, in case of uncertainty, by spectroscopic analysis. Each fluorescent, or other potential plastic particle, that shows no cellular or biologic structure and a clear and homogenic colour (Noren, 2012), was collected and individually stored in microplates (Brand, Wertheim, Germany). Each particle collected was then classified according to surface characteristics (particle type, shape, surface degradation, colour), photographed (Moticam 2, Motic, Hong Kong) and size measured (longest diagonal, Motic Images Plus 3.0, Motic, Hong Kong) (Hidalgo-Ruz et al., 2012; Noren, 2012).

Polymer type identification for a) previously visually determined mesoplastic to coarse microplastic particles, and b) microplastic particles identified via staining-fluorescence procedure, was performed using the Tensor 37 FTIR spectrometer (Bruker Optics, Ettlingen, Germany) combined with a Platinum-ATR-unit (Bruker Optics, Ettlingen, Germany). Measurement was carried out using 20 background scans followed by 20 sample scans for each sample, with a resolution of 4 cm^{-1} in a wavenumber range from 4,000 cm^{-1} to 400 cm^{-1} (Jung et al., 2018; Primpke et al., 2017; Primpke et al., 2018). The ATR-unit used is the limiting factor for the lower size limit of the particles determined in this study, since particles with a size <300 µm have insufficient contact area and are difficult to handle (Weber et al., 2021).

3.5.2.3.3 Contamination prevention

To prevent contamination of the samples with additional plastic particles, the use of plastic equipment in the field and laboratory was avoided. All devices used were made of glass, ceramic or stainless steel. All equipment was thoroughly rinsed with filtered water (>50 µm) after each use, and only filtered NaCl solution (>300 µm) and deionised water (>50 µm) was used. Corn starch bags were used for sample storage and transport, and their spectrum (ATR-FTIR) was compared with all identification spectra for contamination control through potential abrasion from the sample bags used. Furthermore, the sample material was kept under cover whenever possible and cotton lab coats were used to avoid air contamination by synthetic fibres.

During microplastic separation and subsequent analysis steps, control for possible sample contamination was done by means of five blank samples randomly applied during the separation runs. In four of the five blanks, five fragments with an average size of 294.9 µm ± 79.15 µm (SD) (B1: 3 fragments, B2: 1 fragment, B3: 1 fragment) and one filament (B4, length: 449.4 µm) were found via the staining-fluorescence procedure (examples given in Figure A 25). The particles found in blank samples were too small or too degraded for polymer identification by ATR-FTIR. Blank control resulted therefore in an error of 1.2 particles per separation run or sample, but in a particle size below the determination limit of 300 µm, except one single fragment and filament. The calculated concentrations were therefore not adjusted.

3.5.2.3.4 Statistics and data evaluation

Data processing, basic statistical operations and data visualisation operations were conducted using Microsoft Excel (version 1808, Microsoft, Redmond, USA) or RStudio (version 1.3.1093, RStudio, PBC, 2020) within an R environment (version 4.0.3, R Core Team, 2020). Data processing of FTIR spectra was performed in OPUS 7.0 including atmospheric compensation and baseline correction (concave rubber band method) (Bruker Optics, Ettlingen, Germany) and in Spectragryph (Version 1.2.14; Menges, 2020; Oberstdorf, Germany). Spectra identification of pre-processed spectra was done via the OpenSpecy database using full spectra, and Pearson's r with $r^2 > 0.6$ as match quality indicator (Cowger et al., 2021). Spatial data was processed in ArcGIS (ArcMap version 10.8, Esri 2019, West Redlands, CA, United States).

In order to allow an effective assessment of spatial contamination differences between plastics and metals of interest, we calculated the heavy metal "Pollution load index" (PLI) based on "single pollution index" (PI) according to Kowalska et al. (2018) following Eq. (2) and Eq. (3):

$$PI = \frac{\mathrm{HM}}{\mathrm{GB}} \tag{2}$$

$$PLI = \sqrt[n]{PI_1 x\, PI_2 x PI_3 x PI_n} \tag{3}$$

where HM is the concentration (mg kg^{-1}) of individual metals of interest (V, Cr, Co, Ni, Cu, Zn, Cd, Hg, Pb) and the metalloid As, and GB is the geochemical background concentration, calculated for the individual metals (V: 38.25 mg kg^{-1}, Cr: 25.0 mg kg^{-1}, Co: 8.75 mg kg^{-1}, Ni: 24.0 mg kg^{-1}, Cu: 13.25 mg kg^{-1}, Zn: 58.5 mg kg^{-1}, Cd: 0.14 mg kg^{-1}, Hg: 0.04 mg kg^{-1}, Pb: 27.0 mg kg^{-1}, As: 8.0 mg kg^{-1}) based on the average values from 341 soil samples (64 floodplain silt substrates, 277 floodplain sand substrates) from Hessian floodplain soils (Friedrich and Lügger, 2011). In addition, the "Enrichment factor" (EF) was calculated in order to measure the potential impact of anthropogenic metal pollution against geogenic background contents (Kowalska et al., 2018) following Eq. (1):

$$EF = \frac{\left[\frac{HM}{LV}\right]sample}{\left[\frac{HM}{LV}\right]GB} \tag{1}$$

where HM is the concentration of individual heavy metal and LV the reference content of Fe concentration (mg kg^{-1}). Index values were also evaluated according to Kowalska et al. (2018) for PLI levels around 1 as "only baseline levels of pollution" and >1 with "deterioration of soil quality", and for EF with "deficiency to minimal enrichment" at values <2 and "moderate enrichment" at values between 2–5.

Plastic loads were documented as particles per kg soil dry weight (p kg^{-1}), including the total number of sufficient ATR-FTIR identified particles per sample (sample mass 94.0 to 3552.1 g). From 263 particles, previously identified visually (>2 mm, coarse soil fraction) or via staining-fluorescence procedure, 35 particles (13.31 % of all collected particles) were identified as natural organic matter with an R^2 between 0.77 and 0.96 for the spectra correlation by the OpenSpecy database. These organic particles were excluded from the entire data evaluation, which means that 228 particles are counted and evaluated as sufficiently ($r^2 > 0.6$) identified as plastics. Ages of possible earliest occurrence (EPO age) were assigned to the particles identified based on the year of polymer development or start of production, according to Weber and Lechthaler (2021). In the case of identified rubber particles, EPO age were differentiated between natural (EPO: 1820) and synthetic (EPO: 1910) rubbers. Plastics identified as polymers grouped as rubbers or resins were summarized within the respective group. Macro- and mesoplastic loads on soil surfaces from sampling at site OKA were reported as particles per square meter (p m^2).

All data collected do not display a normal distribution (Shapiro-Wilk test) and, in some cases, show significant differences in variance by group. Normality and homoscedasticity of the residuals was checked graphically within R, showing no significant variance differences. Comparison of means was carried out using the Wilcoxon test or Kruskal-Wallis test, using R standard functions. Data visualisation was conducted with R standard functions (R Core Team, 2020), "ggplot2" (Wickham, 2016: https://ggplot2.tidyverse.org) and "corrplot" (Wei and Simko, 2017: https://github.com/taiyun/corrplot).

Spearman correlation was performed with a significance level of $p \leq 0.05$, and correlation coefficients were interpreted as: weak (r_{SP} 0.4 – <0.6), clear (r_{SP} 0.6 – <0.8), and strong (r_{SP} >0.8). Plotting and evaluation of three-dimensional data was carried out using the package “plot3D” (Soetaert, 2019: https://CRAN.R-project.org/package=plot3D) and additional multiple linear regression model.

3.5.3 Results

3.5.3.1 Plastic loads and features

In the floodplain soils along the Nidda River, plastic particles were found at each transect site and sampling point, resulting in a positive rate of 73 % of all samples (n = 100) which contain plastics. In each sample 0 to 20 particles (average: 2.64 particles, SD: 3.49) were found; while overall concentrations ranged from 0 p kg^{-1} up to a maximum of 35.82 p kg^{-1}, with an average of 3.23 p kg^{-1} (± 1.75 p kg^{-1} RSD, n = 100). Samples containing no detectable plastic particles occur mainly at depths > 75 cm, whereas higher concentrations can be found in the upper 30 cm of each soil column (Table 10).The extracted and identified plastic particles appeared as films (45.8 %) and fragments (38.3 %), or as filaments, pellets and foams (Figure 43b), with weathered (49.0 %), fresh (28 %) or incipient alteration (23.0 %) surface structures. The shape composition consists of irregular (71.0 %), regular (25.0 %) or rounded (4.0 %) shapes; particle colour is often transparent or white (49.0 %), or bright red (16.0 %), blue (9.0 %) or pink (8.0 %), followed by different colours with an individual share ≤ 6.0 % (e.g., black, orange, yellow).

Polymer type composition is dominated by low- and high-density polyethylene (LDPE and HDPE) making up 46.0 %, followed by polypropylene (PP, 10.0 %), rubbers (9.0 %), chlorinated or chlorosulfonated polyethylene (CPE, CSM, 7.0 %) and polyethylene terephthalate (PET, 6.0 %) (Figure 43a). All identified polymers show a density of ≤ 1.2 g cm^3 in pure form, except PET with 1.37 g cm^3 (Cutroneo et al., 2021), which was thus only recorded semi-quantitative based on the density separation method with NaCl.

Plastic particles in the coarse soil fraction (>2 mm) occur in a size range between 2.1 mm and 52.0 mm, with an average of 20.68 mm (Figure 43c), while in the fine soil fraction (<2 mm) particle size ranges between 171.0 µm and 1680 µm with an average of 598.6 µm and a clear accumulation of outliers over 1000 µm (Figure 43c).

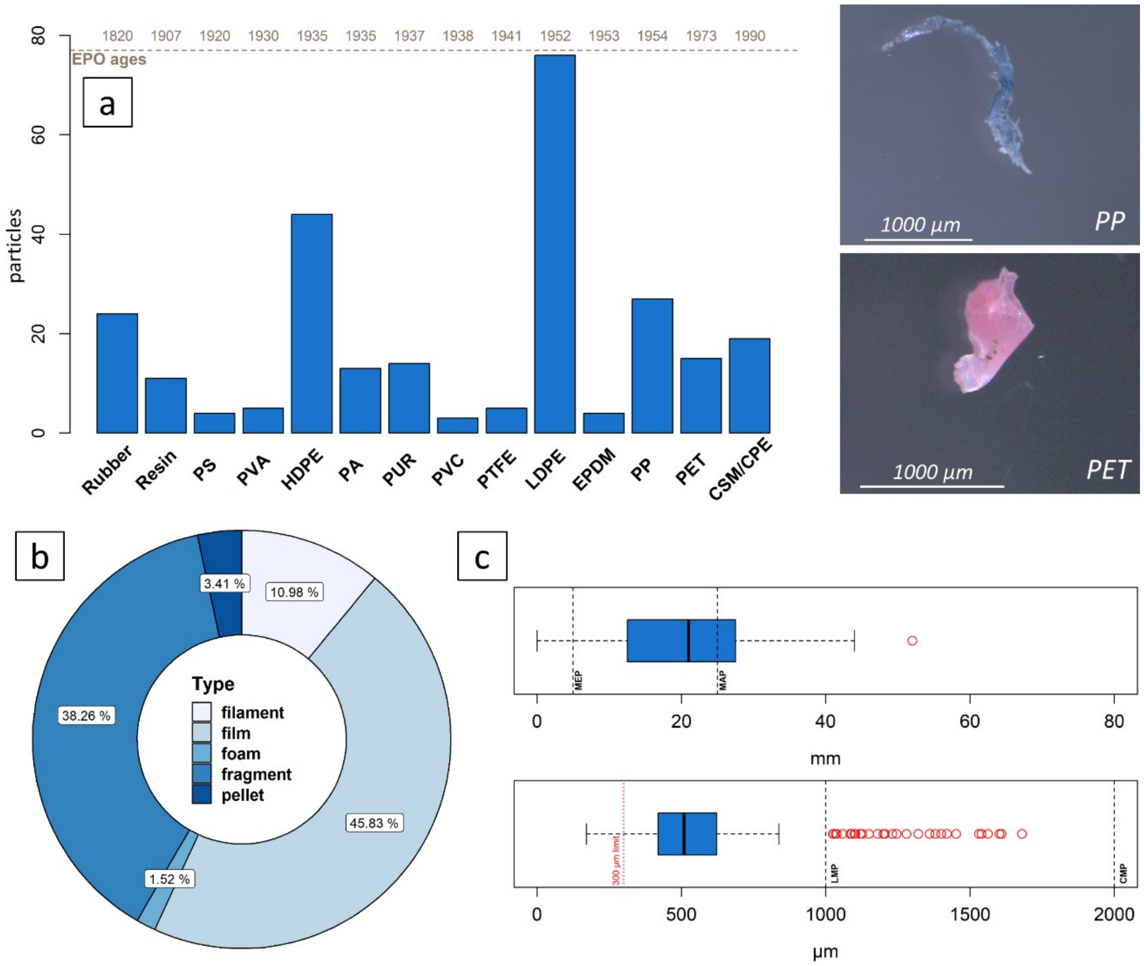

Figure 43: Particle feature composition. a: Number of identified polymer types (n = 228) sorted by age of earliest possible occurrence (EPO ages) with example of a blue PP film and pink PET fragment (Polymer type abbreviations explained in Table S2); b: Particle type composition (n = 228); c: Particle size composition for particles in coarse soil fraction (>2 mm) (upper boxplot, n = 35) and fine soil fraction (<2 mm) (lower boxplot, n = 193).

Additionally, sampling of plastics on the soil surface (site OKA), shows an occurrence of 1 p m^2 (OKA-3) to 1.05 p m^2 (OKA-2). The macroplastics collected occur as films (54.8 %), fragments (38.7 %) or styrofoam (6.5 %), with mainly irregular and weathered surfaces and an average size of 66.3 mm (Table S1). The plastics consist of HDPE (35.5 %), LDPE (16.1 %), PP (12.9 %) and other polymers like PET, polyvinyl chloride (PVC), polystyrene (PS) or polymethyl methacrylate (PMMA). In some cases, the function of plastic items is still identifiable, for example, DIY store shed for flowers, plastic fork, bottle cap or food wraps (Figure A 27).

Table 10: Plastic loads (p kg^{-1}) in soil samples (for plastics size range 171 µm – 52 mm).

Sampling depth (cm)	**Plastic loads (p kg^{-1})**									
	Transect NID		Transect MOK			Transect OKA			Transect FRA	
	1	2	1	2	3	1	2	3	2	1
0–10	2.92	15.14	11.78	0.00	1.10	4.77	35.82	11.44	7.76	5.80
10–20	4.58	3.61	13.86	0.00	0.00	2.48	19.39	4.93	1.40	4.45
20–30	27.25	4.18	1.26	0.00	2.61	5.16	2.76	2.07	3.98	5.43
30–40	2.22	0.71	3.47	2.27	1.94	2.18	2.57	1.81	2.20	21.27
40–50	0.00	12.00	2.32	1.65	1.87	0.00	1.49	1.92	5.83	0.00
50–75	0.55	0.43	0.14	1.04	1.34	0.44	0.00	0.00	1.71	2.36
75–100	1.01	1.57	2.27	0.00	0.00	0.48	0.77	0.00	2.04	1.40
100–125	0.00	0.00	0.00	5.60	5.18	0.00	1.66	0.00	2.09	0.63
125–150	0.70	0.00	5.11	0.00	3.76	1.80	0.00	0.00	1.45	0.59
150–200	0.00	1.59	1.67	0.00	0.00	0.00	0.00	0.00	0.00	0.00

3.5.3.2 Metal concentrations and soil properties

All of the 9 metals of interest analysed, as well as the metalloid As and the metal Fe, were detectable by ICP-MS measurement with contents above the detection limit. In relation to the mean values (n = 100), the content decreases from Fe (21,026.3 mg kg^{-1}) > Zn (55.4 mg kg^{-1}) > Ni (31.17 mg kg^{-1}) > Cr (29.82 mg kg^{-1}) > Pb (23.78 mg kg^{-1}) > Cu (16.58 mg kg^{-1}) > V (16.30 mg kg^{-1}) > Co (10.93 mg kg^{-1}) > As (6.63 mg kg^{-1}) > Cd (0.28 mg kg^{-1}) to Hg (0.11 mg kg^{-1}). A comparison with geogenic background and legislation values is possible for the metals of interest Cr, Ni, Cu, Zn, Cd, Hg and Pb. All of those metals of interest show higher average concentrations in deeper soil (50–200 cm) than in upper soil (0–50 cm) layers (Table 11). Mean and median values fall below the worldwide average contents of surface horizons (Kabata-Pendias, 2011), but exceed the geogenic background values for Hessian floodplain soils in the case of Cr, Ni, Cu, Cd and Hg. Legislative precautionary values are exceeded by all metals of interest except Hg by the respective maxima (Table 11); these levels occur in individual samples at sites FRA-1, MOK-1 to MOK-3, NID-2 and OKA-3 at varying depths between 20 and 200 cm.

With regard to the calculated pollution indices, the Pollution load index (PLI) ranges between 0.4 and 3.2, with a mean of 1.1, just above the limit value of 1 at which baseline levels of pollution begin. The PLI of maximum concentration values of 3.2 indicates a partial deterioration of soil quality (Kowalska et al., 2018). The values of the Enrichment factor (EF) are also comparable, with a mean just above the limit where a moderate enrichment can be assumed, and maximum values indicating a significant pollution enrichment. Moderate enrichment and pollution occur at all sites, irrespective of depth. However, higher PLI and EF average values are also found in deeper soil layers (50–200 cm) (Table 11), and significant pollution enrichment based on EF > 4 occur at all locations except FRA, deeper than 100 cm.

Soil conditions for heavy metal behaviour in the floodplain soils investigated consist of predominantly silty to clayey soils (soil textures: SiCL, SiC, C), OM contents range from 1.57 wt% up to 24.91 wt% with an average of 8.33 wt% and pH values indicate a very weak acidic environment with a total average of 6.33 (range 4.90–7.69, moderate acid to weak alkaline) (Table A 5). Furthermore, in groundwater affected Fluvisols or Gleysols, pedogenic oxides (Fe, Mn) in Bl-horizons as well as reductive conditions occur (Table 9).

Deviations in soil texture occur only in subsoils (>100 cm), where the sand content increases locally, and at the middle and lower reaches, with average values up to 22.0 wt% (OKA-1) or 30.5 wt% (FRA-2). Similarly, organic enrichment occurs through deep peat bands or layers with SOM contents of 16.2 wt% (NID-2, >125 cm) or 24.9 wt% (MOK-1, >100 cm).

Table 11: Summary of metal contents compared to geogenic background levels and legislation values with calculated pollution indices and their thresholds.

		Elemental concentrations								**Indices**	
		Cr	**Ni**	**Cu**	**Zn**	**Cd**	**Hg**	**Pb**		**PLI**[a]	**EF**[b]
					mg kg^{-1}					(-)	(-)
Mean		29.8	31.2	16.6	55.4	0.28	0.11	23.8		1.1	2.2
Median		26.3	27.6	13.5	40.0	0.16	0.07	17.7		0.9	1.8
Min.		9.8	8.7	3.5	17.0	0.05	0.01	8.3		0.4	1.1
Max.		75.4	100.7	55.8	194.5	1.39	0.46	77.1		3.2	5.9
Mean upper soil	0-50 cm	28.6	29.9	15.1	50.1	0.25	0.09	22.9		1.0	2.1
Mean lower soil	50-200 cm	31.1	32.5	18.1	60.8	0.31	0.13	24.6		1.2	2.4
SHW[c]	Average content surface horizons worldwide	60.0	29.0	38.9		0.41		27.0	low[f]	<1	<2
GBHF[d]	Geochemical background in Hessian floodplain soils	25.0	24.0	13.3	58.5	0.14	0.04	27.0	moderate[f]	1	2-5
PV[e]	Precautionary values	60.0	50.0	40.0	150.0	1.00	0.50	70.0	high[f]	>1	>5

[a] Pollution load index; [b] Enrichment factor; [c] Kabata-Pendias (2011); [d] Friedrich & Lügger (2011); [e] German Federal Soil Protection Ordinance - BBodSchV (1998); [f] Pollution assessment according to Kowalska et al. (2018) with low pollution or enrichment, moderate/baseline pollution or enrichment and high/significant pollution or enrichment

3.5.3.3 Spatial distribution

3.5.3.3.1 Plastics along the river course

Plastic loads along the river course show average site loads of 3.92 p kg^{-1} at site NID (upper middle reaches), 2.34 p kg^{-1} at site MOK (middle reaches), 3.46 p kg^{-1} at site OKA (upper lower reaches) and finally 3.52 p kg^{-1} at site FRA (lower reaches). Even though average plastic loads vary by ± 1.58 p kg^{-1} along the course, no significant ($p = 0.5106$) difference exists between the mean values per sampling site. The same applies to the comparison of mean values of proximal (near-channel) floodplain sites to mean values of distal (remote-channel) along the course of the river. For example, the proximal sites show the following mean values in downstream direction: 4.18 p kg^{-1} (NID), 1.78 p kg^{-1} (MOK), 2.22 p kg^{-1} (OKA) and 4.19 p kg^{-1} (FRA), without significant mean differences ($p = 0.6916$); while distal sites reflect the following: 3.92 p kg^{-1} (NID), 4.18 p kg^{-1} (MOK), 1.73 p kg^{-1} (OKA) and 2.84 p kg^{-1} (FRA). Regarding the plastic sums per sampling site (Figure 44), the highest sums for proximal sites are found in the upper middle reaches (39.24 p kg^{-1}) and lower reaches (41.92 p kg^{-1}) (Figure 44a), while distal sites also show high values in upper middle reaches, but differ in the middle reaches (41.87 p kg^{-1}) (Figure 44b). The highest average plastic content occurs in the upper middle and the lower reaches, whereas the higher plastic amounts depend on the position in the floodplain cross-section. Furthermore, sampling points impacted by direct anthropogenic influences (e.g., renaturation, earthworks) show the highest plastic sums (Figure 44). A statistical correlation with the soil textures was not found ($p > 0.63$ for each texture fraction), although the sand content increases from the upper to the lower course while the clay content decreases (Table A 5).

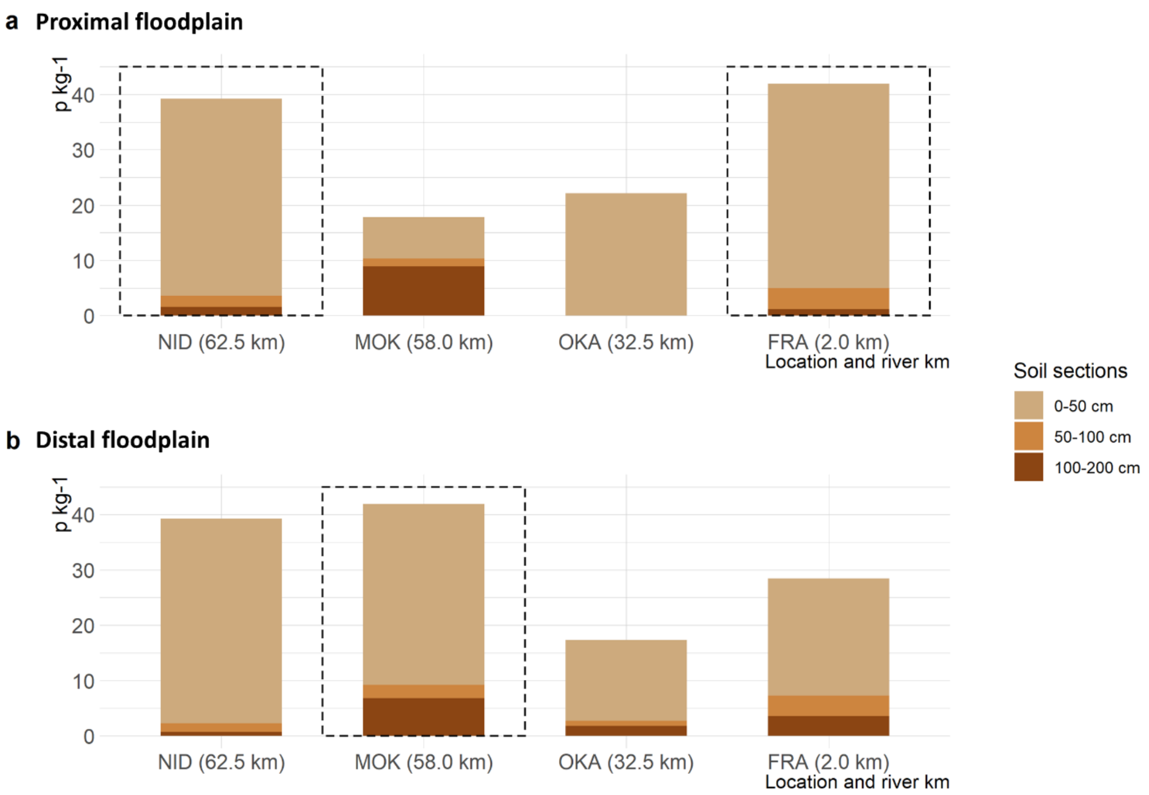

Figure 44: Cumulative sum of plastic loads (p kg^{-1}) per sampling point divided in soil layers (0–50 cm, 50–100 cm, 100–200 cm) along the river course with transect site location and river length (km). a: Proximal sampling points (21.4–35.5 m from active channel); b: Distal sampling points (203.4–859.7 m from active channel); dotted boxes indicate sites exposed to anthropogenic influences (e.g., renaturation, past earthworks).

3.5.3.3.2 Lateral and vertical plastic distribution in floodplain cross-transects

As mentioned before, there are no significant differences in average plastic loads at the lateral level in the floodplain cross-section (Figure 45). Average concentrations range from 4.12 p kg^{-1} (n = 4) at proximal sites, over 6.82 p kg^{-1} (n = 2) at central to 3.97 p kg^{-1} (n = 4) at distal sites, while absolute maxima (35.82 p kg^{-1} or 27.25 p kg^{-1}) occur at central and distal sites (Figure 45c). Increased plastic loads in central floodplain positions are dominated by accumulation of plastics in the arable topsoil of the OKA-2 site (Table 9, Table A 5). A lateral sorting of the plastic sizes, depending on the distance to the channel, could not be determined (Figure A 28). Larger plastic particles within the macro- and mesoplastic size range, only occur isolated within topsoils (plough horizons) of sites OKA-2 (central) and OKA-3 (proximal).

In contrast, clearly significant differences occur in the vertical plastic load distribution (Figure 45a). While the upper soil layers (0–50 cm), consisting of topsoil A-horizons as well as upper B-horizons, show an average plastic load of 6.36 p kg^{-1}, the subsoil layers consisting of B-horizons (50–200 cm) have a significantly lower mean value of 1.73 p kg^{-1} ($p < 0.0000$).

The vertical distribution of plastic loads shows a clear maximum in the uppermost sampling layer (0–10 cm), mostly consistent with A-horizon boundaries, with an average of 9.65 p kg^{-1} continuously decreasing to a depth of 40–50 cm, with an average of 2.71 p kg^{-1} and even lower average values ranging between 1.52 p kg^{-1} and 0.33 p kg^{-1} below that (Figure 46). This vertical decrease is comparable to the decrease in mean organic matter content (with the exception of deeper >100 cm layers which contain peat), and the increase in mean sand content from a depth of 50 cm (Figure 46). Conspicuous accumulation in the vertical distribution occur at sampling site NID-1 (27.25 p kg^{-1} at 20–30 cm), MOK-1 (11.78 p kg^{-1} to 13.86 p kg^{-1} at 0–20 cm), OKA-2 (35.82 p kg^{-1} to 19.39 p kg^{-1} at 0–20 cm) and FRA-1 (21.27 p kg^{-1} at 30–40 cm) (Figure A 29).

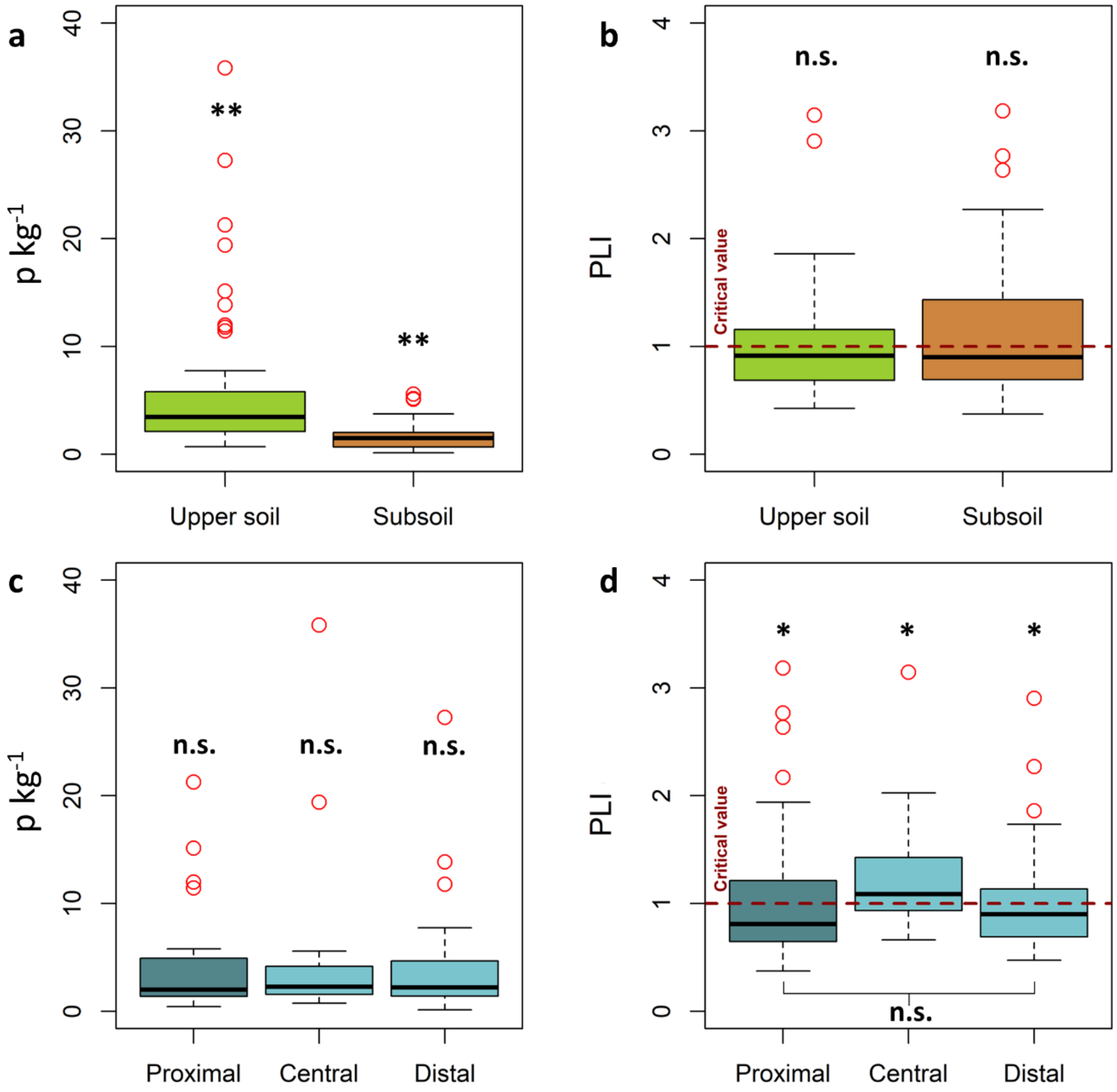

Figure 45: Plastic loads (p kg^{-1}) and Pollution load index values by depth or floodplain position. a: Plastic loads without zero values (empty samples) for upper soil layer (0–50 cm, n = 43) and subsoil layer (50–200 cm, n = 30); b: Pollution load index for upper soil layer (0–50 cm, n = 50) and subsoil layer (50–200 cm, n = 50) with critical value (red dashed line) for significant pollution; c: Plastic loads without blank samples for proximal (n = 30), central (n = 11) and distal (n = 32) sampling points; d: Pollution load index for proximal (n = 40), central (n = 20) and distal (n = 40) sampling points with critical value (red dashed line) for significant pollution. Significance levels: $p < 0.01$ (**); $p < 0.05$ (*); $p > 0.05$ (n.s.).

With regard to the vertical distribution of plastic particle characteristics, differences could be found between upper and deeper soil layers. Figure 47a illustrates that particles with a size >2000 µm (coarse microplastic border) consist mainly of fragments and films, whereas smaller particles show a heterogenous distribution related to particle type, particle size and soil depth. Deepest soil layers are reached only by fragments and filaments: the share of particle types shows higher values of films (46.43 %) and fragments (41.04 %) in lower soil layers than in upper layers (films: 45.40 %, fragments 34.48 %). Overall, the particle size ranged from 171 µm to 52,000 µm (average: 4,566.49 µm) in upper soil layers (0–50 cm), and smaller average sizes of 512.15 µm (242–2,700 µm) in lower (50–200 cm) layers. The share of particle surface characteristics shows an increase for weathered particles with depth, from 45.98% in upper (0–50 cm) to 62.5% in lower (50–200 cm) soil layers, at the cost of fresh and incipient alteration particles.

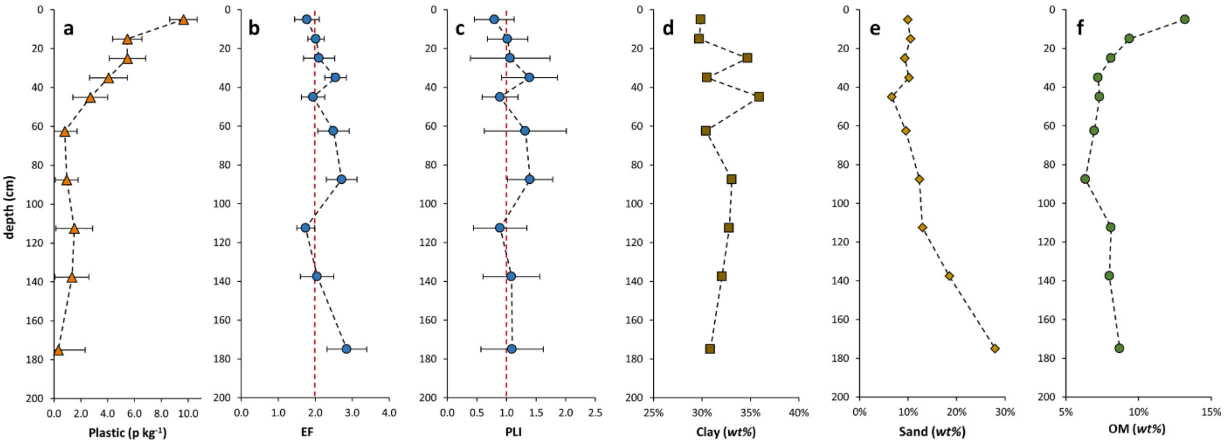

Figure 46: Depth distribution of average plastic loads, pollution indices and soil properties. a: Plastic loads (n = 73); b: Enrichment factor (EF, n = 100) with critical value for significant enrichment (red dashed line); c: Pollution load index (PLI, n = 100) with critical value for significant pollution (red dashed line); d: Clay content (n = 100) in mass-% (wt%); e: Sand content (n = 100) in mass-% (wt%), f: Organic matter content (OM, n = 100) in mass-% (wt%).

EPO ages ranging in upper and lower layers from 1820 to 1990, with an average occurrence of 1938 in upper (0–50 cm), and 1941 in lower (50–200 cm) layers, indicating no significant polymer age differentiation. The vertical distribution of EPO ages (Figure 47b) shows no clustering of polymers of the same age at certain soil depths. There is no dominant polymer type in the deep soil layers, and only two young (>1990) chlorosulfonated or chlorinated polyethylene (CSM/CPE) polymers occur. In general, the depth distribution of the youngest CSM/CPE polymer group shows an average depth of 23.5 cm and an enrichment in soil layers between 0 and 35 cm (third quartile of CSM/CPE depths, n = 24).

With regard to the identified division of plastic content, with values in upper soil layers higher than in deep layers, a statistical correlation with soil textures could not be proven. While in upper soil layers clays (C), silty clays (SiC) and silty clay loams (SiCL) prevail, deeper soil layers show primarily silt loams (SiL), loams (L) or sandy loams (SL), and loamy sands (LS) (Figure A 30).

Comparing the mean plastic contents of both soil texture groups, with 3.26 p kg^{-1} for more clayey (n = 56) and 3.32 p kg^{-1} for rather loamy-sandy (n = 44) samples, no significant (p = 0.3845) difference appears.

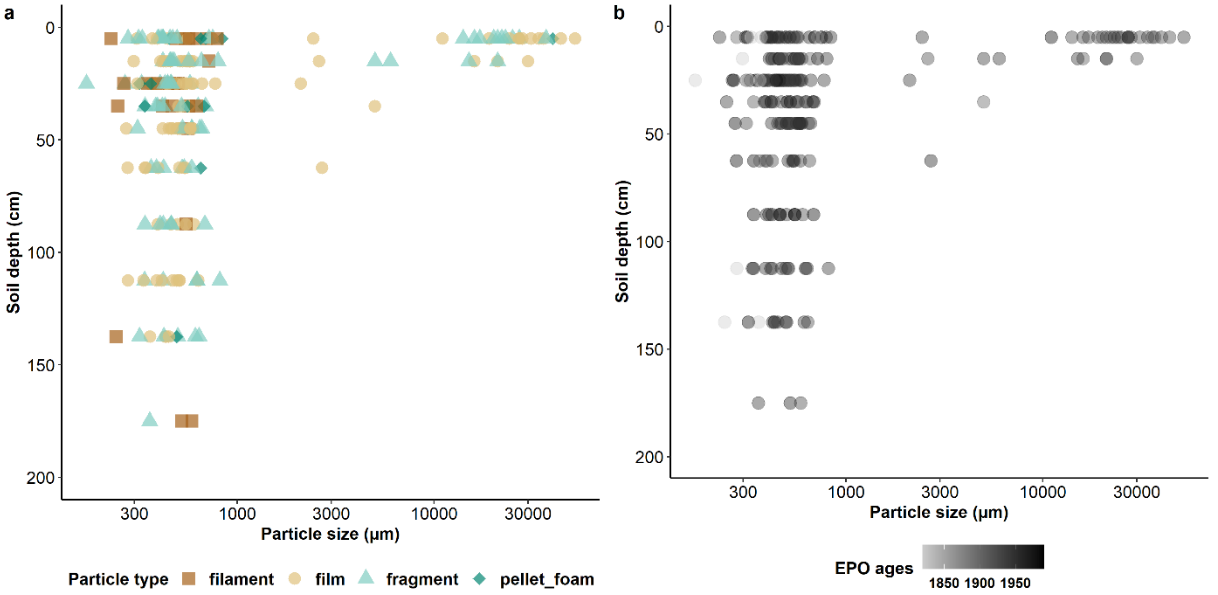

Figure 47: Depth distribution of plastic particle sizes classified according to (a) particle type and (b) age of possible earliest occurrence (EPO ages) for whole particle size range.

3.5.3.3.3 Spatial relationships to metal contamination

As stated earlier, and contrary to the distribution of plastic occurrence, higher PLI and EF values are found in deeper soil layers, with significant pollution enrichments below 100 cm. Figure 48 illustrates the differences between plastic occurrence and PLI loads, showing a clear accumulation of plastics in upper soil layers (0–50 cm). In contrast, the PLI values show enrichment in soil layers between 40 and 120 cm, with EF concentrations showing an additional enrichment in deep soil layers below 150 cm (Figure 46b).

With regard to the lateral distribution of heavy metal enrichment on the catchment scale, average EF values per site increase slightly from NID (upper middle reaches) at 2.06, MOK (middle reaches) at 2.42 and OKA (upper lower reaches) at 2.44, and then decrease to 1.97 at site FRA (lower reaches). The PLI values rank around 1, with a PLI <1 at sites FRA or MOK, and PLI >1 at sites OKA or NID (Table A 5). The lateral distribution on the floodplain cross sections shows slight differences, with an increase from proximal (average PLI: 1.04, average EF: 2.11) to central (average PLI: 1.32, average EF: 2.41), and a decrease from central to distal (average PLI: 1.03, average EF: 2.26) sites.

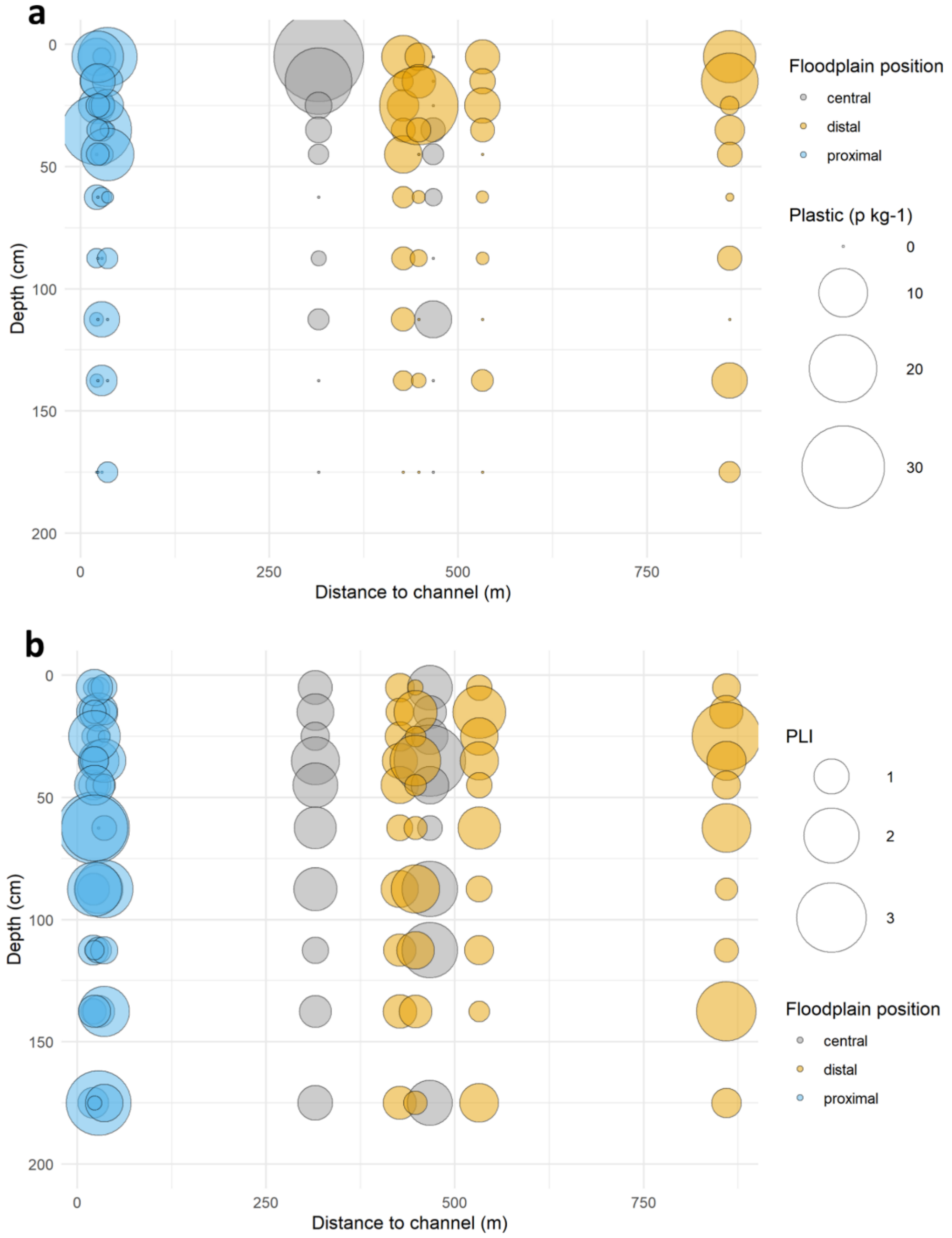

Figure 48: Lateral and vertical distribution of plastic loads and Pollution load index levels (point size as a function of plastic content or PLI levels). a: Plastic load (n = 100); b: PLI levels (n = 100).

A concise assessment of the spatial distribution differences is possible using multiple linear regression models, displayed as regression surfaces in Figure 49. Both regression surfaces show different orientations (slopes) and differences among the variables in terms of their influence on each other. For the first comparison of plastic loads (Figure 49a) a significant influence ($p = 0.0111$) from the predictor variable, soil depth (cm), with regression beta coefficients of -3.0974 (t-value, $p = 0.0028$) and an estimated average effect -0.4094 could be observed. Therefore, changing soil depth is significantly correlated with changes in plastic loads, but the distance to channel shows no significant correlation. For the second comparison with Enrichment factor (EF) values (Figure 49b), no significant correlations were found between EF and the two predictor variables ($p = 0.2066$). Those findings are also visible in the regression surfaces and illustrate the different data distributions.

Whereas the plastic load regression surface (Figure 49a), with an intercept of 7.20, shows a clear slope along the soil depth axis (slope: -0.0493) and a hardly recognisable slope along the distance axis (slope: 0.0002), the EF regression surface (Figure 49b), with an intercept of 1.87, shows very little slope along the depth (slope: 0.0030) and distance (0.0005) axes. Therefore, it can be inferred that the enrichment of metals of interest shows a homogeneous spatial distribution, both to soil depth and across the floodplain width, whereas the distribution of plastic content is found to be heterogeneous and significantly influenced by depth: decreasing with increasing depth.

This spatial connection, and the influence of soil depth on plastic loads, is supported by a significantly ($p < 0.05$) weak negative correlation (r_{SP} = -0.56). Furthermore, plastic loads show slight negative correlations with EF (r_{SP} = -0.19) and PLI values (r_{SP} = -0.12). Slight to weak positive correlations (r_{SP} 0.2–0.6) occur between the river course (km) and distance to channel (m) with clay and OM content, as well as slight negative correlations with sand content. Notable correlations between clay or OM and metals of interest, indicating a strong absorbance to clay minerals or humic substances, could not be found. Inter-element correlations show clear to high positive correlations (r_{SP} 0.6–1.0), except for lower correlation coefficients (r_{SP} <0.4) for Cd, Hg, Pb with V, Cr, Fe, Co, Ni and partly As (Figure A 31).

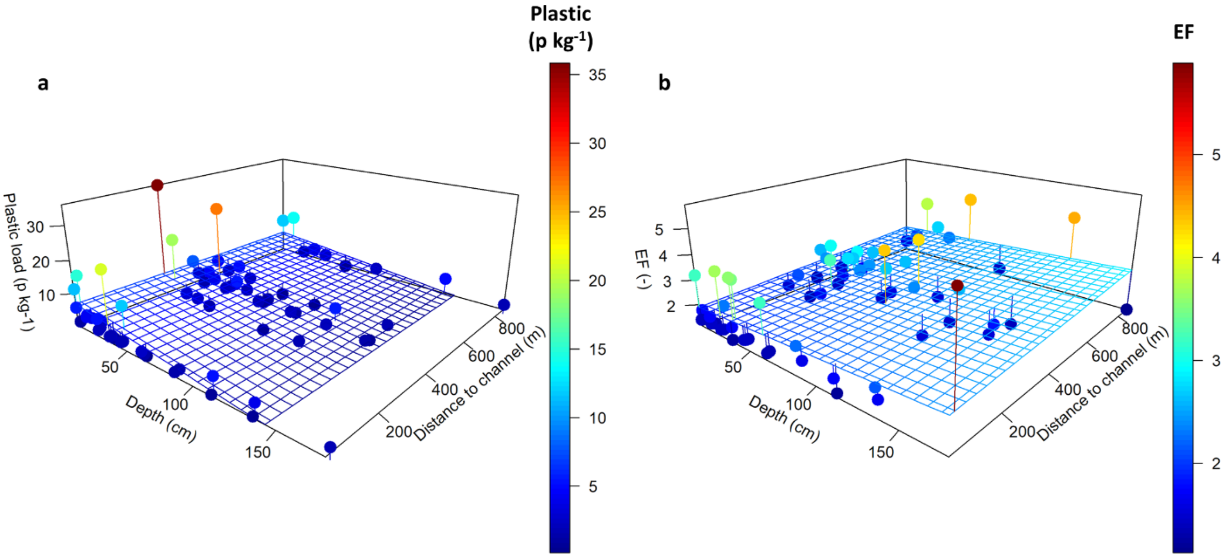

Figure 49: Three-dimensional visualisation of plastic loads and Enrichment factor (EF) levels in dependence of soil depth (cm) and distance to channel (m). Colour scale represents plastic loads or EF level. Regression surface (grid) based on multiple linear regression model for the three included variables. a: Plastic load (n = 100); b: Enrichment factor (n = 100).

3.5.4 Discussion

3.5.4.1 Plastic abundance

Plastics were found at all transect locations along the Nidda River. The observed plastic content, ranging from 0 p kg^{-1} up to a maximum of 35.82 p kg^{-1}, is in the lower range of previously determined plastic contents in floodplain soils. Even if plastic particle abundances recorded for different locations with different methods are difficult to compare, our results can be viewed in relation to other results using comparable methods (density separation) and soils (floodplain soils). For example, Christensen et al. (2020) found plastic loads of 23.0–330.0 p kg^{-1} for average particle sizes of 280–1,160 µm (NaCl solution) in three river floodplains in Virginia (US), whereas Lechthaler et al. (2021) document average loads of 25.4–47.9 p kg^{-1} for plastics with a size of 500–5,000 µm (canola oil separation) in the Inde River floodplain (Germany). Both studies investigated near-channel depositions (bank profiles, levee situations), with a focus on topsoils and single depth profiles. Further investigations, based on the same geospatial sampling approach as in the present study, and conducted in the more rural river system of the Lahn River (Hesse, Germany), found loads of 0.62–5.37 p kg^{-1} for mesoplastics (> 5 mm) and 0.31–8.59 p kg^{-1} for large microplastics (2–5 mm) based on sieving (Weber and Opp, 2020), as well as 0.36–30.46 p kg^{-1} for microplastics sized 219.0–8,321.0 µm based on NaCl separation of the fine soil fraction (<2 mm) (Weber et al., 2021). The average value of all samples from the Nidda catchment at 3.23 p kg^{-1} is comparable to the average values of 2.06 p kg^{-1} (mesoplastics), 1.88 p kg^{-1} (coarse microplastics) or 2.75 p kg^{-1} for microplastics from the Lahn catchment (Weber et al., 2021; Weber and Opp, 2020).

With regard to intensive agriculturally utilised floodplain soils of the lower Yangtze River floodplain, and the lower particle size range investigated, the average of 37.32 p kg^{-1} (100–500 µm) in 0–80 cm soil depth, clearly exceeds the Nidda catchment average (Cao et al., 2021). In comparison to further studies which examine plastic contents in agricultural soils, it becomes clear that these clearly exceed the values from the Nidda floodplain (Liu et al., 2018; Zhang and Liu, 2018; Corradini et al., 2019). This could indicate the role of intensive agriculture in the contribution of plastic inputs. In the Nidda catchment, plastic enrichment through agriculture is also probable. The maximum plastic load (35.83 p kg^{-1}) and higher values, especially for meso- and macroplastic contents, occur where plastic accumulation is also visible at the surface (site OKA, agricultural field). Plastic particles collected on soil surfaces at site OKA (Figure A 26; Table A 6) could be partially identified as parts of consumer articles. The identification of consumer articles may also indicate local littering as a potential source. At this sampling site, the occurrence of plastics on soil surfaces at 1.0–1.05 p m^2 is clearly above the value of 0.021 p m^2 (206 p ha^{-1}) reported by Piehl et al. (2020) for microplastic particles on an agricultural farmland in Germany. Nevertheless, the comparability of the studies is limited, especially because different separation solutions are used, and different particle sizes are considered. Higher plastic contents in agricultural soils could therefore also be caused by the consideration of particles <300 µm in other studies.

With a view to the entire aquatic-terrestrial interface, it seems that floodplain soils contain lower plastic loads than river sediments in the active channel (riverbed, shore). For example, shore sediments of the Main River contain plastic loads of 786.0–1,368.0 p kg^{-1} (63–5,000 µm) and values >50 p kg^{-1} for particles >200 µm directly before and after the inflow of the Nidda River (Klein et al., 2015). Even in more rural areas, such as the Tisza River (eastern central Europe) contents reach values of 3,808 ± 1,605 p kg^{-1} (90–5,000 µm, zinc chloride solution) already in the upper reaches (Kiss et al., 2021). Both examples exceed the plastic loads in the Nidda River floodplain by a multiple factor which, however, may be traceable in part to the examination of smaller particles in the comparative studies. Up to now, only the results of Christensen et al. (2020) suggest equal or slightly increased levels in floodplain samples instead of channel samples, while larger plastic particles occur in floodplain deposits.

Plastic particle characteristics found in floodplain soils of the Nidda River are comparable to other findings from floodplain soils, as well as river sediments. Films and fragments prevail, followed by filaments and pellets, with a typical distribution for soils, with the exception that filaments are sometimes dominant in other studies (Christensen et al., 2020; Corradini et al., 2019). Most of the particles show a weathered or incipient alteration of surface structure, indicating prolonged exposure to degradation factors (e.g., physical break, UV-light) (Hidalgo-Ruz et al., 2012; Napper and Thompson, 2019; Chamas et al., 2020). The increase in the number of particles with smaller particle size also shows a typical distribution independent of the environmental media studied (Kooi and Koelmans, 2019). Due to the method used, particles <300 µm could only be detected semi-quantitatively here if their size and degradation state allowed a manual ATR-FTIR measurement. Therefore, it can be assumed that plastic loads would still increase significantly at a lower detection limit, as in studies quantifying particles <300 µm (Cao et al., 2021).

The dominant polymer types found correspond to those of commonly produced and used polymers in Europe (top 10 ranking), like polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET) or rubbers (PlasticsEurope, 2020). This polymer composition, resulting from the frequency of use in everyday life, industry, agriculture and infrastructure (e.g., rubber car tires), is also found in most soil studies, with fluctuations around the most dominant polymer type (Koutnik et al., 2021). Furthermore, a composition following the frequency of use is also found in channel bed sediments and seems to overlap in different river systems (Koutnik et al., 2021). For river shore sediments of the Main River, Klein et al. (2015) found a composition of PE, PP, PVC and dominant polystyrene (PS) which occupies only a small share <6 % in Nidda floodplain samples. Based on the density separation fluid used here, polymers with a density >1.2 g cm^3 can only be detected semi-quantitatively (e.g., PET). However, except for PET, and without taking additives into account, the common polymer types show a density <1.2 g cm^3. Considering the binding of plastic particles to and in soil aggregates, the question arises whether all particles could be separated (Rehm et al., 2021; Zhang and Liu, 2018)?

Although manual mortaring allows a gentle sample preparation, it does not dissolve soil microaggregates in which plastic might still be retained (Möller et al., 2020).

Besides the methodological limitations described, the comparison of plastic contents with other investigations, results frequently in restrictions based on methodical differences. These differences arise from different sampling concepts, the sample quantity examined, size classes, and the different separation methods. It is therefore difficult to evaluate the plastic content against the background of a contamination assessment, as is usual for other pollutants. In the previous discussion, mainly studies on floodplain soils (mostly near bank and topsoil), which work by means of density separation (NaCl or canola oil), were consulted. Against the background of the comparisons made, it can be cautiously assumed that the contamination level of plastics over the entire soil depth of 2 meters is in the lower range of known contamination, also with regard to smaller particles. Thus, the Nidda floodplain and its soils could be classified as less contaminated against river sediments of larger rivers (e.g., Rhine, Main) and soils under intensive agricultural usage. However, the composition of the plastic particles in terms of shapes, size and polymers shows a typical composition for soils or fluvial sediments in general.

3.5.4.2 Metal abundance

Metals of interest and the metalloid As are present in the floodplain soils of the Nidda River catchment. Even if the average concentrations of Cr, Ni, Cu, Zn, Cd, Hg and Pb fall below the average contents of surface (topsoil) horizons worldwide (Kabata-Pendias, 2011), the exceeding of local geochemical background values of Cr, Ni, Cd and Hg indicates a contamination enrichment of those metals of interest compared to other regional floodplains in Hesse (Germany) (Table 11) (Friedrich and Lügger, 2011). From a legal perspective, only individual breaches of the precautionary values require legal measures (e.g., further investigations, risk designation), traceable to the absolute maximum values and therefore single enriched samples (Bundesregierung, 1998). A pronounced contamination from a single element could not be detected.

Pollution indices, like the Enrichment factor (EF), or Pollution load index (PLI), enable an assessment of the possible anthropogenic impact on heavy metal concentrations (Kowalska et al., 2018). Both indices show average values just above the threshold values for moderate enrichment (EF; >2) and baseline pollution (PLI; >1), with a significant enrichment for single samples with EF >5. As both indices require a geochemical background value for calculation, the exceeding of the thresholds indicates a deviation of heavy metal loads from the theoretical natural background variation (Kowalska et al., 2018; Alloway, 2013). Elemental concentrations and pollution indices show higher mean values and maxima in lower soil layers (>50 cm) than in upper soil layers (0–50 cm) (Table 10). This pattern could indicate older contamination in deeper floodplain sediments, or mobilised metals of interest that reach deeper soil horizons through relocation processes (Alloway, 2013; Dudka and Adriano, 1997). However, against the background of possible heavy metal displacements, the soil properties indicate adsorption tendencies.

Dominant silty to clayey, organic rich Fluvisols and Gleysols, provide good adsorption potentials on clay minerals, humic-substances and the formation of metal-humus-complexes (Alloway, 2013; Blume et al., 2016). Furthermore, adsorbent pedogenic-oxides, and reductive conditions in groundwater effected layers, with single peat layers in deeper soil sections, can increase the retention of metals of interest (Blume et al., 2016; Alloway, 2013; Calmano et al., 1993). Additionally, the very weak acid environment falls below the pH values for incipient mobilisation of Cd, Zn, Ni, but not for Cu, As, Cr, Pb and Hg, even in the minima (Blume et al., 2016; Calmano et al., 1993).

Due to spatially widespread moderate enrichment, and baseline pollution by metals of interest under strong adsorption tendencies, anthropogenic impacts on heavy metal enrichment can be assumed. Because of the vertical differences observed, this vertical pattern could also be due to an historical heavy metal enrichment in deeper soil layers (higher mean contents and maxima), and a more recent one in upper soil layers. Possible older sources of heavy metal enrichment may include mining in the headwaters of the Nidda River (Vogelsberg mountains: iron ore and basalt mining), as well as early industrial metal processing throughout the river catchment (Dudka and Adriano, 1997). Mining and metal industry represent one of the main sources of historical heavy metal enrichment in river floodplains before, and especially during the Industrial Revolution from the 1850s onwards (Kern et al., 2021). In contrast, recent sources could be related to wastewater treatment plants, industrial and traffic discharges as point sources, or uptake of polluted legacy sediments, as well as erosion on agricultural land (Alloway, 2013; Martin, 2015; Pejman et al., 2015; Hahn et al., 2016). Former studies, assessing the ecological quality and ecotoxicological effects from channel sediments along the Nidda River, concluded that, other than the headwaters, the whole Nidda River is affected by anthropogenic chemical pollution (e.g., PAH, PCB, metals) (Schweizer et al., 2018; Brettschneider et al., 2019). A relationship between anthropogenic point sources and ecotoxicological effects could not be proved, which leads to the assumption of diffuse sources for chemicals and consequently also for metals of interest.

3.5.4.3 Spatial differences between plastic and metal contamination

The spatial pattern of plastic and metal contamination observed, differs along the lateral as well as vertical spatial extension. First, no enrichment of plastic loads along the river course could be found, whereas heavy metal enrichment increases slightly with the course of the river (Figure 44). Second, no significant differences in plastic loads occur in the floodplain cross-section, whereas heavy metal enrichment increases slightly from proximal to central, and decreases to distal floodplain soils (Figure 45). Therefore, the hypothesis that plastics accumulate with the river course cannot be supported, as also found for the Lahn River catchment by Weber et al. (2021).

Although plastic loads in floodplain soils could be related to the population densities in the river catchments (Scheurer and Bigalke, 2018; Christensen et al., 2020), and microplastic loads in river water show higher abundance near urbanised areas (Xiong et al., 2018), these patterns do not appear to be applicable on the Nidda River. Highest plastic occurrence was found at the proximal floodplain sites in the upper middle reaches (NID) and lower reaches (FRA). For riverbed sediments, Kiss et al. (2021) found plastic enrichment in tributaries of the Tisza River, indicating the contribution of plastic in suburban areas. Although the Nidda rises in a rural landscape, passes through agricultural heartland and reaches the highly urbanised agglomeration area around Frankfurt, a simple source-to-sink downstream increase does not occur. Although, suburban to rural areas also seem to provide potential plastic sources. In contrast, heavy metal abundance seems to follow a downstream increase, which could be attributed to the increasing number of possible point sources, or the increasing deposition of legacy sediments (Ciszewski and Grygar, 2016).

With regard to the floodplain cross-section patterns of plastic loads, no significant differentiation or lateral sorting of plastic characteristics or relationships to lateral soil texture changes were found. Here the issue arises that no previous studies have examined plastic levels in floodplain cross transects, except the study of Weber and Opp (2020), for coarse microplastics and mesoplastics, and the study of Weber et al. (2021) for medium and large microplastics in the Lahn River catchment. Both studies found a clear enrichment of plastic loads at near-channel (proximal) floodplain sites, interpreted as a consequence of frequent flood occurrence at levee situations, and easier plastic retention during floods, due to higher vegetation density. In contrast, plastic loads in the Nidda floodplain seem to be much more homogeneously distributed over the floodplain area, and no differentiation based on flood dynamics and related sediment deposition occur. The slight increase of heavy metal enrichment could be traced back to the clear association of metal loads with sediment particles, reaching the floodplain when flood water overflows the riverbank (Ciszewski and Grygar, 2016). Following the diffusion mixing model, and water-flow velocity slowing with increasing distance from the channel, metals associated with finer sediment fractions show higher concentrations in floodplain zones behind the levee (central, distal) (Ciszewski and Grygar, 2016). Assuming flood delivery to be the dominant source of plastic as well as heavy metal contamination, it can be stated that transport and deposition of both contaminants by floodwater is conceivable. The spatial patterns of the metal distribution correspond to well-known distribution patterns, whereas the plastic distribution shows differences to previous findings.

A clear and statistically significant separation of spatial patterns between the two contaminants, proved by mean differences and correlations, occurs when considering vertical distribution in floodplain soils; plastic loads showing a clear distinction between upper (0–50 cm) and lower (50–200 cm) soil layers (Figure 45, Figure 46). The accumulation of plastics in the uppermost topsoils, and an overall decrease in concentrations with increasing depth, was also found by the few studies that have investigated different soil depths (Liu et al., 2018; Weber and Opp, 2020).

In contrast, the recent work of Cao et al. (2021) documents renewed increases of concentration below 40 cm depth in agricultural soils. In contrast, heavy metal concentrations, which are found throughout the soil column, show significant pollution tendencies between 40 and 120 cm based on PLI, and higher enrichment below 150 cm based on EF. Assuming a more or less low mobility of metals of interest, due to good adsorption conditions in the floodplain soils examined, this pattern can probably be attributed to deposition processes of metals of interest bound to sediments (Lair et al., 2009; Ciszewski and Grygar, 2016). With regard to the assumption that fluvial processes lead to the deposition and accumulation of plastics as well as metals of interest in floodplain soils, no further indicator, like a relationship to soil texture (Cao et al., 2021; Lechthaler et al., 2021), or a clear stratigraphic distinction, could be found. Nevertheless, other surface discharge pathways for microplastics, such as surface runoff on slopes, can be excluded for the studied floodplains. Beside agricultural activities contributing to plastic deposits, plastic can originate from the river and deposited via flood water since further, laminar sources are excludable.

Since the vertical formation of floodplain sediments always reflects a temporal sequence of dynamic sedimentation and erosion processes, the question arises whether different time periods for the input of the two contaminants could be relevant? Although no clear temporal differentiation could be established by EPO ages, the increase in plastic loads between 50 and 30 cm, depending on the sampling point, suggests that deposition of plastic started at these depths, beginning in the 1950s at the earliest. Assuming plastics load increases as a general marker for sediment dating, the upper soil layers containing significant enriched plastic loads could have been deposited after the 1950s (Turner et al., 2019; Weber and Lechthaler, 2021). The application as a general marker also works when plastic is shifted vertically (e.g., by bioturbation), as significant content increases can be seen in the upper soil section (Weber and Lechthaler, 2021). In contrast, and although the heavy metal inputs have not stopped in recent times, deeper metal accumulations may indicate earlier impacts (e.g., mining, industry), with maximum accumulation since the 1850s, and before widespread environmental protection laws in the 1960s (Alloway, 2013). This assumption could be supported by the, in some cases, strong inter-element correlations (Figure A 31), indicating a combined metal pollution from similar long-term sources with the same origin and controlling factors (Manta et al., 2002; Lu and Bai, 2010).

Even though the concentrations in deeper soil layers decrease significantly, the results from the Nidda River indicate that plastic particles can shift vertically, as was also shown for larger particles by Weber and Opp (2020), and smaller particles by Cao et al. (2021) and Weber et al. (2021). The size distribution of plastic particles found here, with the occurrence of coarse microplastics (>2000 µm) only in upper soil layers and a considerably smaller particle size average in deep layers, suggests that smaller particles can more easily reach deeper soil sections. This result is supported by the findings of Rehm et al. (2021), showing that microplastic particles with a size of 53–100 µm tend to be carried vertically in soils more than larger particles.

Possible transport paths through the soil, depending on the particle size, are assumed to be the pore space (macropores) or preferential flow paths, but also transport by soil organisms (earthworms) (Rillig et al., 2017a; Rehm et al., 2021; van Schaik et al., 2014; Yu et al., 2019).

In general, it could be stated that a spatial homogenous distribution of both contaminants in floodplains exists. However, in the case of plastic contents, this only concerns the basic occurrence, since the vertical distribution is clearly influenced by the depth. Whereas the contamination of metals of interest is probably the result of multiple historic to recent sources, including point and diffuse sources, a clear source of plastic inputs is not identifiable based on this study. However, the widespread distribution of plastics indicates that they can enter fluvial systems anywhere and at any time (Lechthaler et al., 2021), independent of point sources, and can accumulate temporarily in floodplains.

Despite spatial comparisons, possible interactions between plastics and metals of interest could not be identified in this study. Although the spatial differences of both contaminants were studied, no correlations between plastic content and individual elements were found, which would indicate relationships like adsorption or desorption processes (Verla et al., 2019). Slight negative correlation between EF and PLI values with plastic loads may indicate that emissions of metals of interest from plastics plays no role or at most a subordinate role here compared to other metal sources. Therefore, further studies should perform a targeted analysis of metals of interest adsorbed on plastic surfaces and within plastic particles, and consider geochemical interactions between adsorbed metals and the soil matrix in addition to spatial connections.

3.5.4.4 Anthropogenic activities might directly impact distribution of plastics

Despite the general spatial distribution of plastic loads in floodplain soils of the Nidda River, the question arises whether there are high accumulations of plastics and sums per site (Figure 44, Figure 45), exclusively related to the vertical distribution? Heavy metal concentrations and pollution indices show only minor outliers, which can usually be associated with individual deep-lying soil layers and single-element enrichments (Figure 49). In contrast, four significant, vertical outliers of plastic loads could be found in the cores NID-1, MOK-1, OKA-2 and FRA-1. Thus, at each sampling site one soil column shows a concentration of 13.86–27.25 p kg^{-1}, exceeding the average value of the respective profile by 3.3 to 6.9 times (Figure A 29). The first assumption that these enrichments are attributed to flood processes could not be confirmed, because none of the four sites has a special micro-morphology (e.g., flood channel, depression) (Figure A 21) (Blettler et al., 2017; Lair et al., 2009). Also, an influence from outside the floodplain, such as slope erosion and surface flow (Rehm et al., 2021) can be excluded, since either no lower slopes are present (sites: FRA, OKA) or these are separated by roads (sites: NID, MOK).

In contrast, a relationship is evident at the OKA site between macro- and mesoplastic accumulations on the soil surface of the agricultural fields at OKA-2 (distal) as well as OKA-3 (proximal) and the enrichment of microplastic loads ranging between 35.82–19.39 p kg^{-1} (0–20 cm, OKA-2) or 11.44–4.93 p kg^{-1} (10–20 cm, OKA-3) in ploughed topsoil. The marked decrease of concentrations with depth could be due to compaction by tillage below the Ap horizons (Weber and Opp, 2020). Even if it is obvious to seek the source for this enrichment in agriculture, local littering cannot be ruled out. As no plasticulture was carried out on the field, the findings of macro- and mesoplastic may indicate an application of a compost or sewage sludge (origin of some plastic pieces still recognisable) (Braun et al., 2021; Steinmetz et al., 2016). However, according to information provided by the land tenant (anonymous for data protection reasons), only fertilization with manure has been carried out in recent years. Because this information is not verifiable, the entire range of possible agricultural plastic input, from fertilizer application to machine abrasion, or local littering cannot be retraced.

For the remaining enriched sites, the soil stratigraphy shows slight layer differences for the sites MOK-1 and FRA-1, but not in NID-1, and likewise without changes in soil texture. However, with consideration of land use changes (Figure A 22, Figure A 23), it becomes clear that these sites were immediately adjacent to earthworks for construction purposes (bridge construction, site FRA-1) and floodplain and river restoration (sites NID-1 and MOK-1) during the 2000s and 2010s. The influence of restoration on microplastic loads in near-channel deposits, through a remobilisation of deposited plastics and a high and young sedimentary activity, was also found in the lower reaches of the Inde River (Germany) (Lechthaler et al., 2021). Therefore, direct anthropogenic impacts like tillage and fertilization, as well as earthworks for building or restoration purposes, might have an influence on the microplastic abundances found in this study.

3.5.5 Conclusion

Floodplains and their soils can act as temporal sinks for plastics and metals of interest entering floodplain areas through flood water and flood depositions, or through agriculture. The spatially widespread and homogenous enrichment of plastics in upper floodplain soil layers indicates plastic input and distribution in fluvial systems which influences the whole floodplain soilscape. Simple interpretive hypotheses, such as increasing plastic levels with river flow following the potential increase in plastic sources, cannot be supported; rather, plastic inputs already appear to be increasing in rural and suburban areas. Furthermore, anthropogenic heavy metal enrichments, in addition to geogenic abundances, occur in the floodplain soils of the Nidda River and follow known distribution patterns resulting from fluvial transport and deposition in floodplain soils. Floodplains, as highly affected landscapes, due to their natural sink function for sediments, nutrients and pollutions, now appear to be exposed to additional contamination, resulting in a multiple contamination framework. Therefore, plastic loads should be included in future evaluations of floodplain conditions, ecological quality and preliminary studies for renaturation measures or construction projects.

The vertical sequence of plastic enrichment in the topsoil and upper soil layers, followed by deeper heavy metal enrichments, indicates deposition and contamination of different time periods. The floodplain soils are now contaminated with both metals of interest and plastics, although the levels are in the lower range of known concentrations in floodplain soils and soils in general. However, since the environmental impacts and consequences for humans of plastic contamination in soils, are still not entirely understood, even low levels of accumulation should not be ignored. Not least because a further increase in plastic production, and thus, an increase in plastic emissions into the environment, can be expected. Further areal and spatially representative monitoring of plastic contents in soils, their input pathways, and the investigation of possible interrelationships with other pollutants, will be necessary in the future in order to provide risk assessments in case of upcoming legislation.

Finally, direct short and long-term anthropogenic impacts, like tillage and probably soil fertilization, as well as earthworks and floodplain restoration could affect plastic enrichment. While agriculture and tillage can be interpreted as an emitting and spreading agent, earthworks and renaturation could be seen as redistributing agents for plastic deposits. Against the background of the manifold conflicts of use in floodplains, and the increasing renaturation and withdrawal of watercourse structures for nature conservation and flood protection purposes, the question arises as to whether these measures encourage the temporary storage of plastics in floodplain soils? Relocation of legacy sediments, increase in erosion due to channel relocation, or removal of bank stabilisers, could result in renewed plastic discharges, resulting in further inputs into aquatic and marine ecosystems that are already severely affected by plastic contaminations.

Based on our case study, the methodological limitations and our findings, the following recommendations can be made for further research and the management of floodplains:

- Multiple plastic monitoring in soils should be carried out in a spatially representative manner. Those studies can contribute to the understanding of interrelationships and influences across soilscapes, improve knowledge of sources and transport routes, and implement targeted containment measures in the future.
- Plastic contamination in soils should be considered in construction and landscape planning. In terms of precautionary soil protection, consideration should be given to the consequences of anthropogenic interventions such as renaturation on the storage or discharge of plastics. This does not mean to dispute the benefits of restoration projects, but to introduce the examination of plastic residues and to work out a management system for these residues in case of high concentration.

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3.6 Plastics as a stratigraphic marker in fluvial deposit systems

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Abstract

Plastics as purely human-made materials have entered the environment for at least 70 years. They are detectable in a wide variety of ecosystems worldwide. Due to the global occurrence of plastics, the long-lasting presence, the clear temporal delineation and the lack of a geogenic background, plastics have also been considered as a potential marker for the proposed Anthropocene. Fluvial depositional systems are transport pathways for anthropogenic plastic residues through the environment, and they provide opportunities for the storage and accumulation of plastics. Despite the potential negative effects that originate from pollution to the environment and its biota, the presence of plastic in fluvial environments is also potentially useful for a scientific advantage. The viewpoint presented in this paper raises the question of whether plastic particles are also usable as a new stratigraphic marker within fluvial systems of the "Anthropocene", and thus for dating the youngest sedimentary deposits. We elaborate on the theory of conditions for using plastic as a stratigraphic marker, as well as its use as a general marker (from 1950) and as a specific marker based on polymer types and the associated age on earliest possible occurrence (1910–1990). Benefits and limitations in practical and interdisciplinary application include an inexpensive and rapid approach with combinable existing methods, that may be limited by disturbance of the investigated legacy sediments or in-situ relocation of plastic.

Keywords

Anthropocene, Strata, Microplastics, Mesoplastics, Floodplain, River sediments, Wetland

3.6.1 Introduction and background

Plastics are present in all ecosystems and therefore are found worldwide in a various range of environments (Karbalaei et al. 2018; Souza Machado et al. 2018a) the first scientific evidence of plastics in the ocean in the 1970s, the detections of plastic in all ecosystems have steadily increased (Andrady 2017). The abundance of plastics is now documented for marine, fluvial, terrestrial and atmospheric areas (Bancone et al. 2020; Evangeliou et al. 2020; Lechthaler et al. 2020; Weber und Opp 2020). The threat to ecosystems and organisms is still poorly understood, but initial studies have suggested possible eco-toxicological consequences in aquatic and terrestrial environments (Souza Machado et al. 2018b; Rillig et al. 2019; Ragusa et al. 2021). Basically, the worldwide evidence of plastic in the environment is not astounding. After the development of polymers in the late 19th century (e.g., synthetic rubber) and early 20th century (e.g., resins, polyvinyl chloride), global plastic production, which began on an industrial scale in the 1950s, has multiplied from 1.7 kg x 10^6 to 368 kg x 10^6 in 2019 (PlasticsEurope 2018, 2020) and thus leading consequently to a possible increase for environmental entry of plastics (Figure 50). Therefore, plastics have a very clear time limit on their environmental occurrence, as they could only be released into the environment in sporadic settings before 1950.

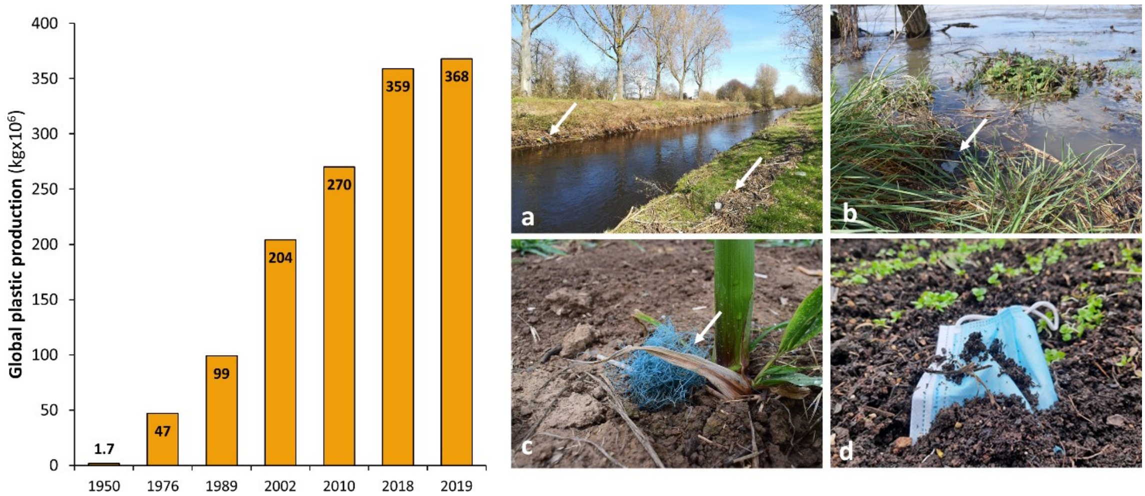


Figure 50: Global plastic production (PlasticsEurope, 2018, 2020) and records of macro- and mesoplastic particles in fluvial environments: a) Plastic debris on the banks of the Inde river (North Rhine-Westphalia, Germany); b) Single white macroplastic particle at the edge of the flooding area during the spring flood 2020 on the river Lahn (Hesse, Germany); c) Mesoplastic particles on a maize field in the floodplain of the Nidda River after flood discharge 2020 (Hesse, Germany); d) Covid-19 protection mask on the riverbank of the river Lahn Nida (Hesse, Germany) recorded in summer 2020. Photos by S.E. Lechthaler and C.J. Weber.

Plastics in the environment are described in an overarching way as human-made, polymeric or co-polymeric, solid and insoluble materials either created (primary form) or fragmented (secondary form) to a defined particle size (Andrady 2017; Bancone et al. 2020). Plastics research distinguishes mainly between macroplastics (>25 mm), mesoplastics (>5–25 mm), microplastics (5000–1 µm) and nano-plastics (<1 µm), although no standardized size definition and consideration of size ranges is available so far (Andrady 2017).

Furthermore, they are purely anthropogenically created synthetic polymers whose origin is natural materials (e.g., petroleum, natural gas or, in the case of biopolymers, in parts organic components), but whose creation through polymerization, polycondensation and polyaddition is purely human (Zalasiewicz et al. 2016; Bancone et al. 2020). Unlike other foreign substances in the environment, plastics as purely human-made materials have no natural or geogenic background content and can only enter nature through human activity (littering) or through natural processes (e.g., erosion, relocation) following anthropogenic deposition (e.g., landfills). On the other hand, the properties of plastic, especially its manifold applications and the inclusion of countless additives (e.g., slip agents, pigments, metals), lead to a very slow degradation of plastic in the environment (Barnes et al. 2009). Modelling experiments suggest that the half-life of particle degradation can range from a few years to >2500 years (Chamas et al. 2020). However, since plastics are degraded and fragmented by environmental impacts and not dissolved, residence times are very long in particulate and thus detectable form, at least from a human time perspective (Zalasiewicz et al. 2016). Conservation, for example in sediments (buried), can significantly prolong conservation as important decomposition factors (e.g., UV light, oxygen availability) are reduced or absent (Zalasiewicz et al. 2016; Bergmann et al. 2017).

The global abundance of plastics, the long-lasting impact, the clear temporal delineation of plastics, and the lack of a geogenic background have also led to the consideration of plastics as a potential marker of a proposed new post-Holocene Cenozoic era, the “Anthropocene” (Corcoran et al. 2014; Geyer et al. 2017; Waters et al. 2016; Zalasiewicz et al. 2021; Zalasiewicz et al. 2008). Beginning with the work of Zalasiewicz et al. (2016) and discussed further, researchers have developed concepts on how plastics can be usable as a possible primary or auxiliary marker of a Global Boundary Stratotype Section and Point (GSSP) for the start of an “Anthropocene” epoch, from the mid-twentieth century (Lewis und Maslin 2015; Zalasiewicz et al. 2021). With the ongoing discussion, it has become clear that plastic can fulfill the requirements of a marker in the sense of a GSSP due to the above-mentioned properties and conditions, despite the unclear long-term preservation, especially in sediments or even in rocks (Zalasiewicz et al. 2016; Ehlers und Ellrich 2020; De-la-Torre et al. 2021a; Ehlers et al. 2021).

With the consideration and discussion of plastics as a possible temporal marker for the lower limit of the “Anthropocene”, scholars have simultaneously recognized plastic as part of the geological cycle (Zalasiewicz et al. 2016). In principle, the first discovered plastic deposits in the marine environment can only be understood as the end point of a plastic transport system that extends from the land via rivers into the world’s oceans (Siegfried et al. 2017; Xiong et al. 2018). Since the majority of global plastic production is both produced and consumed on land, it has been shown that rivers and river systems are the main corridor and transport route for plastics in the environment (Siegfried et al. 2017; Lechthaler et al. 2020).

The detection of plastics in freshwater systems and fluvial sediments allows the following research questions:

a) Are plastics temporarily stored and accumulated in fluvial systems and their sediments?

Initial research on the quantification and spatial abundance of meso- and microplastic in floodplain soils and sediments showed that plastic is deposited and enriched in floodplain sediments through flood water delivery (Lechthaler et al. 2021; Weber und Opp 2020). This process is already known for sediments per se, as well as for other nutrients and pollutants (e.g., heavy metals) (Bridge 2003; Brierley und Fryirs 2007). The concept of plastic as a marker of the "Anthropocene" therefore also raises the question:

b) Are plastic particles usable as new stratigraphic marker, especially in fluvial deposits?

Floodplains and their associated river systems are highly dynamic systems. They are subject to sediment deposition and erosion, depending on their location within the river system and the area of influx, as well as human influences resulting in anthropogenic river systems (Bridge 2003; Edgeworth 2011; James 2013; DeBoer et al. 2020). Above all, the reconstruction of floodplain dynamics and sediment deposition in recent times has so far only been possible on the basis of radiometric chronological approaches (Gałuszka et al. 2014; Bancone et al. 2020). Even if these approaches provide often valid results, they are not free from natural and anthropogenic disturbances, especially in legacy sediments, reaching their limits in very juvenile sediments. They are furthermore cost and time consuming.

Therefore, the possibility exists to establish a new method to date recent sediment depositions of the "Anthropocene" (assuming a start point in the mid-twentieth century) in fluvial systems (Zalasiewicz et al. 2016), generate specific sedimentation rates, and foster interdisciplinary research from hydrology to archaeology. Also, for the study of microplastics in fluvial systems themselves, its use as a stratigraphic marker can lead to a better assessment of microplastic deposition and transport dynamics. Based on two initial considerations (Weber 2020; Weber et al. 2021b), this viewpoint article introduces the theory behind the application of plastic as a stratigraphic marker in fluvial systems of the "Anthropocene". It discusses possible benefits and limitations of the practical application to stimulate scientific discourse. Even if plastics and especially microplastics represent a foreign substance, and thus a contamination in the natural environment, their occurrence in fluvial systems in combination with the specific material properties is therefore usable for a scientific advantage.

3.6.2 Theory

The idea of using plastics in the environment, and especially in soils, as evidence of recent anthropogenic influence is not new, but it is not very common in practical application. To cite two examples, plastic particles are considered as anthropogenic artefacts in soil science (FAO 2006; IUSS Working Group 2015), or applied in archaeology as evidence of modern recently disturbed deposits (Edgeworth et al. 2015). Nevertheless, previous considerations of the application of plastic as a stratigraphic marker were mostly limited to general discussion on its use as a marker for the "Anthropocene", in marine and limnic systems (Bancone et al. 2020; Bensaude-Vincent 2021; Zalasiewicz et al. 2021).

If these approaches are applicable to fluvial systems for recording the stratigraphy and chronology of recent sedimentary deposits, four basic conditions must be fulfilled, which are valid throughout all markers in environmental archives. (1) Recordable and clearly identifiable material must be available. (2) The chronological occurrence must be clear and precisely delimited in terms of time. (3) Their presence and preservation in the environment must be long, with the lowest possible mobility after deposition. (4) The anthropogenic material must have no geogenic background content in the case of recent timelines.

Those requirements are fulfilled by plastic particles in fluvial deposits and sediments. Plastics, especially macro- or mesoplastics (MEP), are easily identifiable and are also already purely visible in the field. MEP particles (Figure 50) are often observable and sampled directly in the upper sediment layers of embankments, for example. For comprehensive sampling, the fluvial sediments can be sampled by drilling (Weber et al. 2020). Furthermore, microplastics, both coarse microplastics (CMP, >2 mm) and large or medium microplastics (LMP, >1 mm or MMP, >0.5 mm), are extractable from soil and sediment samples by separation and analysis methods, as demonstrated in reviews (e.g., Hidalgo-Ruz et al., 2012; Prata et al., 2019; Stock et al., 2019; Weber et al., 2020). With regard to floodplains and river systems, plastics of different size classes can reach concentrations from 0 to 55.5 mg kg^{-1} or 0–186.3 particles kg^{-1}, and have a spatially heterogenous distribution down to a depth of 2 m (Scheurer und Bigalke 2018; Weber und Opp 2020; Lechthaler et al. 2021). One major problem that occurs in the field of especially microplastic analytics is the method of standardization among the great variety of possible methodologies (Stock et al. 2019).

Furthermore, more detailed analysis of plastic particles (e.g., Fourier-transform infrared or Raman spectroscopy) enables assignment of a particle precisely to a polymer type. This approach is thus analogous to a chemical fingerprint. As already pointed out, plastic has a clear temporal demarcation due to the comparatively late development and production by humans. This can be based on the increasing production of plastics from the 1950s onwards, or more specifically on the development of each type of polymer, based on the age of earliest possible occurrence ("earliest possible occurrence", EPO).

Bancone et al. (2020) also introduced this age with regard to the abundance of zones of plastics. The EPO age is equivalent to the start of development or production of a polymer, whereby the exact years vary (Table 12). Therefore, two different markers—(i) a general marker (meaning stratigraphically: distinction between young and older sediments around 1950, above or under the plastic-bearing layers) and (ii) a specific marker (allocation of the EPO age)— are applicable to access recent sediment chronologies between the 1910s and 1990s, as well as recent sedimentation rates in case of the specific marker (Figure 51). With regard to the specific marker (ii), a further distinction is possible: bans of several additives due to health or environmental concerns give hints of a 'latest possible occurrence'. Azodicarboxylic acid diamide or the flame retardants octa- and pentabromodiphenyl ether and short-chain chlorinated paraffins, for example, have been prohibited since 2005 and 2004, respectively (Maier und Schiller 2016).

With regard to the environmental preservation of plastic particles, no definitive timeframe is currently available from research. It is clear, however, that the stable properties of plastic materials must lead to comparatively long residence times, even if a steady disintegration of the particles (for example from meso- to microplastics) is assumed. Workers have suggested that buried particles are preservable over significantly longer timeframes, since the most important chemical decomposition factors are thus inhibited (Napper und Thompson 2019; Chamas et al. 2020). In addition, the high-molecular-weight organic chains of polymers should resemble persistent organic fossils (e.g., wood, spores) and could be received as 'technofossils' in sediments (Zalasiewicz et al. 2016). Although this preservation may only be long-lasting on human time scales, and it cannot be confirmed at the moment whether they remain detectable in geological records, plastics are now usable as a stratigraphic marker of recent depositional periods in fluvial systems.

Table 12: Earliest possible occurrence (EPO) ages for different polymers and with regard to different references.

Polymer	EPO-ages	References
ABS (Acrylonitrile Butadiene Styrene)	1948	British Plastic Federation 2020
CA (Cellulose Acetate)	1938	Zalasiewicz et al. 2016
CSM (Chlorosulfonated Polyethylene)	1990	British Plastic Federation 2020
EPS (Expanded Polystyrene)	1954, 1949	Zalasiewicz et al. 2016, Crawford, Quinn 2017
HDPE (High-density Polyethylene)	1955, 1935	PlasticsEurope 2017, British Plastic Federation 2020
LDPE (Low-density Polyethylene)	1939, 1952	PlasticsEurope 2017, British Plastic Federation 2020
PA (Polyamide)	1938, 1935	PlasticsEurope 2017, British Plastic Federation 2020 and Hopmann, Michaeli 2017
PAN (Polyacrylnitrile)	1930	Crawford, Quinn 2017
PC (Polycarbonate)	1956, 1955	PlasticsEurope 2017, Crawford, Quinn 2017
PE (Polyethylene)	1933/39	Zalasiewicz et al. 2016
PET (Polyethylene Terephthalate)	1941/73 (bottles), 1973	Zalasiewicz et al. 2016, British Plastic Federation 2020
PMMA (Polymethyl Methacrylate)	1933, 1931	Hopmann, Michaeli 2017, Crawford, Quinn 2017
POM (Polyoxymethylene)	1920/56 (patent)	Crawford, Quinn 2017
PP (Polypropylene)	1959, 1957, 1954	Zalasiewicz et al. 2016, PlasticsEurope 2017, British Plastic Federation 2020
PS (Polystyrene)	1937, 1931, 1930, 1920	Zalasiewicz et al. 2016, Caterbow, Speranskaya 2019, Hopmann, Michaeli 2017, PlasticsEurope 2017
PTFE (Polytetrafluoroethylene)	1941	British Plastic Federation 2020 and PlasticsEurope 2017
PU (Polyurethane)	1940, 1937	PlasticsEurope 2017, British Plastic Federation 2020
PVC (Polyvinyl Chloride)	1940, 1938, 1927	Zalasiewicz et al. 2016, PlasticsEurope 2017, Hopmann, Michaeli 2017
Resin	1910, 1907	Caterbow, Speranskaya 2019, Crawford, Quinn 2017
Silicone	1943	PlasticsEurope 2017
UP (Unsaturated Polyester)	1941	PlasticsEurope 2017

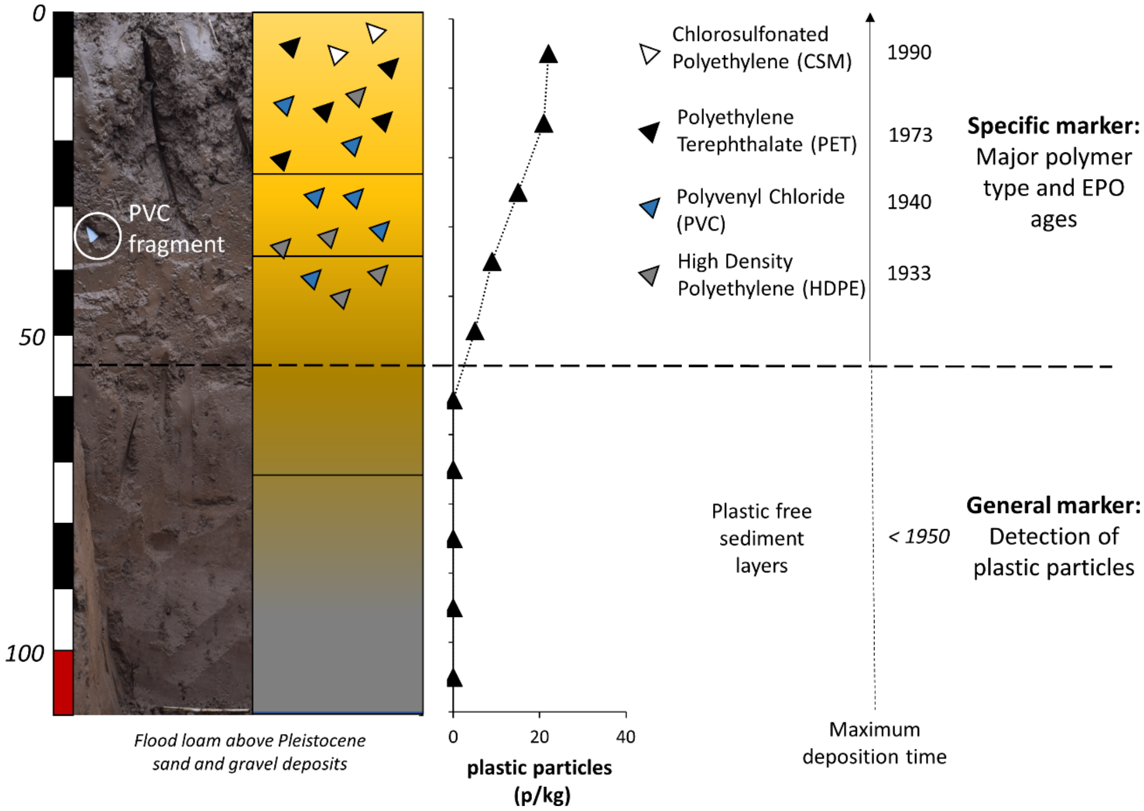


Figure 51: Ideal chronology for establishing a stratigraphy with the help of plastic particles using the example of a floodplain soil profile with visual detectable polyvinyl chloride (PVC) fragment (Fluvisol, Lahn catchment, Germany).

Finally, among the most valuable advantages, if considering plastics as potential stratigraphic markers, is the absence of geogenic background contents. Frequently applied anthropogenic contaminants, such as heavy metals, are subject to the problem that no clear distinction is possible between natural and anthropogenic inputs, especially in fluvial systems (Hürkamp et al. 2009; Kowalska et al. 2018). Although other pollutants are present in the environment, especially anthropogenic organic pollutants that do not show a geogenic background content, their detection is often more difficult than that of plastics, since only plastics in particulate form is detectable. The same circumstance in terms of analytical effort arises for geochemical dating methods in the form of radionuclide analyses like Cesium-137 (^{137}Cs) or Lead-210 (^{210}Pb) that cover the same time interval (Weckström et al. 2017).

3.6.3 Benefits and limitations

Besides the fact that plastics as long-lasting human made materials in Earth's surfaces are usable as possible indicators for the beginning of the "Anthropocene" (Bancone et al. 2020; Bensaude-Vincent 2021), several advantages are evident in using plastic deposits for the stratigraphic investigation of recent sediment dynamics in fluvial systems. It is an inexpensive, comparatively rapid analytical alternative or addition to established dating methods.

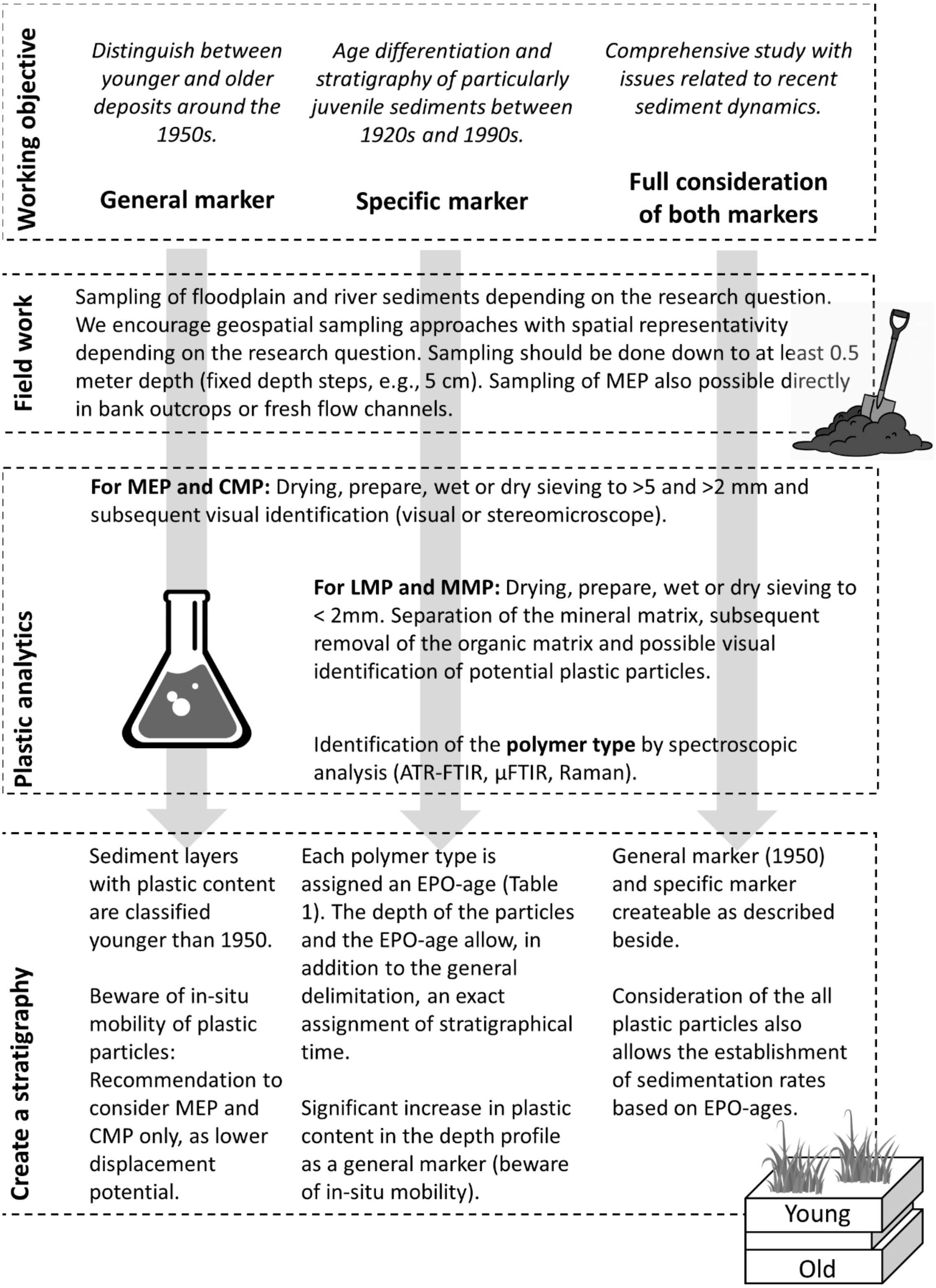
It relies on an easily identifiable (especially for MEP and CMP particles) persistent marker and provides dual results in terms of further knowledge of plastic contaminants in fluvial systems and the establishment of a stratigraphy, along with dating and sedimentation rates for the youngest fluvial sediments. Although research to date is limited, it has been shown, through the combination with established dating methods, that the plastic input and the increase of concentrations in different environmental archives (marine or limnic depositions) started after the 1950s, with very good agreement with the increase in global plastic production (Brandon et al. 2019; Turner et al. 2019; Dong et al. 2020).

From a conceptual point of view, however, first limitations are also identified. They include the archive in the fluvial system itself as well as remobilization and relocation of plastics, especially smaller particles. First, when extracting plastic particles from legacy sediment, human activities might have influenced fluvial systems in such a way that the sediments were deposited through a combination of both natural and anthropogenic processes (Edgeworth 2011; James 2013). Furthermore, Zalasiewicz et al. (2016) stated that sedimentary bodies of both marine and fluvial systems are still accumulating within the “Anthropocene”.

Despite direct anthropogenic influences on watercourses, one must deal with dynamic systems and search for plastics in sediment archives whose formation is by no means completed. Therefore, opportunity exists to monitor active sedimentation processes. The understanding and exploration of these recent deposits, however, is precisely at the core of the approach. This is why the uncertainty of the future stability of the archive is manageable for the approach presented in this paper, as opposed to its application in the “Anthropocene” stratification. Nevertheless, undisturbed sampling sites where plastic input is to be expected are ideal study sites on the basis of a geospatial approach.

A different situation arises with the limitation of possible remobilization or relocation of the archive, the sediments themselves, or the plastic in them (in-situ relocation). Sites where recent erosion processes (bank or lateral erosion) have occurred minimize the success of finding legacy sediments containing plastic and establishing a closed stratigraphy (Lechthaler et al. 2021). Furthermore, former dumped plastic material (e.g., post usage of quarries for landfills) can enter the fluvial system after longer retention, through bank erosion (Brand et al. 2018), or leachate movement (He et al. 2019). In addition, studies have already documented in-situ relocation processes for microplastics in soils and sediments (Rillig et al. 2017b; Alimi et al. 2018; Weber und Opp 2020). This process can occur through infiltration, preferential flow, groundwater or bioturbation (Rillig et al. 2017b; Engdahl 2018; Yu et al. 2019). However, comparable limitations, especially with regard to bioturbation, also apply to other dating methods (e.g., radionuclide dating, carbon dating, luminescence dating) and may hinder them altogether (Weckström et al. 2017). In the case of plastic particles, the displacement tendency and mobility depend mainly on the particle size.

Therefore, the postulated advantage of considering microplastics, since their small size enables them to enter all environmental media more easily, can also become a disadvantage (Zalasiewicz et al. 2016). Both MEP and CMP particles are only displaceable by bioturbation in floodplain soils, as they are often too large for the pore space with a diameter of >2 mm (Weber und Opp 2020). Since the analysis of microplastic particles is also much more complex, it is worth considering whether the focus should not be on particles >2 mm for stratigraphic and dating purposes. Here, too, as in the case of the application of established methods, undisturbed sites with regard to traceable anthropogenic direct disturbances should be preferred, also with regard to relocation or bioturbation processes. Figure 52 gives an overview of the three possible working objectives for the application of plastics as stratigraphic marker. It must be noted against the background of plastics mobility within sediments or erosion (remobilization) of former landfill deposits, that the general marker or specific EPO ages, may only provide a ‘terminus post quem’ to the date after the sediment was deposited and no precise deposition date.



Distinguish between younger and older deposits around the 1950s.

Age differentiation and stratigraphy of particularly juvenile sediments between 1920s and 1990s.

Comprehensive study with issues related to recent sediment dynamics.

Sampling of floodplain and river sediments depending on the research question. We encourage geospatial sampling approaches with spatial representativity depending on the research question. Sampling should be done down to at least 0.5 meter depth (fixed depth steps, e.g., 5 cm). Sampling of MEP also possible directly in bank outcrops or fresh flow channels.

For MEP and CMP: Drying, prepare, wet or dry sieving to >5 and >2 mm and subsequent visual identification (visual or stereomicroscope).

For LMP and MMP: Drying, prepare, wet or dry sieving to < 2mm. Separation of the mineral matrix, subsequent removal of the organic matrix and possible visual identification of potential plastic particles.

Identification of the **polymer type** by spectroscopic analysis (ATR-FTIR, µFTIR, Raman).

Sediment layers with plastic content are classified younger than 1950.

Beware of in-situ mobility of plastic particles: Recommendation to consider MEP and CMP only, as lower displacement potential.

Each polymer type is assigned an EPO-age (Table 1). The depth of the particles and the EPO-age allow, in addition to the general delimitation, an exact assignment of stratigraphical time.

Significant increase in plastic content in the depth profile as a general marker (beware of in-situ mobility).

General marker (1950) and specific marker createable as described beside.

Consideration of the all plastic particles also allows the establishment of sedimentation rates based on EPO-ages.

Figure 52: Flow chart for the use of plastic particles as a stratigraphic sediment marker in fluvial environments from working objectives to final application.

3.6.4 Outlook

Ubiquitous in the environment, (micro-)plastics have potential to become a ’novel’ stratigraphic marker for recent sediments, and especially fluvial sediments. This potential is due to their occurrence in fluvial systems, their properties, and their preservation. Even though plastic, and especially microplastics, are an environmental contaminant and a potential pollutant, one can consider plastic particles beyond that light. Nevertheless, due to limited studies so far and the numerous open research questions, it is important to define (micro-)plastic hotspots within the environment, whereby soils and sediments play an important role. Thus, the detection of plastic particles are usable in two different ways: as a proxy of environmental contamination, and as marker in a sedimentary context. In the future, it will be possible to record recent sediment dynamics in fluvial systems, to classify them stratigraphically, and to monitor them. The highlighted limitations, however, due to plastic relocation and the disturbance of already human-influenced environmental archives, also requires further investigation. With the emerging Covid-19 pandemic, the protective mask (Figure 50) has entered the environment as a new specific marker. It may emerge in the future as a 2020 marker due to its visual properties and specific composition (Dharmaraj et al. 2021). Despite the widespread use of face masks in certain regions or during previous virus outbreaks, the explosive global increase in mask production in 2020 is accompanied by a worldwide spread and high potential for littering of used masks (Chen et al. 2021a). Perhaps this will not be the last clearly assignable marker in fluvial systems that can be used in a stratigraphic context. Finally, we would like to call for the ideas around the use of plastic as a stratigraphic marker for application in practice, for validation, and to enable further progress among disciplines.

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4. Key findings and summary

The individual Chapters 3.1 to 3.6 contain different contributions to an improved understanding of the spatial distribution of meso- and microplastics within floodplain soilscapes. Each chapter includes conceptual developments and new scientific findings, which are in-depth discussed within each respective chapter. All chapters and scientific findings contribute to the overall goal of unravelling the role of floodplain soilscapes as depositional areas for meso- and microplastic debris within the global plastic cycle. Within this summarizing chapter, the key scientific outcomes will be presented with a special focus on the objectives and hypotheses introduced at the beginning of this thesis.

Against the background of the first objective stated at the beginning of this thesis (Chapter 1.3.1), both the scientific problem and the objectives derived from it overlap with the key findings of Chapter 3.1. The conceptual starting point for this work was the finding that, within environmental (micro-)plastic research, a lack of spatial representative studies exists so far. This circumstance has made it necessary to think about potential conceptual solution approaches. From an environmental, geographic, and especially soil geographic view, environmental processes and the contamination of soils by plastic residues can only be considered comprehensively in the context of soils as a spatial phenomenon and their influencing or resulting soilscape properties. A major outcome from the systematic literature review (Chapter 3.1) and my own conceptual considerations was that a transition from “explorative” to systematic (micro-)plastic studies, based on geospatial sampling approaches, becomes necessary to access the spatial dynamics of (micro-)plastics in soils (Figure 53, **key finding 1**). Derived from this key finding, the geospatial sampling approach, based on a classification of river courses according to soilscape conditions and the determination of meso- and microplastics in floodplain cross-sections as well as the consideration of deeper soil-sections were conducted. This framework forms a process-oriented sampling approach providing more sophisticated research on (micro-)plastics in floodplain soilscapes as a response to the overall scientific problem (**Objective 1**).

The implementation of the developed geospatial sampling approach is reflected in the following case studies for the model regions of the Lahn and Nidda Rivers (Chapters 3.2, 3.3, and 3.5). Within these case studies, several key scientific findings regarding the further objectives and respective scientific questions of this thesis were derived (Chapter 1.3.1). Following the further objectives, with a focus on the determination of environmental drivers through the spatial distribution of meso- and microplastics in floodplain soils (**Objective 2**) and the investigation of temporal enrichments and spatial correlations to other contaminations (**Objective 3**), the following key findings can be summarized:

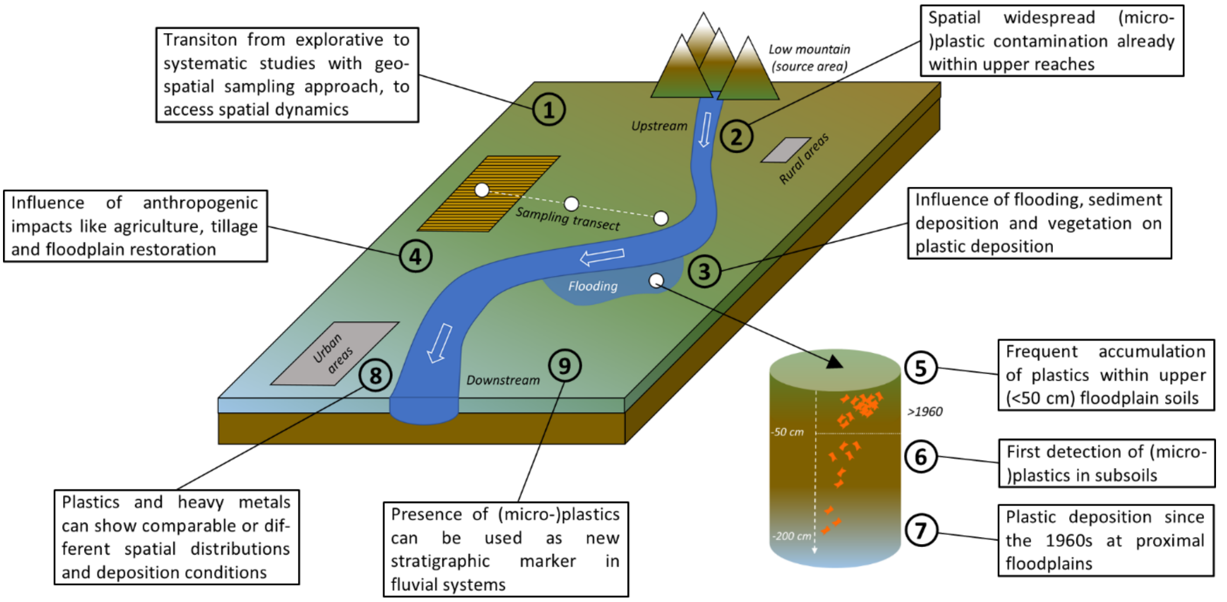

Figure 53: Graphical summary of key findings from Chapters 3.1 through 3.6.

First, on the lateral catchment scale, it was found, that meso- and microplastic contaminations already occur within the upper reaches (Figure 53, **key finding 2**) of both studied catchments and their respective floodplain soilscapes. This finding contradicts previously assumed linear increases in plastic contamination from freshwater and sediments. Even if maximum meso- and microplastic levels occur within the floodplain soilscapes of the lower reaches, a non-negligible contamination already exists where the riverine floodplains and the associated sink function are only slightly developed. In general, a spatial widespread but heterogenous contamination of floodplain soilscapes could be proofed, thus challenging simple, linear source-to-sink assumptions about plastic transport and deposition. This finding raising further questions on the origin of the found meso- and microplastics as common assumptions, such as major inputs from urban or traffic runoff, WWTPs, and agricultural inputs being only slightly pronounced in the headwaters of the most, low mountain range rivers in Central Europe.

Second, on the lateral floodplain scale expressed through floodplain cross-transects, it was possible to determine an influence of flooding, sediment deposition, and vegetation on the plastic deposition dynamics (Figure 53, **key finding 3**). Already during the investigation of mesoplastics and the newly introduced classification term *coarse microplastics* (Chapter 3.2), it has become clear that higher concentrations of both plastic size classes can be found at proximal, near-channel floodplain sites with a tendency to lower concentrations at distal sites. This spatial pattern, in combination with the calculated sedimentation rates, gave the first indication that flood processes as a diffuse input pathway from the waterbody could play a major role for plastic depositions in floodplain soils. This finding was also supported from the continuation of the analysis including smaller microplastic particles within the Lahn River (Chapter 3.3) and Nidda River (Chapter 3.5) floodplains.

Generally, it can be summarized that larger amounts of microplastics occur within areas that are (i) flooded more frequently and where (ii) larger amounts of sediments are deposited and (iii) where the vegetation cover of floodplain soils shows a greater roughness. Those natural conditions occur within the proximal floodplain riparian corridor, built up from young sediment deposits and showing a morphological levee situation, including riparian or grassland vegetation. Therefore, the frequency of floods, their dynamics, and the retention properties against microplastics transported within floodwater affect meso- and microplastic deposition within floodplain soilscapes.

Third, and despite the previous key finding 3, already within the first case studies (Chapter 3.2), it becomes obvious that flood related sedimentation processes alone could not explain the found spatial contamination patterns in a sufficient way. Differences between meso- and microplastic concentrations also occur in comparison with different land uses (here: riparian, grassland, and cropland) in both studied catchments. For the Lahn River floodplains, the influence of land use on the spatial distribution remains an indication, but within the Nidda River floodplain, which is even more strongly influenced by agriculture and urbanization, these indications could be unraveled more clearly. Based on maximum meso- and microplastic concentrations, surface accumulations of macroplastic residues and deviations in the vertical plastic distribution, it becomes distinct that short- to long-term anthropogenic impacts such as agriculture in general, tillage, and floodplain restoration measures have an effect on (micro-)plastic distribution patterns in floodplain soilscape (Figure 53, **key finding 4**). Therefore, a combination of natural, primary flood-related, and anthropogenic (both land use and impact effected) processes seem to affect the spatial distribution of meso- and microplastics in floodplain soilscapes on the lateral and vertical scale. This summarized finding also leads to further questions about the quantitative contribution of each single effect and the environmental drivers on the entirety of (micro-)plastic contaminations. Finally, other proposed input pathways of (micro-)plastics to soils, like atmospheric deposition, erosion from surrounding slopes, or the simple anthropogenic littering can be part of the identified combined source and influencing factors.

Fourth, leaving the lateral dimension and focusing on the vertical scale, two key findings and other insights can be summarized, findings that are perhaps the most important ones within the overall background of this thesis. Regarding the vertical distribution of meso- and microplastics in floodplain soils, a frequent accumulation within all investigated soils was found within the first half meter (0–50 cm) of the soil column (Figure 53, **key finding 5**). Furthermore, the reported records of meso- and coarse microplastic within subsoils at depths of 50 to 100 cm (Chapter 3.2) and the evidence of microplastics within deep subsoils, reaching depths down to 2 meters (Chapters 3.3 and 3.5), were the first detections of plastics in subsoils worldwide (Figure 53, **key finding 6**). Based on the geospatial sampling approach, which considers soil as a three-dimensional spatial phenomenon and going beyond the often-conducted topsoil-studies, those key findings were enabled. Based on these findings, further insights can be derived concerning the deposition and behavior of plastics in floodplain soils.

The frequent accumulation within upper soil sections leads to the inference that (micro-)plastics entering floodplain soils through the above-mentioned combined processes are stored within the upper soils sections first. However, the sole evidence of (micro-)plastics in deeper soil sections (subsoils) at lower concentration levels and a tendency towards smaller particles in deeper layers indicates the role of natural processes that transfer plastic into deeper soil layers. Given the fact that comprehensively larger meso- or coarse microplastic particles reach depths of one meter, different in-situ relocation processes become conceivable, as discussed within Chapters 3.2, 3.3, and 3.5. It can therefore be summarized that (micro-)plastics become accumulated and stored within floodplain soilscapes but can also become mobile and transferable within the soil. These key findings raise further research questions regarding the underlying environmental processes, as well as the extent of the relocation processes.

Fifth, a further elaboration of the previous key findings became feasible by including dating methods. To investigate the temporal component of meso- and microplastic enrichment (**Objective 3**), dating recent floodplain sediment deposition was possible for two exemplary soil columns within the Lahn River catchment. Those analyses have shown that (micro-)plastics are accumulated within the youngest floodplain sediments, which correspond to the upper accumulation layer (0–max. 50 cm) since the 1960s, which is in line with the global increase in plastic production (Figure 53, **key finding 7**). This key finding is linked to proximal floodplain positions within the upper and lower reaches (Chapter 3.3) and can be transferred to the wider floodplain only via the distributed evidence of accumulation in upper soil layers. Furthermore, this key finding proves under the given spatial restrictions that deeper plastic deposits cannot have been deposited by sedimentary processes but must have been vertically displaced in the existing sediment and the soil developed in it. Regarding the temporal occurrence of (micro-)plastic depositions in floodplain soilscapes, it can be summarized that floodplains act as accumulation sites since the early period (1960s) of the *Plastic Age* and onwards.

Sixth, the analysis of spatial correlations between the new contaminant plastics and the well-recognized contaminant of metals of interest or heavy metals, form the basis for a further key finding within the framework of this thesis. Within both model regions and their floodplain soilscapes, both contaminants were found all-encompassing within the investigated soils (Chapter 3.4). Because metal contents can be evaluated (e.g., legal requirements) very well in contrast to (micro-)plastics, low-to-moderate metal contaminations were found. Regarding the spatial correlations of both contaminants, comparable or different spatial distributions and deposition conditions were found, which vary depending on the model region considered (Figure 53, **key finding 8**). For the Lahn River floodplains, the spatial correlations found comparable variability across the catchment and floodplain cross-sections, as well as a comparable accumulation of both contaminants within upper (0–50) and therefore recent floodplain sediment deposits (Chapter 3.4). In contrast, within the Nidda River floodplains, both contaminants show a different spatial distribution on the lateral scales and significantly deeper metal enrichments than plastic accumulations (Chapter 3.5).

Because metals reaching floodplains soils mainly through flood related deposition processes, this key finding leads to further insights to the deposition dynamics of both contaminants. Whereas within the Lahn catchment comparable deposition processes and time periods (recent, last 6–7 decades) are probable, different deposition conditions and different time periods can be assumed for the Nidda catchment. Furthermore, the finding that macro- and coarse microplastics contain heavy metals of adsorbed or additive origin and that the mutual presence of both contaminants in floodplain soilscapes raises further questions about the interaction of both substances in floodplain soils and the resulting environmental risks.

Finally, and as a perspective developed from the overall framework of the thesis, a scientific outlook can be derived as a key finding. The presence of meso- and microplastics in floodplain soilscapes can be applied to scientific advantage, namely as the application of plastics as a stratigraphic maker for fluvial deposits (Figure 53, **key finding 9**). Based on the former key findings regarding the lateral and vertical distribution of (micro-)plastics and their temporal occurrence within floodplain soilscapes, a methodological approach could be developed. Despite given limitations (Chapter 3.6), plastics are usable as a new stratigraphic marker within fluvial systems of the *Anthropocene*. This approach enables a further method for dating youngest sedimentary deposits and poses the possibility to monitor active sedimentation processes within floodplains.

Summarizing the new insights and the key findings achieved within the framework of this thesis, it can be stated that the general presence of meso- and microplastics within considerable concentrations confirm the hypothesis that floodplains can be considered a part of the global plastic cycle and act as temporal accumulation sites (**Hypothesis 1**, Chapter 1.3.1). The detection and identification of typical, every-day-use thermoplastic polymers such as PEs, PP, or PA, as well as several resins or rubbers, contributes on the assumption that floodplain soilscapes are affected by the global plastic crisis in the same way as other environmental systems and that they are not subject to specific or isolated plastic contaminations. The spatial widespread occurrence of meso- and microplastics besides enrichments at certain spatial positions, contributes to the prior assumption that plastics occur within the entire catchment and soil column (**Hypothesis 2**). Furthermore, the combined effects of natural and anthropogenic factors on the three-dimensional spatial distribution patterns of meso- and microplastics, proof the interaction of fluvial, terrestrial, and anthropogenic drivers in view of the plastic input pathways and dispersion to floodplain soilscapes (**Hypothesis 3**). The coherent key findings of meso- and microplastic accumulation within upper soils, the evidence in subsoils, the associated relocation processes, and finally the deposition of plastics since the 1960s confirm that floodplain soilscapes are affected through meso- and microplastic inputs since the “Great Acceleration”; once in cooperated into the soil, plastic particles became subject to vertical shifts and therefore mobile (**Hypothesis 4**). Lastly, the identified spatial correlations between meso- and microplastics and metals of interest demonstrate a partial spatial connection between both contaminants (**Hypothesis 5**).

5. Conclusions

5.1 Discussions on the conceptual and methodological approaches

The conceptual framework of this thesis is based on a geospatial approach (Chapter. 2.2.1) and a combination of analytical strategies from the fields of meso- and microplastic analysis (Chapter 2.2.2.3), soil and metal analysis (Chapters 2.2.2.2 and 2.2.2.4), and sediment dating (Chapter 2.2.2.5). The scientific data obtained during this thesis and the respective key findings must therefore be examined against the background of the conceptual considerations and the limitations of the methodology applied (Chapter 2.2.3). First, the geospatial sampling approach, whose foundation lies in the lack of systematic spatial studies, allows a first spatial assessment on meso- and microplastic contaminations in floodplain soilcapes. Consequently, interpretations of the obtained data—depending on spatial contexts and differences—can be considered against the background of the dynamic and interacting environmental processes within the aquatic-terrestrial interface. After this first attempt, it becomes clear that the spatial representativeness of (micro-)plastic related studies can be widened through methodological implications in the future. Nevertheless, the geospatial sampling approach has to deal with given constraints, such as a limited number of samples that can be examined (cost- and time constrains) and limited knowledge about sampling site history (knowledge constraint). Although the influence of flood-related processes and anthropogenic influences on the meso- and microplastic distributions could initially be identified, a detailed quantitative assessment of the (micro-)plastic inputs derived from both factors and other influencing factors were rendered unsatisfactory by the given constraints.

Although the conceptual geospatial approach allows a spatially based analysis of meso- and microplastic contents and initial assessments of environmental drivers, the adapted (micro-)plastic analysis itself is primarily limited (Chapter 2.2.3). Results on meso- and microplastic abundance within floodplain soilscapes is mainly limited through the investigated plastic particle size range and through the considered particles' density. Consequently, even if a state-of-the art analysis were performed, suitable for large parts of the common thermoplastics in the environment, the goal of a truly comprehensive (micro-)plastic analysis still seems to be a long way off. The overwhelming number and variety of polymers, their additives, and the resulting chemical and physical properties make it difficult to carry out an all-encompassing comprehensive analysis. Nevertheless, a target-oriented application of existing analysis methods enables the acquisition of initial research data and findings.

What is considered profitable within the framework of this thesis and for (micro-)plastic research within soil environments could be the application of combined and interdisciplinary method approaches. Despite the consideration of meso- and microplastics in a stand-alone way, the combination of different methodological skills enables a combination of environmental data and further conclusions about the spatial distribution and initial insights about the responsible environmental drivers of (micro-)plastic dispersal in floodplain soilscapes.

Within the emerging and highly dynamic research field dealing with plastics in soils, the global plastic cycle, and the global plastic crisis, the results and insights of this thesis should be considered a snapshot of the state of knowledge. Further perspectives for the geographic, spatial-, and environment-oriented research will therefore be described in detail in the next chapter.

5.2 Perspectives for future research

The scientific findings and new insights about the spatial distribution of meso- and microplastics in floodplain soilscapes that were presented throughout this thesis have generated new research questions. In addition to further and in-depth research questions, the findings can also be used to derive recommendations for further research on (micro-)plastic in floodplain soilscapes and soils in general. In general, further and more detailed research on (micro-)plastics at the interface of aquatic and terrestrial systems is clearly needed to improve the understanding of their role in global plastic cycles in the future.

Methodological implications: Geospatial access to (micro-)plastics in soils

In this thesis, just as in numerous other research investigations, the need for improvement of analytical methods for (micro-)plastic detection, their validation, and final standardization, especially for complex sample matrices such as soils, has already been highlighted. Furthermore, the importance of spatially adequate sampling strategies and the proposed geospatial sampling approach was discussed (Chapter 3.1). Beyond that, and from an environmental geography and soil geography point of view, geospatial sampling approaches could be enhanced in the future through the increased use of geo-information systems and the automation of spatial selection procedures. With the increasing knowledge about the occurrence, fate, and behavior of (micro-)plastics within the environment, it becomes possible to apply geostatistical methods and modelling approaches for the question-oriented selection of suitable study areas, sampling sites and soil sections. Those approaches should be based on sufficient, spatial data about (micro-)plastics, whose database is slowly emerging. Furthermore, modelling and spatial predictions approaches will become suitable in future, if a satisfying database, derived from both field and laboratory studies exists. As the plastic crisis and plastics as part of Earth's processes are a global phenomenon, it becomes even more important to share basic research data and make it freely available worldwide. Only when global spatial datasets are available can geospatial approaches contribute to further research and method improvements.

Environmental drivers of (micro-)plastic dispersal in floodplain soilscapes

The key findings of this thesis proved the presence of meso- and microplastic in floodplain soilscapes and indicates that a complex spatial contamination pattern results from combined sources and drivers within the aquatic-terrestrial interface (Chapter 3.2, 3.3, and 3.5). Within this context, the question about the extent and contribution of single environmental and anthropogenic drivers for (micro-)plastic sources, spatial dispersal, and deposition arises.

Action is needed to quantify the contribution of single (micro-)plastic sources (e.g., flood dynamics, land use, littering) to the contamination of floodplain soilscapes. Furthermore, quantifications of influencing factors that contribute to deposition and remobilization in floodplain soils must be performed. Future studies should initially focus on single drivers to perform a holistic combined assessment in a later step. However, it should be clear that any consideration of single drivers cannot be done in isolation because different drivers interact within the aquatic-terrestrial interface. Based on the interacting and often highly dynamic drivers over space and time, the question about the temporal dimension also arises (Chapters 3.3 and 3.6). Methods such as sampling in time series and event-based sampling (e.g., during flood events) and analysis can be applied here. Nevertheless, it should be considered that the sampling of natural archives, like floodplain soils, is always disturbed by sampling, which makes sampling in time series difficult against the background of spatial representativeness. Further conceptual studies are therefore necessary. Regarding the possible spatial and biogeochemical interactions between plastics and metals of interest, further research should consider the different chemical and physical binding and release options (e.g., application of different digestion protocols during elemental analysis) and focus on the resulting environmental risks (e.g., plastic as an additional source of metals, or as a carrier for metals) (Chapter 3.4). In summary, a combination of target oriented and systematic case-studies within different model regions and soilscapes, studying in-situ processes in combination with the investigation of environmental drivers under controlled laboratory conditions (e.g., flume experiments) will contribute to an enhanced understanding of the responsible environmental drivers.

Going deeper: Vertical mobility of plastics in floodplain soils

The first attempt and the subsequent first evidence of meso- and microplastics in subsoils, contributed by the findings of other studies, raises several questions on how (micro-)plastic relocation takes place in soils (Chapter 3.2, 3.3, and 3.5). To address these questions in the future, the shift from examining topsoil alone to examining the entire soil column must be continued. Future case-studies should monitor the vertical distribution of (micro-)plastics based on high vertical sampling resolution within different soils. Additionally, soil-related data influencing the transport processes within soils (e.g., texture composition, pore spaces, pore characteristics, soil organisms) should be analysed together with plastic abundance and characteristics to obtain initial findings on influencing factors. Again, the combination of in-situ investigations and laboratory experiments (e.g., infiltration tests) will contribute to a satisfactory gain of further knowledge about the mobility of plastics in soils in the future. Because floodplain subsoils and deeper fluvial sediment layers could contribute to a long-term storage of (micro-)plastics and because an accumulation in those “deep” soils poses a risk to groundwater and water supply, this research field is of particular urgency.

The temporal component: A novel plastic-stratigraphy

Within the framework of this thesis, one of the first attempts was made to use meso- and microplastics as novel stratigraphic markers within fluvial systems. Different contributions from other scholars within the fields of marine or limnic and archaeological research contribute to the finding that plastics are generally usable as a stratigraphic marker (Chapter 3.3 and 3.6). Despite the role of (micro-)plastics as environmental pollutants, this opportunity bears a huge (earth) scientific progress. In the future, it will be necessary to quantitatively validate the previous approaches using various environmental archives. Limitations (e.g., plastic mobility) and open questions (e.g., long-term preservation) could also be investigated in this way. Combined method approaches—like the combination of plastic analytics, soil stratigraphy, and dating methods suitable for the period beginning in 1950 to the present—could also be applied to other environmental archives. In general, the role of plastics as potential markers within the current scientific debate about the proposed *Anthropocene* epoch must be further discussed. In addition to other case studies, it must be discussed on a conceptual level what role and function plastics can play in relation to other markers of the Anthropocene.

5.3 Implications for floodplain protection and policy makers

Despite the environmental and health risks posed by the global plastic crisis, it must be clear that a general condemnation of plastics cannot become a targeted solution of this crisis. Plastics as a material, as well as recent developments including biopolymers, is so widespread and useful that even after only 70 years it is hardly replaceable. Nevertheless, society and politics have become aware of the global crisis, and several measures to contain the crisis have already been taken (Chapter 1.1). Not least of all, the recently adopted United Nations Environment Assembly resolution to end plastic pollution with an international legally binding agreement by 2024 during UNEA-5.2 gives hope for further reduction of plastic mismanagement and input into the global environment.

Nevertheless, the scientific outcome and conclusions of this thesis illustrate that plastics have entered the environment and especially floodplain soils over a period of six to seven decades so far. Although further reduction and prevention of plastic inputs into the environment are urgently needed, action is also needed to deal with the contamination that already exists. Because floodplains are one of the most threatened ecosystems worldwide and are subject to a distinct conflict of use, many measures have already been taken in the past for the protection and restoration of floodplains and will be pushed forward against the background of climate change. With the new scientific insights gained within this thesis on meso- and microplastics in floodplain soils, implications for floodplain protection arise that should be considered in the future:

Specific implications for floodplain protection

- The presence and possible environmental consequences of (micro-)plastics in floodplains and their soils must be brought to the attention of society and politicians. Decision makers need to be informed about new findings to integrate them into their strategies.
- To protect floodplains as an ecosystem, further (micro-)plastic inputs must be prevented. Even if the input pathways of plastics to floodplains seems complex, the principle that clean rivers and clean landscapes led to "clean" floodplains, as a result of the essential connection between rivers and floodplains, applies here. Although certain input pathways can be prevented through regulation or technical innovation, littering can only be brought about through improved social awareness and strategies for the use of recovered plastic materials.
- In the case of existing contamination and possible hotspots, such as proximal floodplain sites close to the riverbank, special care is required for interventions, such as restoration measures. Proximal floodplains are often strongly affected by measures, such as the creation of near-natural banks, and bear the risk for renewed remobilization of deposited plastics. It is necessary to consider how to deal with plastic contaminated soil and sediment material in the future.
- Because the impact of direct anthropogenic influences on plastic abundance is traceable, known measures of soil protection should also be implemented with regard to plastics. Examples would be the monitoring of plastic contamination before any construction and renaturation activities, the identification of hotspots, and the proper handling of heavily contaminated material. This does not mean questioning the advantages of floodplain restoration measures but rather identifying possible ways of dealing with plastics, even against the comparatively low contents of plastics.

In addition to the protection of floodplains and their soils, there are further implications for society and politics, which can be pronounced based on the conceptual work and key findings of this thesis within a in a broader context:

General implications

i. Plastics in the environment and especially within floodplains and soils **have to be understood as what they are: anthropogenic contaminants**. Even if their role as pollutants has not been comprehensively understood so far, they are foreign substances that have been introduced into the environment by humans. This fundamental understanding must be the guiding principle for all measures, regulations, or even laws that may be developed in the future.
ii. The extent of the global plastic crisis with all proven or possible environmental risks is so far-reaching that **containment measures must be taken immediately**. Global environments, natural processes, and soils as the foundation of terrestrial and human life are already affected to such an extent that further damage to the global soil system, which may also be accelerated by plastic, must be prevented in a timely manner.
iii. To understand the whole extent of (micro-)plastic contamination of floodplain soils, but also of all terrestrial soils, **spatial and quantitative monitoring of plastics in soils is mandatory**. Although legislation relies on the standardization of analytical methods, this does not apply to (official) monitoring programs. The use of already existing soil permanent monitoring sites could be an and their sample databases and could be a powerful tool for spatially representative and timely monitoring at the regional to national level.
iv. For existing (micro-)plastic contaminations, it is necessary to **find a suitable management strategy**. In addition to plastic monitoring, this also requires regulations and legislation on handling. Basic principles of precautionary soil protection and proven measures for dealing with contaminated soils should be applied to the "new pollutant" plastic in the future.
v. Finally, **scientific and technical progress must be supported**. At this stage, a sufficient data base on (micro-)plastics in floodplain soils and terrestrial ecosystems in general is clearly a long way off. Research and technical innovation are the only ways to cope with the global plastic crisis and protect the environment more effectively in the future. Because it is a global crisis, free access to new knowledge (*Open Data*) becomes indispensable.

Furthermore, the socio-economic dimension of the global plastic crisis cannot be neglected. Although there is already widespread social awareness of this crisis, it needs simply to be better communicated. Marine plastic issues are still more prominent than the problem of plastic in soils. Because part of the problem lies in society's handling of plastic, improved communication of scientific findings, public involvement in research (citizen science), and broad information campaigns can be essential.

In conclusion, the given implications can be summarized with the triad of **"protect – monitor – develop"** with the meaning of (i) protect floodplains and soils for further (micro-)plastic contamination, (ii) monitor (micro-)plastic contaminations within the aquatic-terrestrial interface, and (iii) develop strategies to deal with existing (micro-)plastic contaminations.

In view of the ongoing research about (micro-)plastics within soil environments, this thesis is equally an appeal to think beyond the trending approaches of environmental science and consider soils and their contamination as results of spatial interacting processes and spatial phenomenon. Soil geography is not limited to spatial surveys of soils but rather allows approaches to thoughts about the influence of the processes in the space, on the space, and the scientific investigation targets. The role of geospatial approaches with target-oriented and validated sampling and analysis provides a powerful tool for creating valuable insights within the previously unknown fate of plastics in the environment.

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Appendix

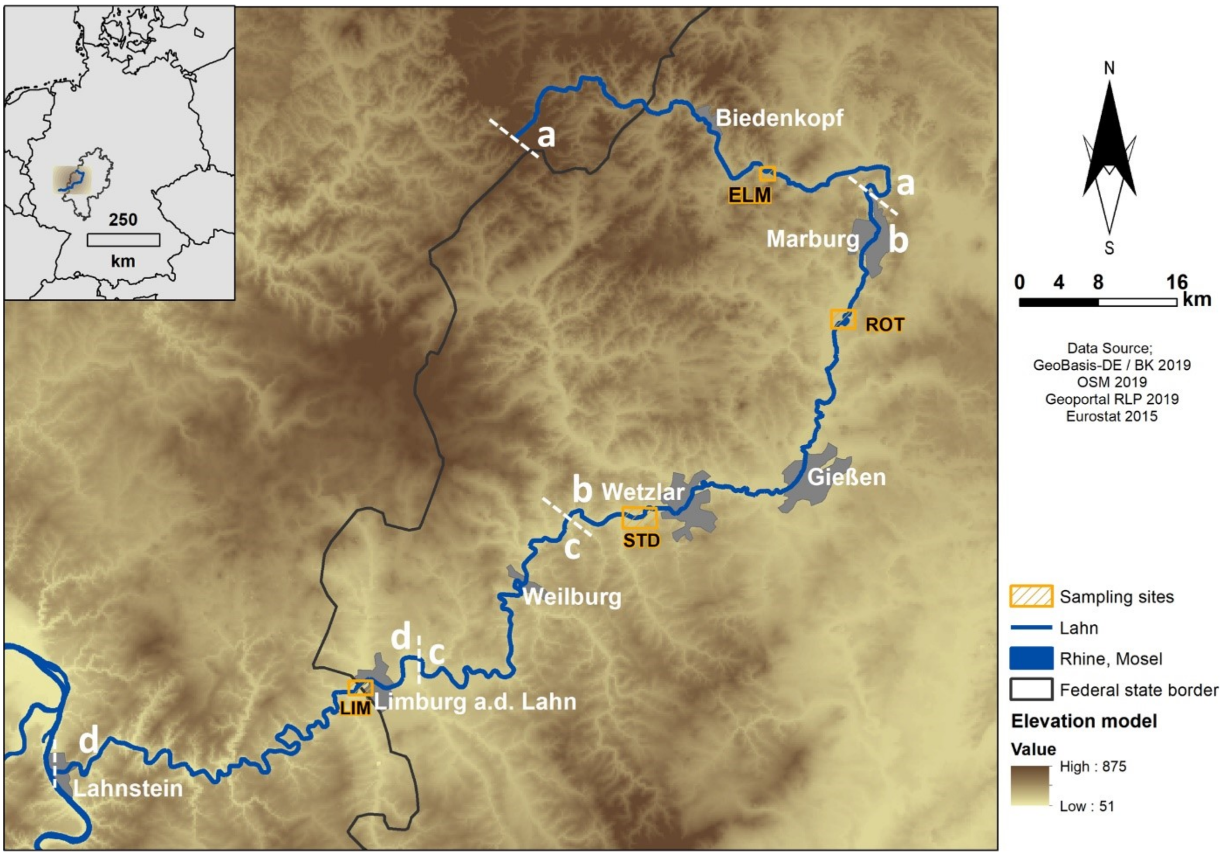


Figure A 1: Location of sampling sites inside the Lahn River catchment (ELM: “Elmshausen”; ROT: “Roth”; STD: “Steindorf”; LIM: “Limburg”). In addition, the dotted lines show the boundaries of the river and landscape sections which are explained in chapter Study area (a = upper course; b = middle course; c = narrow valley; d = lower course). [Original part of the supplementary material of chapter 3.2]

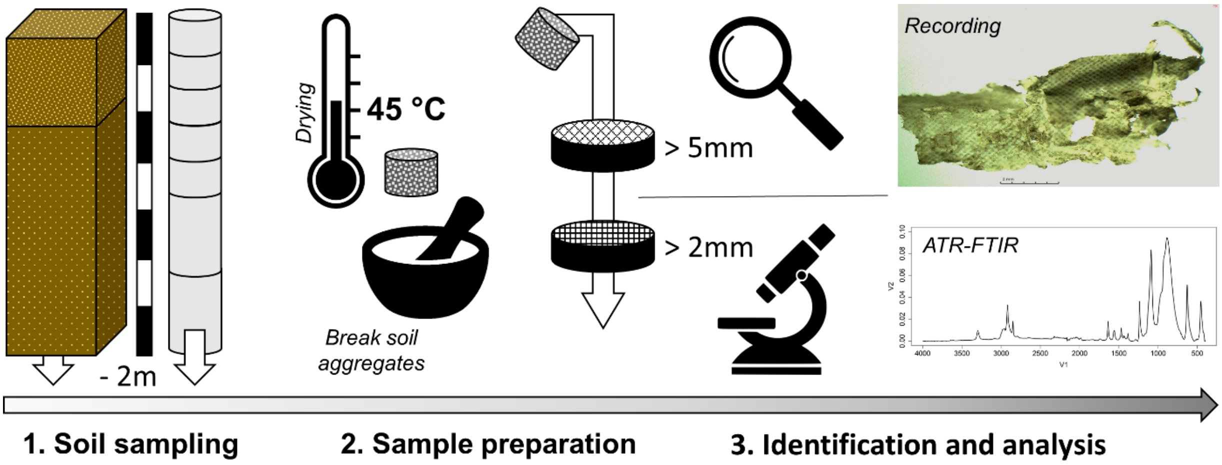


Figure A 2: Procedure for MAP and CMP analysis. [Original part of the supplementary material of chapter 3.2]

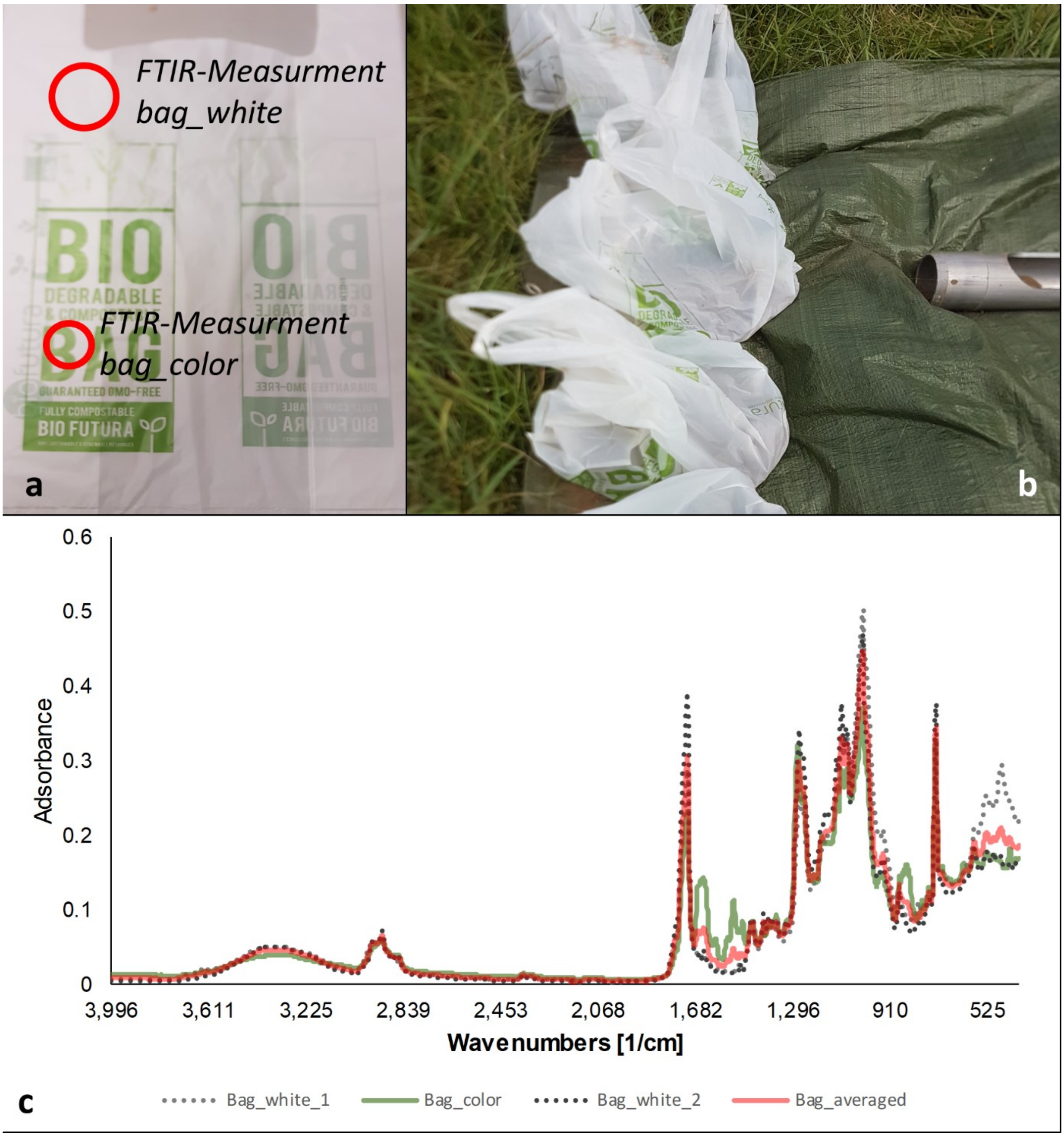
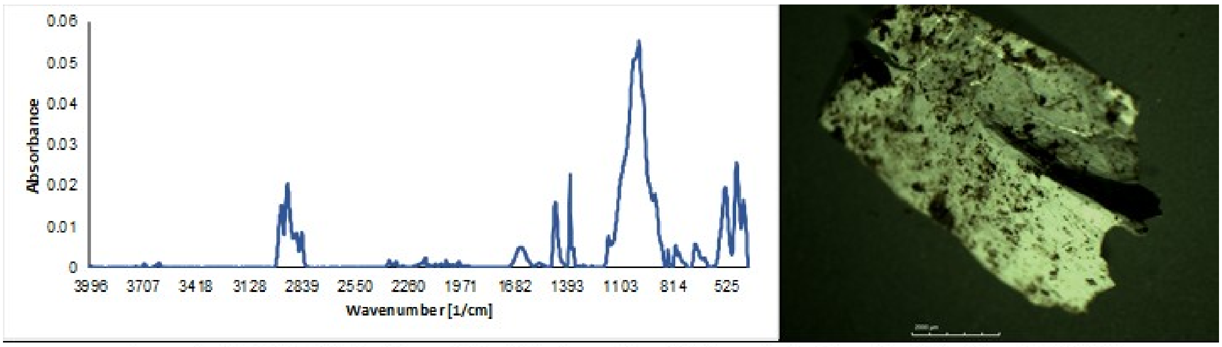
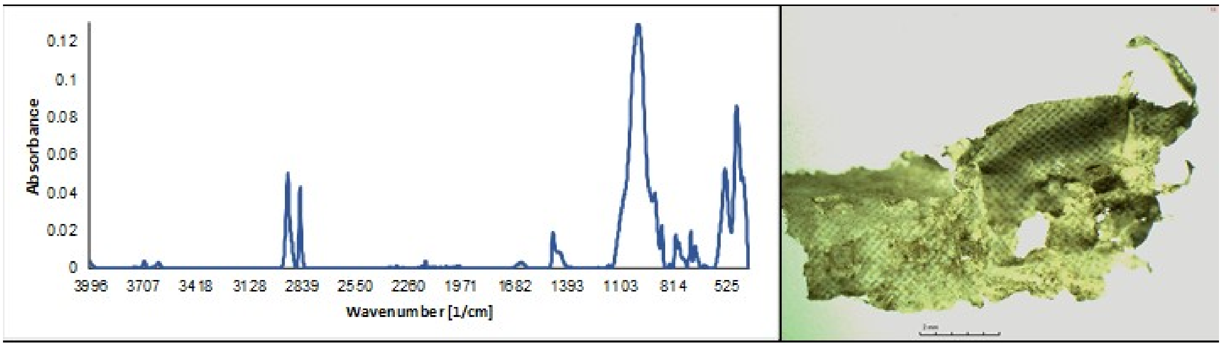


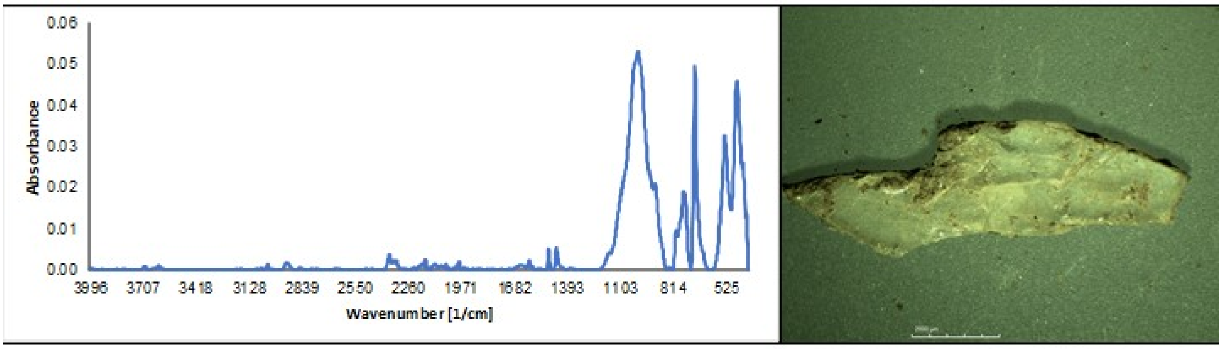
Figure A 3: Bioplastic bag features: a) Bioplastic bag Mater-Bi bags, Bio Futura B.V., Rotterdam, Netherlands) and sample parts FTIR analysis; b) Bioplastic bag during field work; c) FTIR spectra of Mater-Bi bioplastic bags. [Original part of the supplementary material of chapter 3.2]



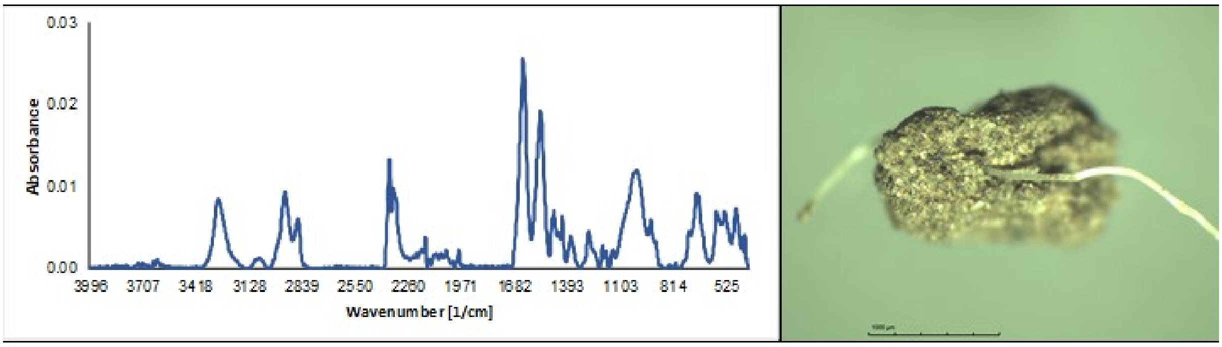
*Sample-ID: **LIM-1-1** (0-10 cm); Particle type: film (white color), size: Identification: **PP** (505)*



*Sample-ID: **STD-1-5** (40-50 cm); Particle type: film, size: ,Identification: **PE-LD** (356)*



*Sample-ID: **STD-1-1** (0-10 cm); Particle type: fragment, size: ,Identification: **PA** (318)*



*Sample-ID: **ELM-1-3** (20-30 cm); Particle type: filalment stocked in macroaggregate,
size: Identification: **PA** (430)*

Figure A 4: Examples for identified CMP particles in floodplain soils (Pictures of CMP particles were taken after visual identification and before selective cleaning for ATR-FTIR analyses). [Original part of the supplementary material of chapter 3.2]

Figure A 5: Visible MEP and CMP in floodplain soils: a) Fluvisol at sampling site STD riparian zone with young sandy layers (0-3 cm) containing plastic particles; b) Fluvisol (Arenic) at sampling site STD with single microplastic particle (white) at the bottom of plough topsoil horizon (0-32 cm). [Original part of the supplementary material of chapter 3.2]

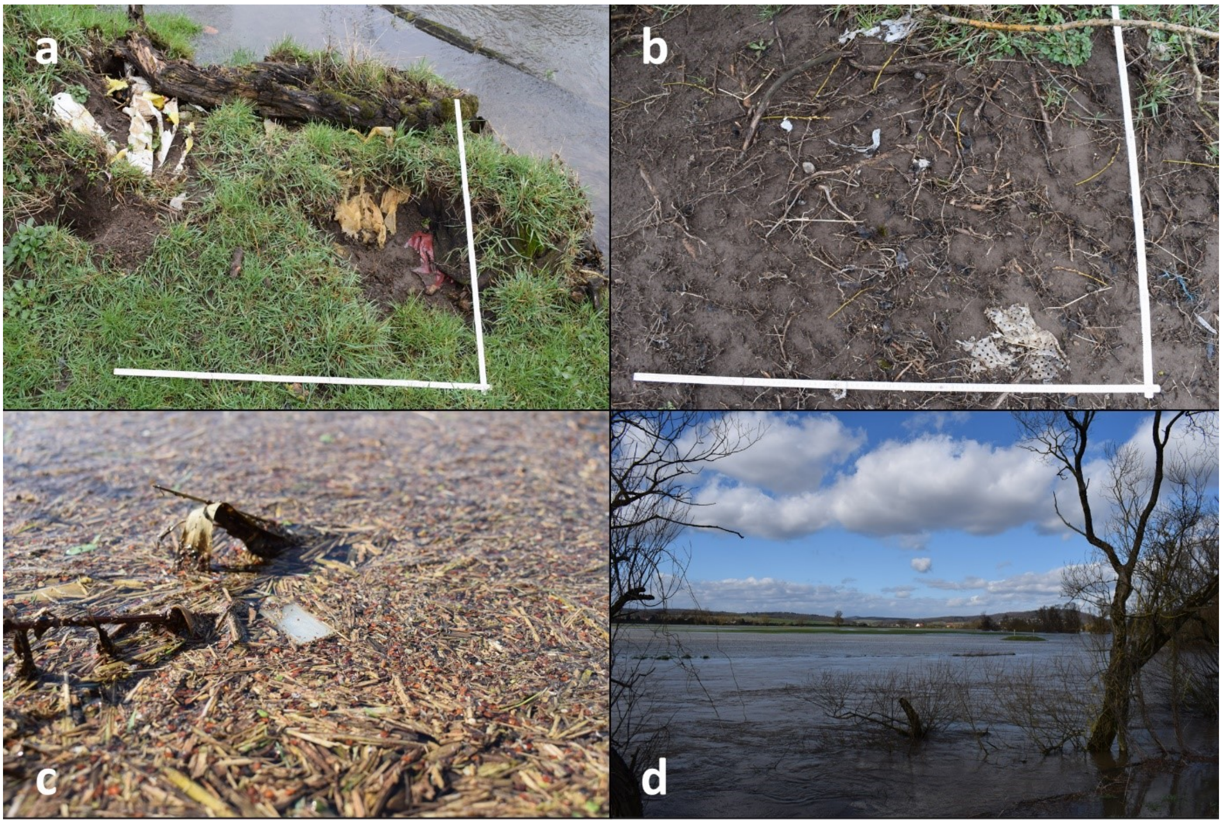


Figure A 6: Plastic particles deposited by overbank floods: a) Riparian zone at sampling site STD with mesoplastics after spring flood events in 2019 (03.2019); b) Floodplain zone at sampling site STD with meso- and microplastic accumulation on topsoils after spring flood events in 2019 (03.2019); c) Macroplastic particle on water surface during flood event at sampling site ROT (13.03.2020); d) Sampling site ROT during flood event in March 2020 (13.03.2020). [Original part of the supplementary material of chapter 3.2]

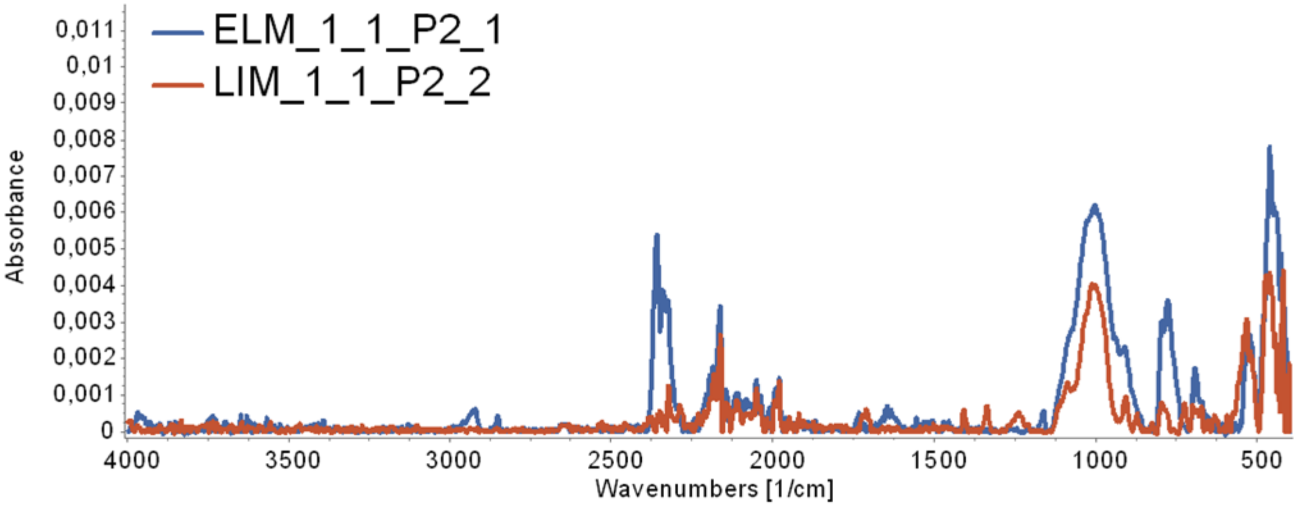


Figure A 7: Examples of FTIR spectra for two unidentified CMP particles in floodplain soils (hit quality < 300 in comparison with OPUS 7.0 internal spectra database). [Original part of the supplementary material of chapter 3.2]

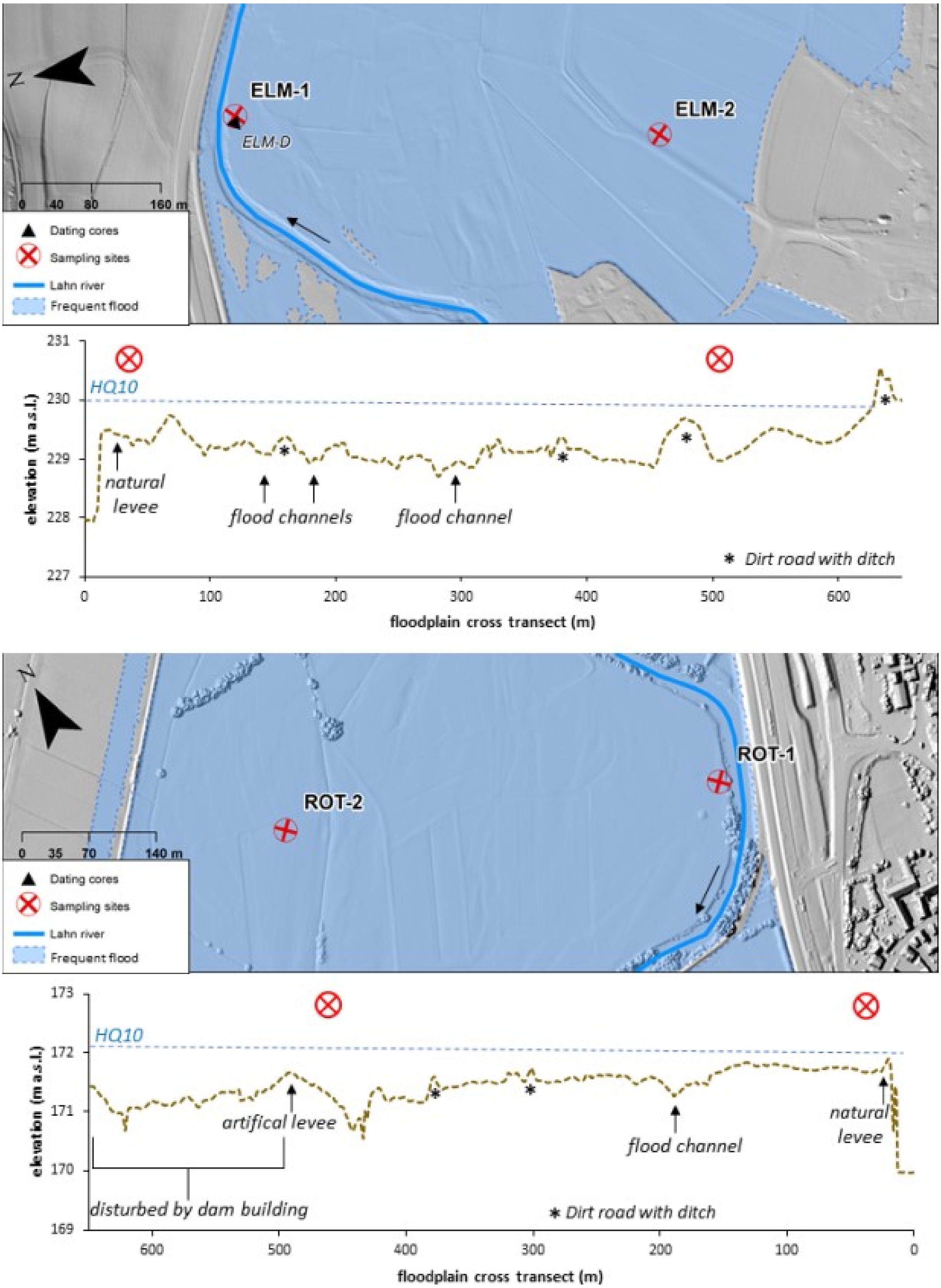


Figure A 8: Detailed maps and elevation profile of transect sites ELM (upper reaches) and ROT (upper middle reaches) with location of sampling points. Frequent flood shows the area of a 10-year flood (HQ10). Elevation profile follows the sampling points. Data basis: Digital elevation model (DEM) received from and with permission of the Hessian Administration for Land Management and Geoinformation (2019). [Original part of the supplementary material of chapter 3.3]

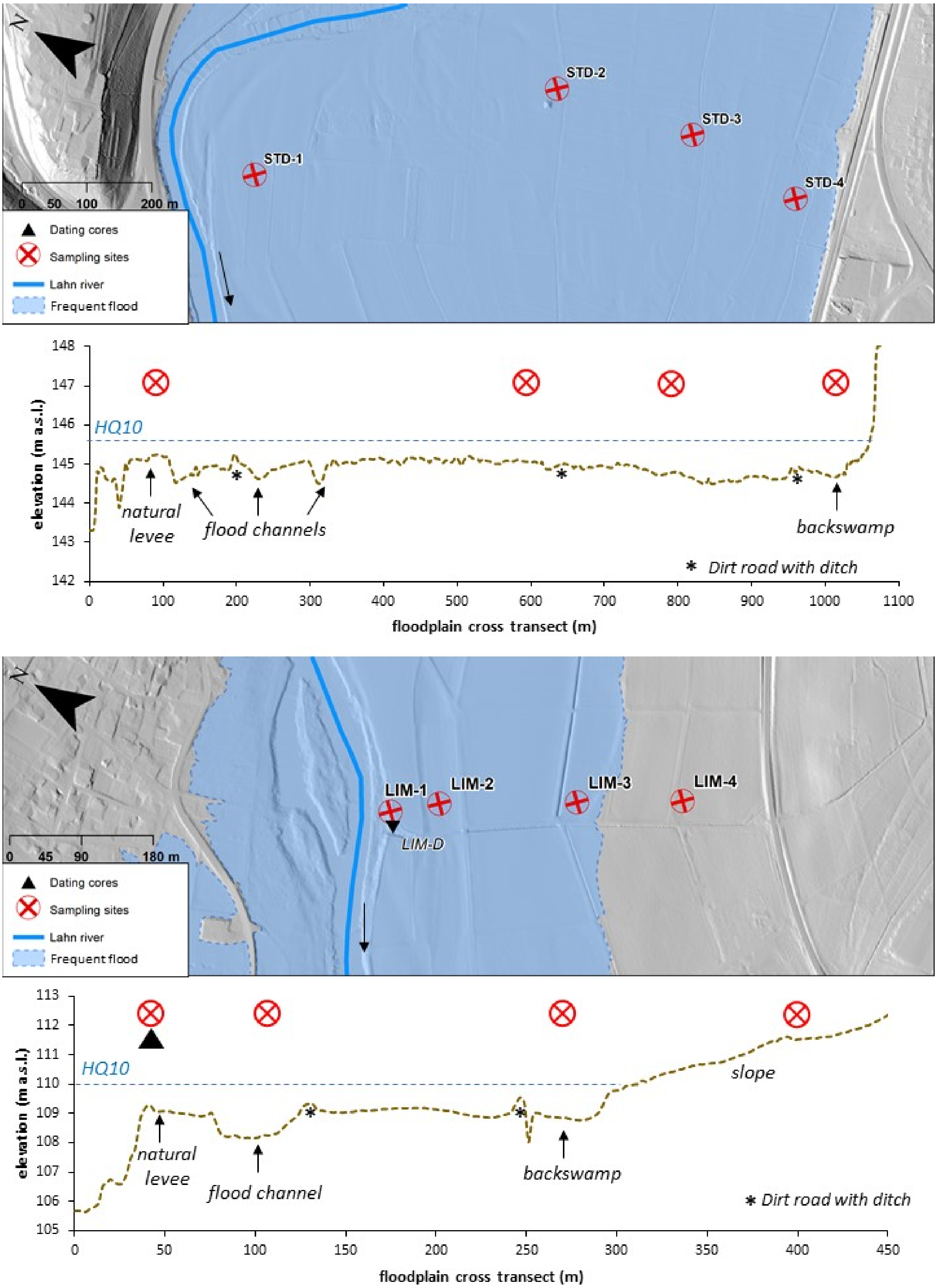


Figure A 9: Detailed maps and elevation profile of transect sites STD (lower middle reaches) and LIM (lower middle reaches) with location of sampling points. Frequent flood shows the area of a 10-year flood (HQ10). Elevation profile follows the sampling points. Data basis: Digital elevation model (DEM) received from and with permission of the Hessian Administration for Land Management and Geoinformation (2019). [Original part of the supplementary material of chapter 3.3]

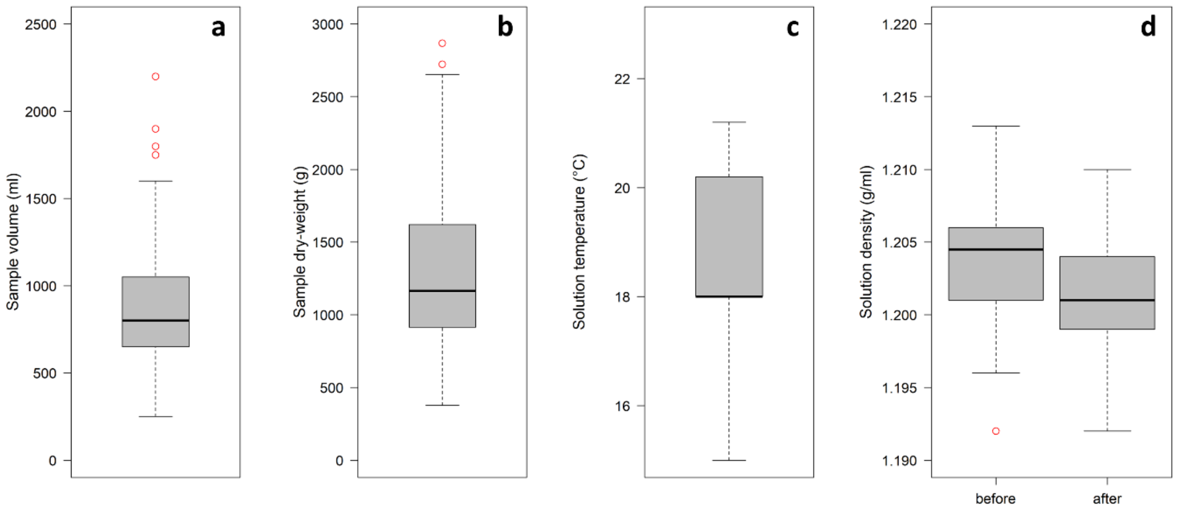


Figure A 10: MPSS control parameters. (a) Sample volume (ml). (b) Sample dry-weight (g). (c) Temperature of NaCl-solution. (d) Density of NaCl-solution before and after separation process. [Original part of the supplementary material of chapter 3.3]

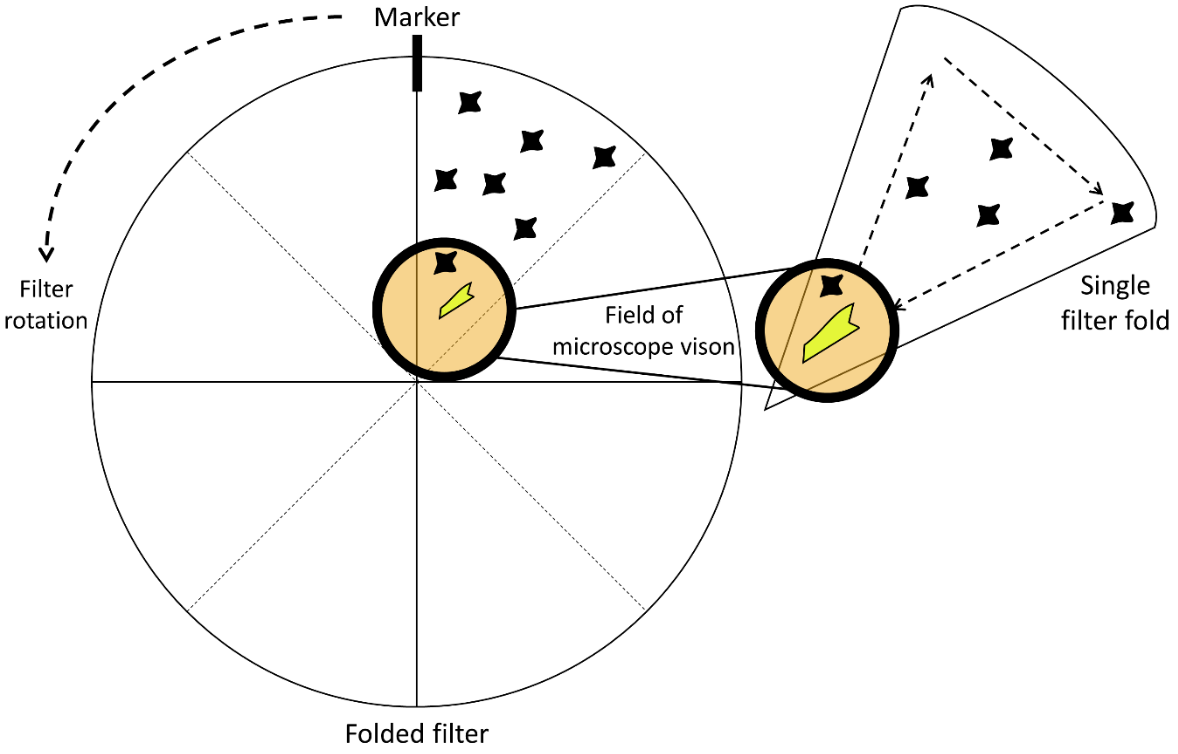


Figure A 11: Systematic scanning procedure for the pleated filter (15cm diameter). [Original part of the supplementary material of chapter 3.3]

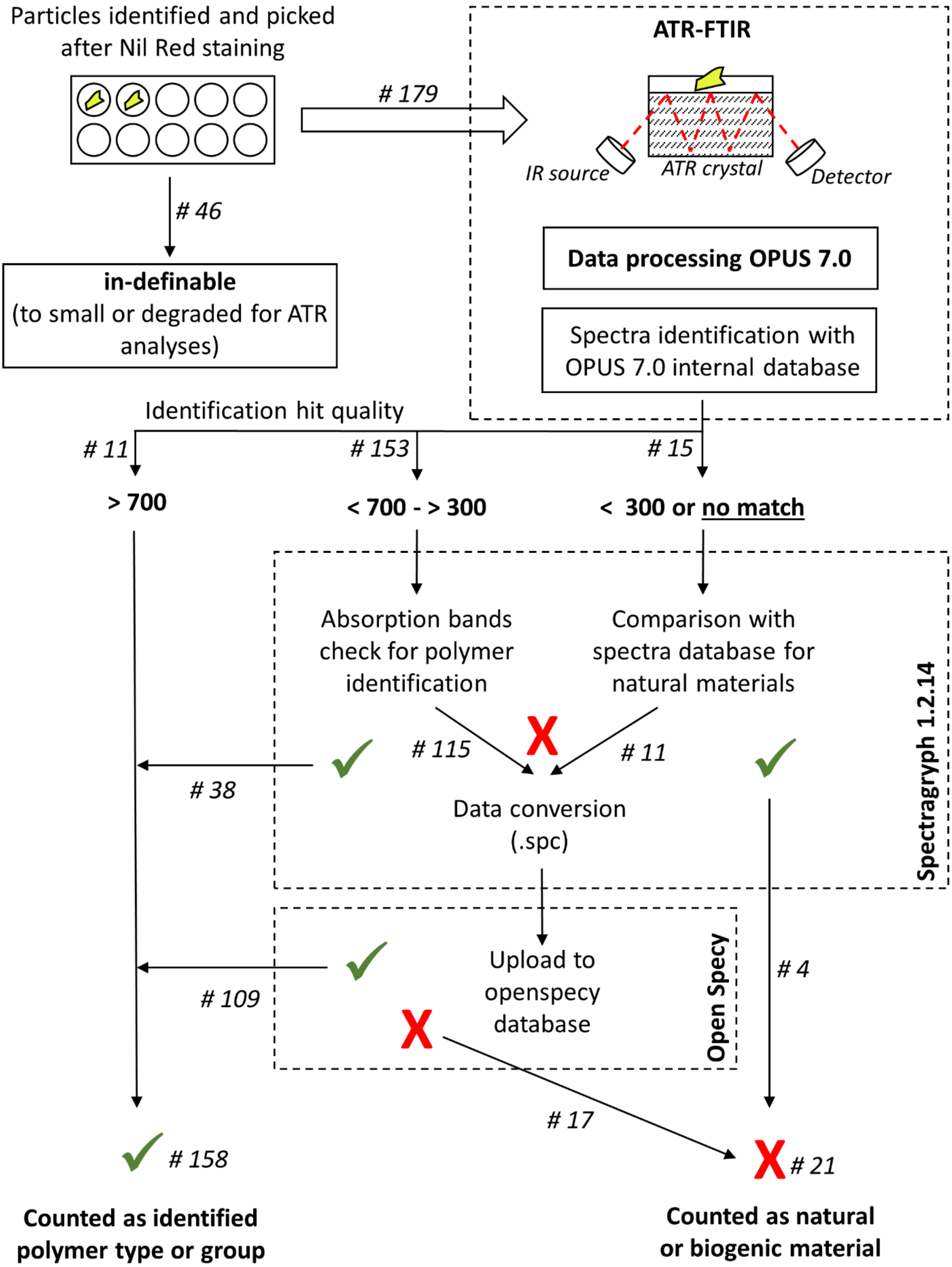


Figure A 12: Identification scheme for FTIR spectra (numbers with # indicate the total number of particles passing each junction). [Original part of the supplementary material of chapter 3.3]

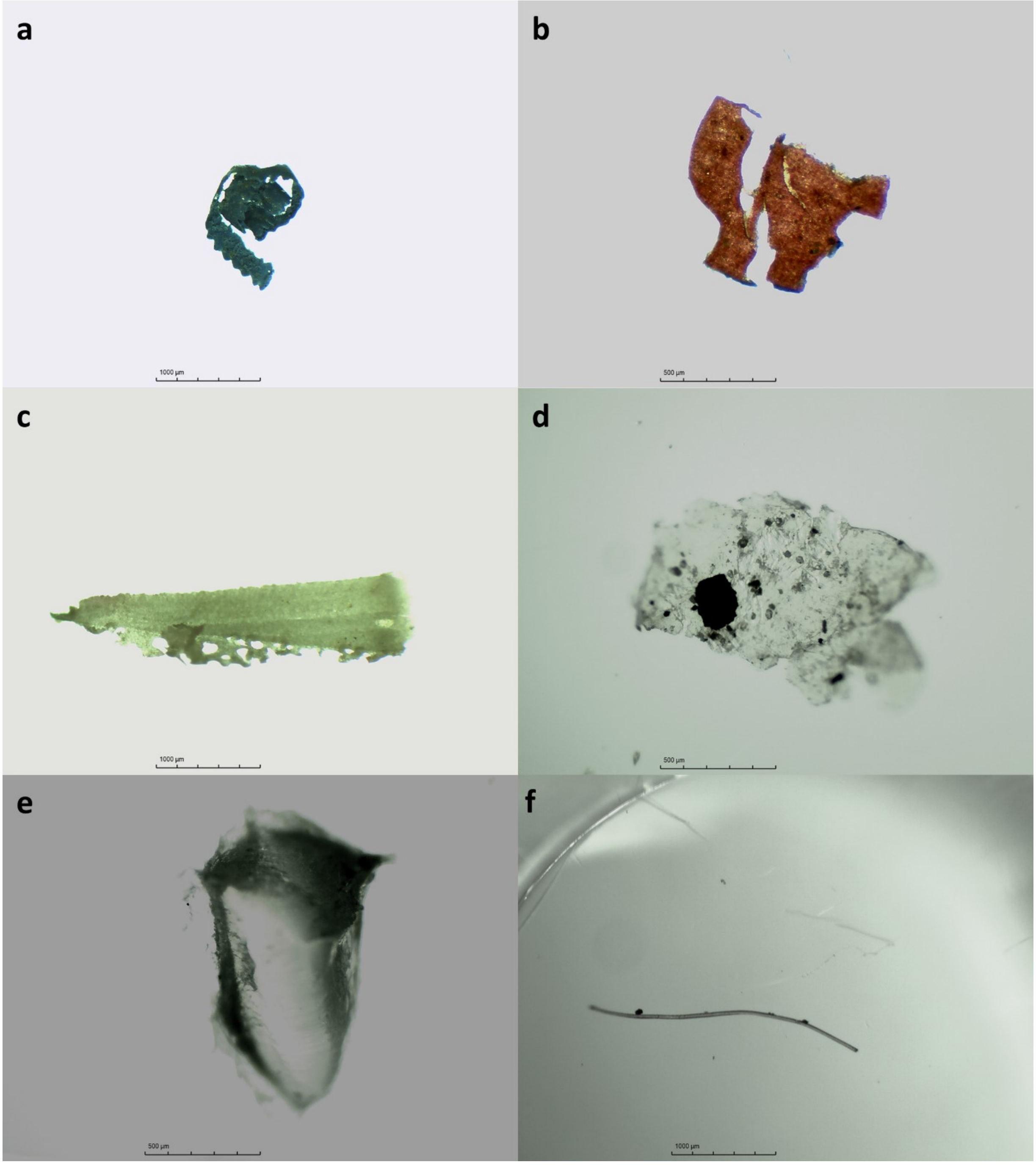


Figure A 13: Microplastic particle examples. (a) resin fragment (sample: LIM-2-1, 0-10 cm depth). (b) PUR fragment (sample: LIM-1-9, 125-150 cm depth). (c) PVC fragment (sample: STD-3-5, 40-50 cm depth). (d) HDPE film (sample: LIM-1-9, 125-150 cm depth). (e) LDPE fragment (sample: LIM20-30 cm depth). (f) PA (Nylon-6) filament (sample: STD-2-2, 10-20 cm depth). [Original part of the supplementary material of chapter 3.3]

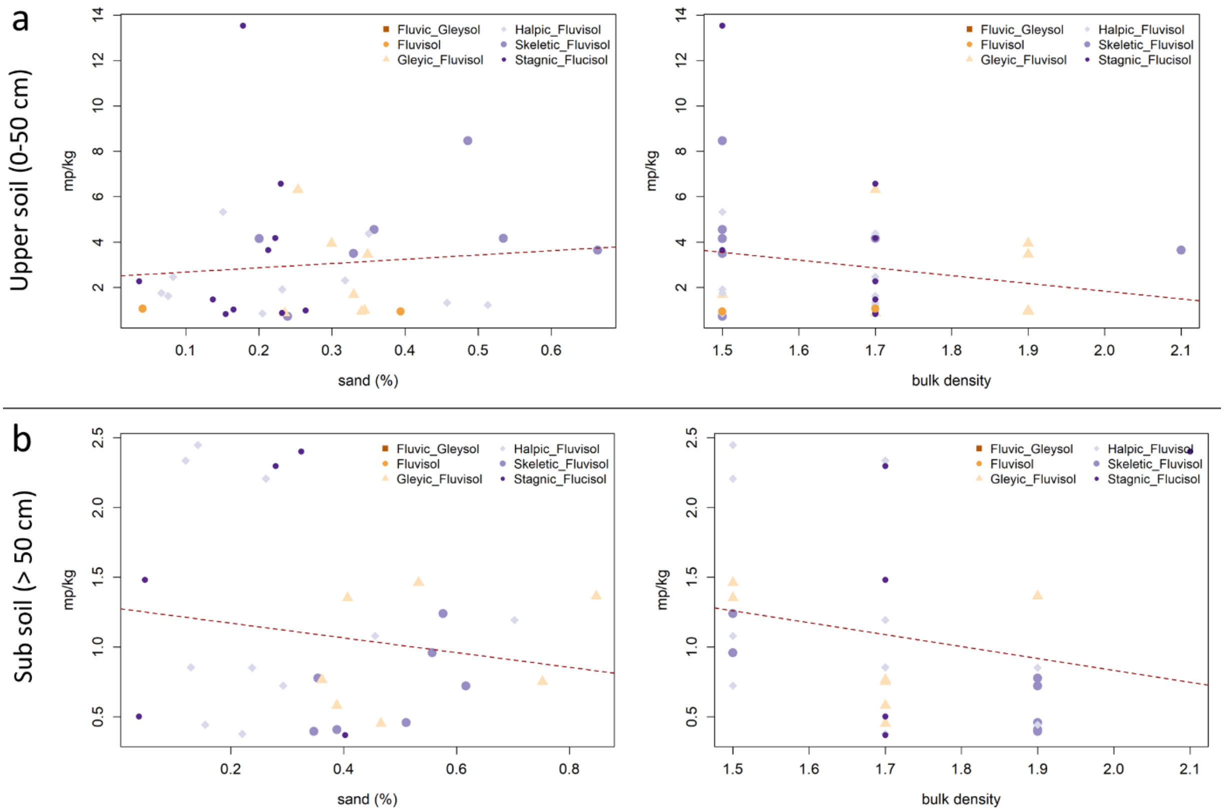


Figure A 14: Comparison of sand content (%) and bulk density (g cm³) with microplastic concentration (p kg^{-1}). (a) For upper soil samples (0-50 cm) (b) For sub soil samples (50-200 cm). Linear regression added via red line. [Original part of the supplementary material of chapter 3.3]

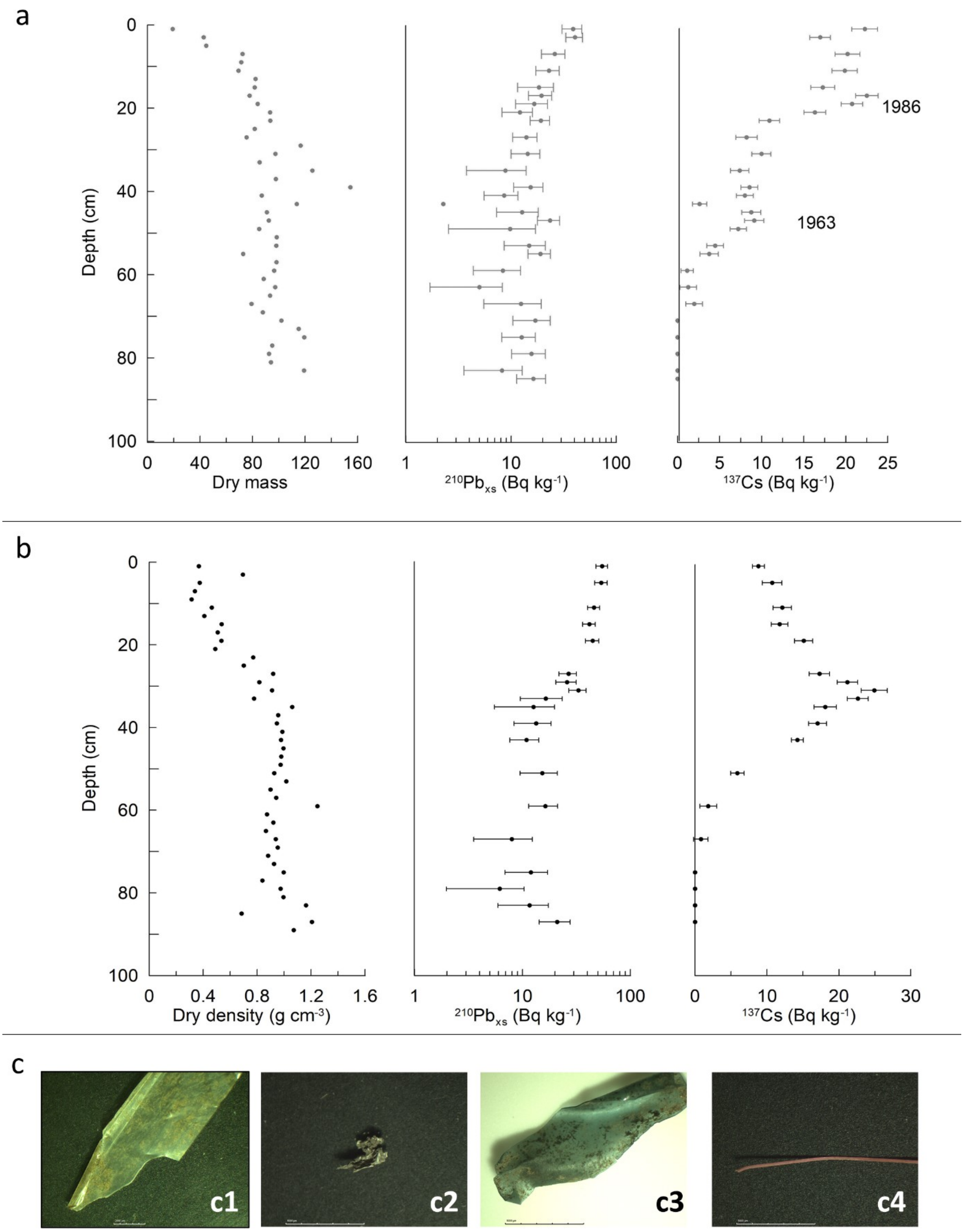


Figure A 15: Radiometric data of dating cores and mesoplastic particles. (a) Dry mass and radiometric data of core ELM-D. (b) Dry density and radiometric data of core LIM-D. (c) Mesoplastic particles documented during sample preparation from core LIM-D: c1 film (15 cm depth), c2 films (19 cm depth), c3 fragment (27 cm depth), and c4 filament (29 cm depth). [Original part of the supplementary material of chapter 3.3]

Table A 1: Soil properties and microplastic loads. [Original part of the supplementary material of chapter 3.3]

				Soil propertiesc							
			horizont limit	clay	silt	sand	OM	bulk density	root_dens	**MPd loads**	**n**
Sampling site	**Soil typea**	**Horizont sequenceb**	cm	mass-%				g/cm³	roots/dm²	mp/kg	
ELM-1	Skeletic Fluvisol (Technic, Arenic)	Ah	13.00	0.07	0.57	0.36	11.48	1.50	8.00	4.55	1
		B. Bl	105.00	0.02	0.06	0.05	0.79	0.18	1.96	2.51	5
ELM-2	Endogleyic Skeletic Fluvisol (Anthric. Siltic)	Ap	30.00	0.25	0.50	0.26	8.36	1.50	8.00	2.79	3
		B. Bl	105.00	0.16	0.47	0.37	5.22	1.90	1.50	0.19	4
ROT-1	Halpic Fluvisol (Arenic)	Ah	10.00	0.23	0.47	0.30	9.88	1.90	35.50	3.95	1
		B. B. Bl	200.00	0.15	0.41	0.43	3.67	1.72	4.39	0.78	9
ROT-2	Stagnic Fluvisol (Anthric. Tephric. Loamic)	Ap	32.00	0.20	0.47	0.33	4.31	1.50	4.00	0.56	3
		B. Bl. Bgl. Bgr	200.00	0.14	0.40	0.46	2.97	1.67	0.10	0.40	7
STD-1	Fluvisol (Anthric. Arenic)	Ap	35.00	2.40	2.78	3.22	3.95	3.53	4.44	2.53	4
		B. Bl. Bl. Br	200.00	0.14	0.47	0.38	4.40	1.64	0.10	1.01	7
STD-2	Skeletic Fluvisol (Loamic)	Ap. Abp	25.00	0.08	0.39	0.53	4.17	1.63	7.83	0.85	3
		B. Bl. Bl. Blr	200.00	0.09	0.26	0.65	3.88	1.68	2.71	0.47	7
STD-3	Epigleyic Fluvisol (Silitc)	Abp	25.00	0.29	0.55	0.16	10.12	1.50	11.67	1.78	3
		Bl. Bl. Brl. Br	200.00	0.26	0.39	0.35	4.81	1.55	2.54	1.00	7
STD-4	Fluvic Gleysol (Clayic)	Ahl	8.00	0.24	0.70	0.07	13.66	1.50	15.50	1.75	1
		Bl. Brl. Br	200.00	0.38	0.50	0.12	8.27	1.70	4.80	0.87	9
LIM-1	Haplic Fluvisol (Arenic)	Ah	15.00	0.22	0.58	0.20	7.32	1.50	15.50	8.59	2
		B. B	200.00	0.16	0.65	0.18	5.47	1.63	2.74	2.06	8
LIM-2	Endogleyic Fluvisol (Silitc)	Ah	10.00	0.22	0.64	0.14	9.91	1.70	15.50	1.47	1
		B. Blg. Blg. Bl. Bl	200.00	0.18	0.58	0.25	4.85	1.72	4.03	0.60	9
LIM-3	Fluvic Gleysol (Loamic)	Ah	13.00	0.27	0.69	0.04	11.77	1.70	15.50	0.00	1
		B. Bl. Brl. Br	200.00	0.23	0.71	0.06	5.25	1.70	2.48	0.59	9
LIM-4	Skeletic Stagnic Fluvisol (Densic. Clayic)	Ap	30.00	0.23	0.37	0.39	6.40	1.50	8.00	0.31	3
		Bg. Bg. C	140.00	0.27	0.36	0.36	3.23	1.78	3.22	0.55	6

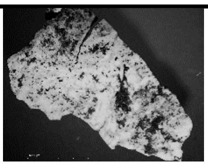
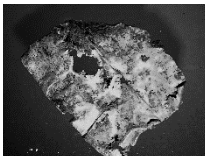
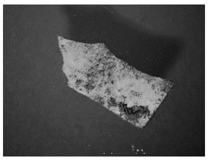
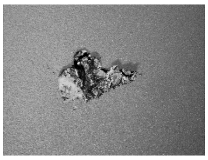
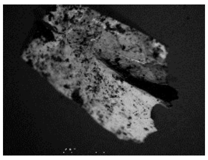
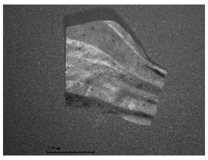
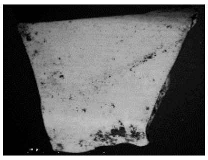
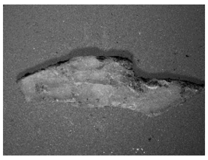
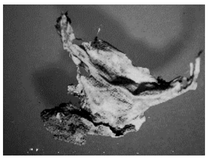
Table A 2: Polymer types abbreviations (order following mention within Figure 31). [Original part of the supplementary material of chapter 3.3]

Abbreviation	Polymer type
PVC	Polyvinyl chloride
PS	Polystyrene
HDPE	High-density polyethylene
PA	Polyamides
PUR	Polyurethane
PTFE	Polytetrafluoroethylene
ABS	Acrylonitrile butadiene styrene
LDPE	Low-density polyethylene
PP	Polypropylene
PET	Polyethylene terephthalate
CSM	Chlorosulfonated polyethylene

Table A 3: Sampling plot elevations and elevation differences. [Original part of the supplementary material of chapter 3.3]

Site	Sampling plot elevation (m a.s.l.)			
	1	2	3	4
ELM	229.4	229.0		
Difference		*-0.4*		
ROT	171.8	171.4		
Difference		*-0.4*		
STD	145.2	145.0	144.7	144.6
Difference		*-0.2*	*-0.3*	*-0.1*
LIM	116.6	114.8	114.6	118.9
Difference		*-1.8*	*-0.2*	*4.3*

Table A 4: Mesoplastic and coarce microplastic particles for metal detection. [Original part of the supplementary material of chapter 3.4]

Size class[a]	Sample	Depth (cm)[b]	Particle mass (mg)	Description	Polymer type	Picture
5	ELM-1-1	0-10	16.50	fragments (white)	PMMA	
5	ELM-1-3	20-30	11.30	plate (silver)	POM	
2	ELM-1-3	20-30	30.40	films and fragments (white/transparent)	PA	
2	ELM-1-4	30-40	23.50	fragments (silver/white)	CSM	
5	LIM-1-1	0-10	42.10	fragments (white/transparent)	PP	
5	LIM-1-2	10-20	17.00	films (transparent)	PE-LD	
5	ROT-1-2	0-10	131.40	fragment (white. massive)	PE-LD	
5	STD-1-2	10-20	42.10	fragment and film (transparent /colored)	CSM	
5	STD-1-3	20-30	40.90	film (white)	PE-LD	
5	STD-4-1	0-10	120.90	film (transparent/blue)	PP	

[a] Sieved size class of plastic particles. [b] Depth of sampling section within soil profile

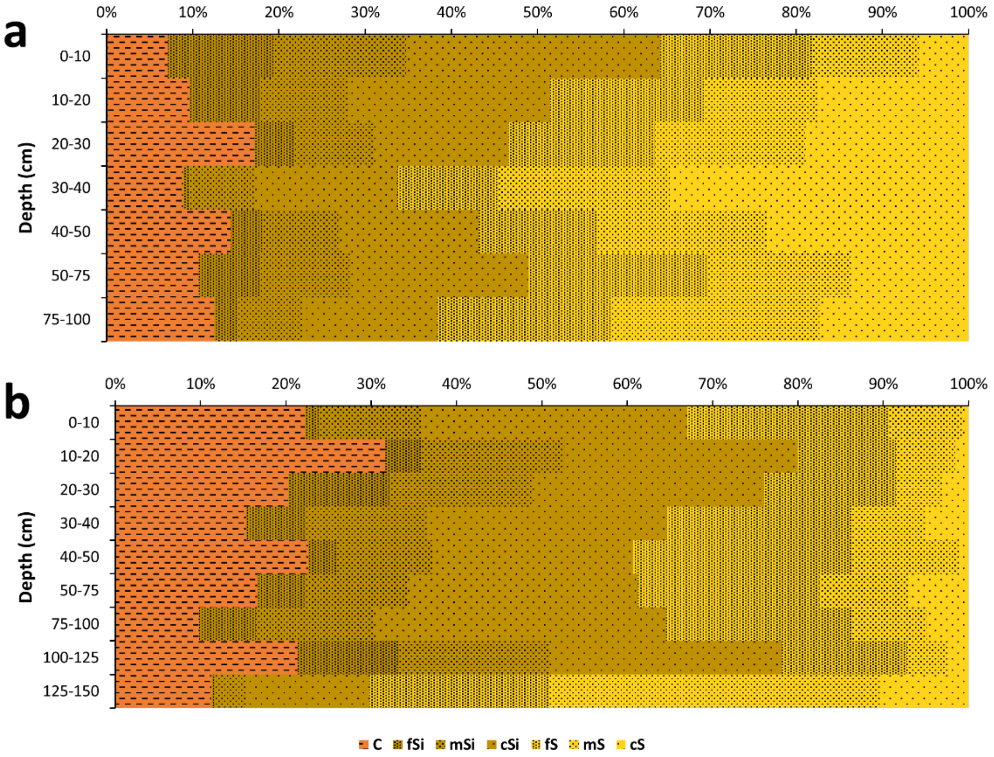


Figure A 16: Grain size distribution for soil profiles of site ELM. a: Profile ELM-1. b: Profile ELM-2. [Original part of the supplementary material of chapter 3.4]

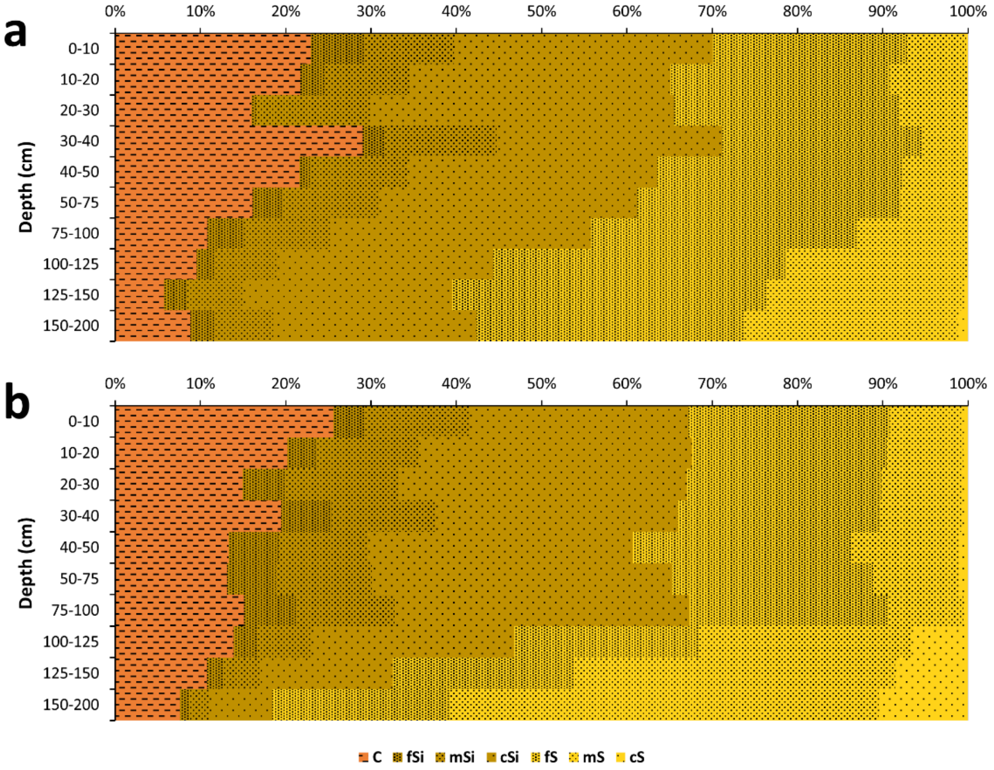


Figure A 17: Grain size distribution for soil profiles of site ROT. a: Profile ROT-1. b: Profile ROT-2. [Original part of the supplementary material of chapter 3.4]

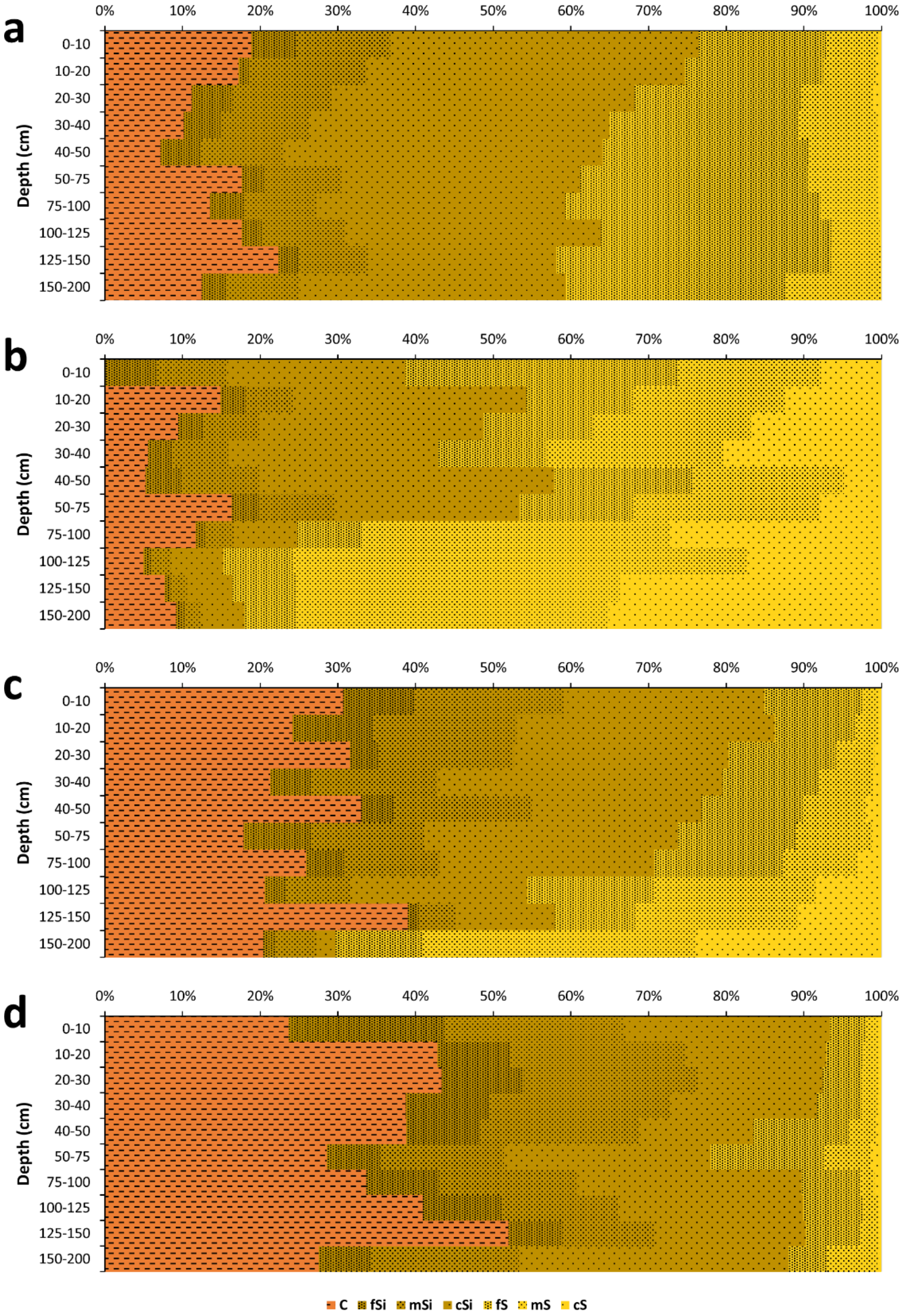


Figure A 18: Grain size distribution for soil profiles of site STD. a: Profile STD-1. b: Profile STD-2. c: Profile STD-3. d: Profile STD-4. [Original part of the supplementary material of chapter 3.4]

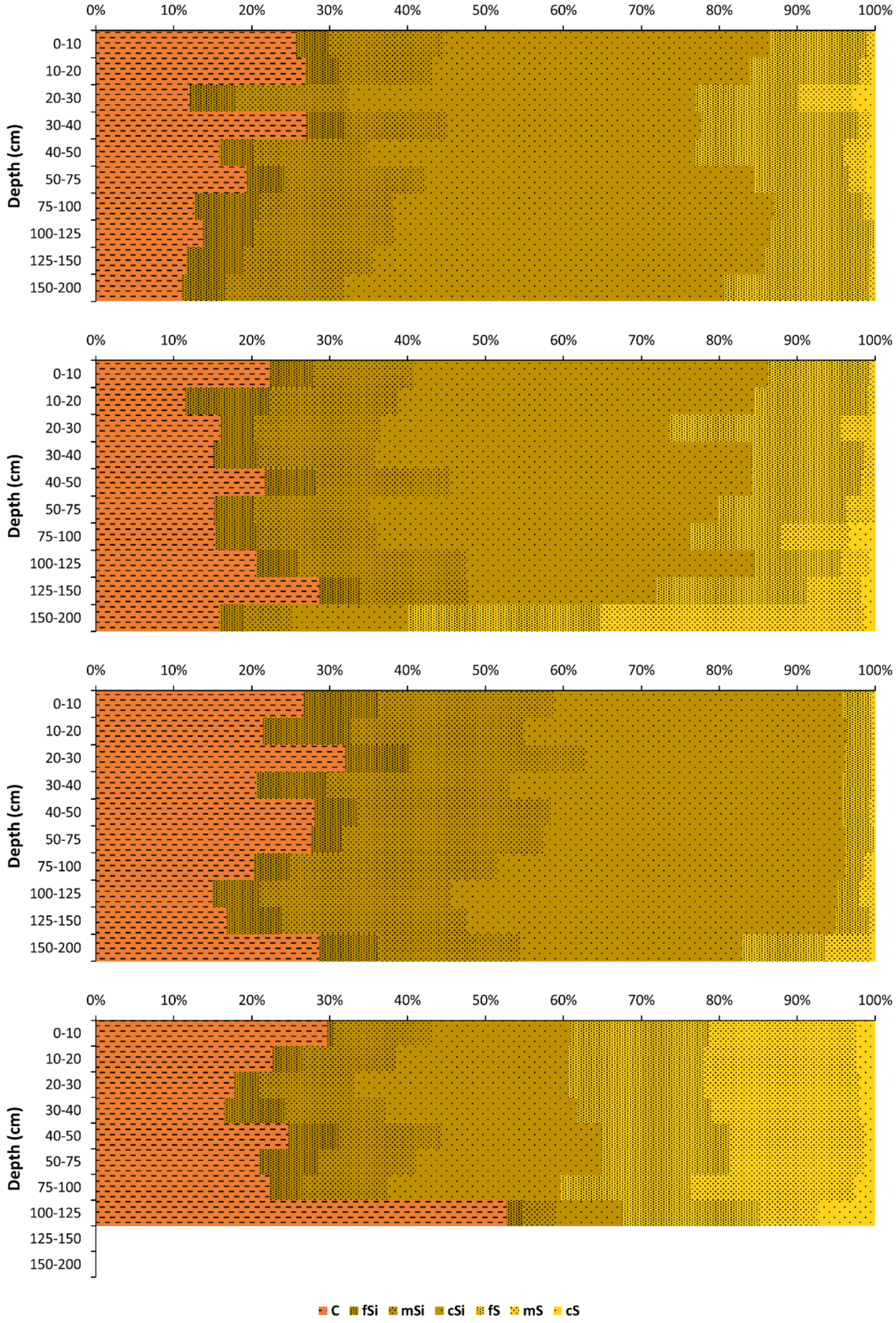


Figure A 19: Grain size distribution for soil profiles of site LIM. a: Profile LIM-1. b: Profile LIM-2. c: Profile LIM-3. d: Profile LIM-4. [Original part of the supplementary material of chapter 3.4]

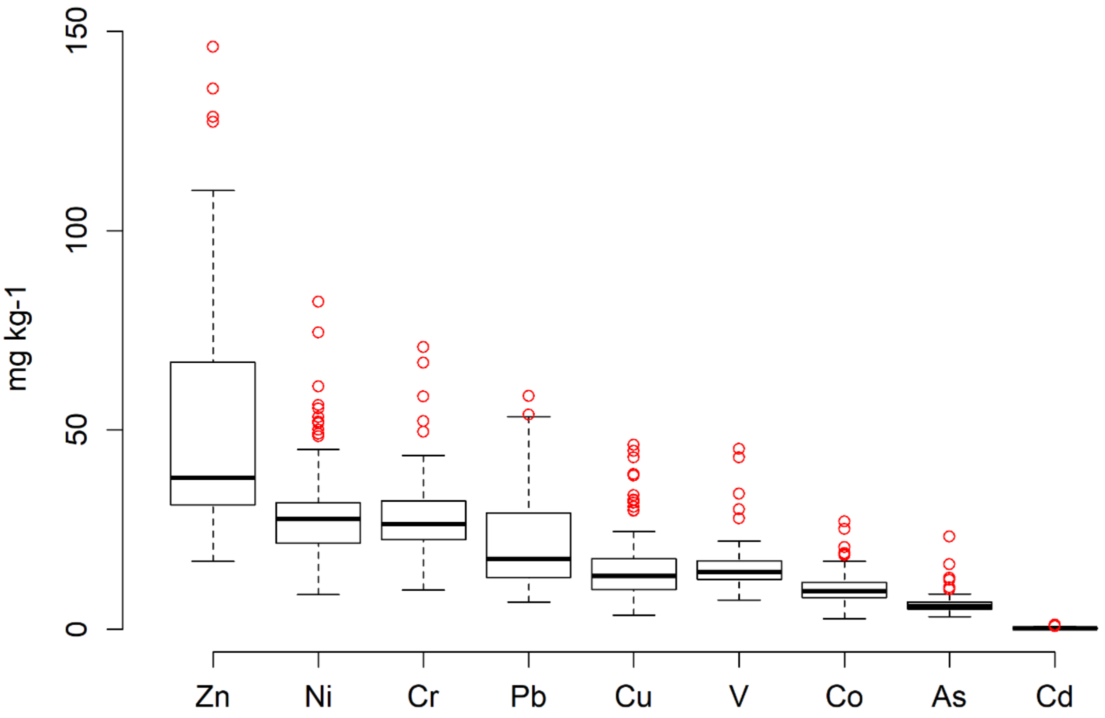


Figure A 20: Heavy metal and metalloid As concentrations (mg kg^{-1}) from floodplain soils samples (*n = 112*) ordered by descending mean concentration. [Original part of the supplementary material of chapter 3.4]

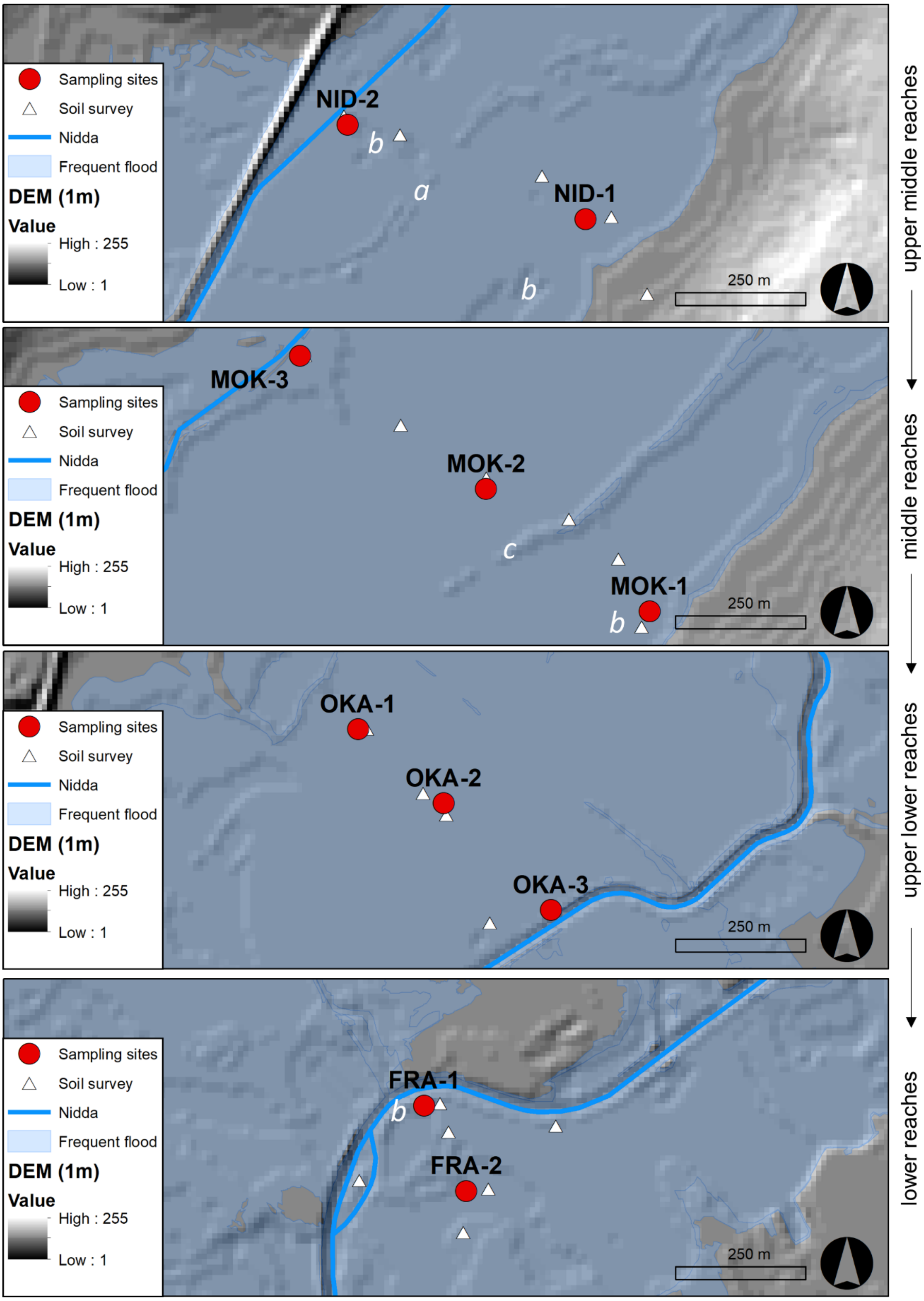


Figure A 21: Detailed maps of transect sites NID, MOK, OKA and FRA with a: inactive flood channels; b: river renaturation structures; c: flood protection dam. Data source: © OpenStreetMap contributors 2021. Distributed under the Open Data Commons Open Database License (ODbL) v1.0. and Hessian Administration for Soil Management and Geoinformation 2021. [Original part of the supplementary material of chapter 3.5]

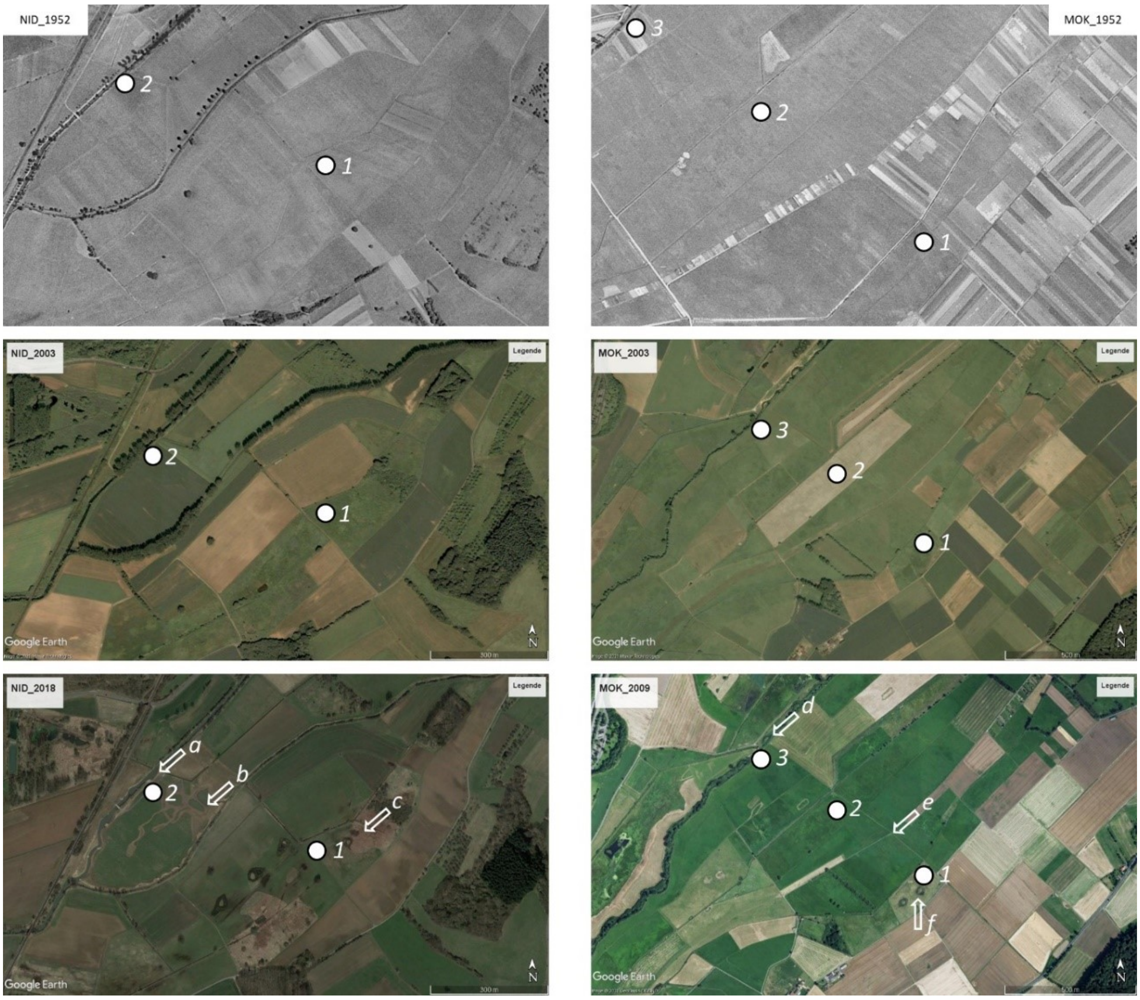


Figure A 22: Floodplain and land use change between 1952 and 2018 for transect sites NID and MOK. Left site: Transect NID (1952, 2003, 2018) with a: river renaturation, b: floodplain renaturation (earth works) and c: floodplain renaturation. Right site: Transect MOK (1952, 2003, 2009) with d: river renaturation, e: flood protection dam and f: floodplain renaturation. Data source: © 1952 NATUREG Viewer Hessen 2021, recent images © Google Earth. [Original part of the supplementary material of chapter 3.5]

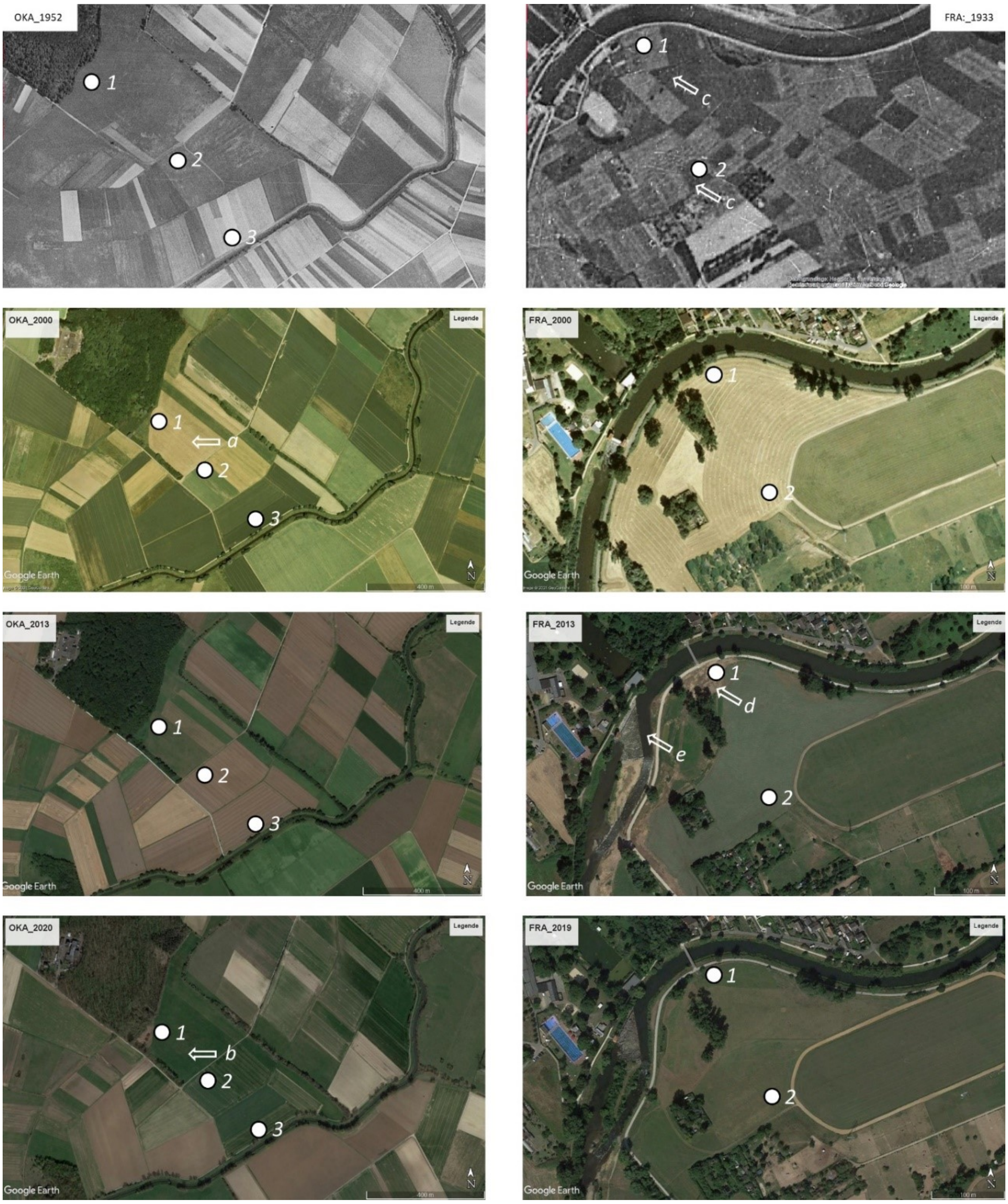


Figure A 23: Floodplain and land use change between 1933 and 2020 for transect sites OKA and FRA. Left site: Transect OKA (1952, 2000, 2013, 2020) with a: arable land changed to b: grassland between 2000 and 2013. Right site: Transect FRA (1933, 2000, 2013, 2019) with c: arable land (small plots) changed later to grassland, d: earth works for bridge construction and e: river weir renaturation. Data source: © 1952 NATUREG Viewer Hessen 2021, recent images © Google Earth. [Original part of the supplementary material of chapter 3.5]

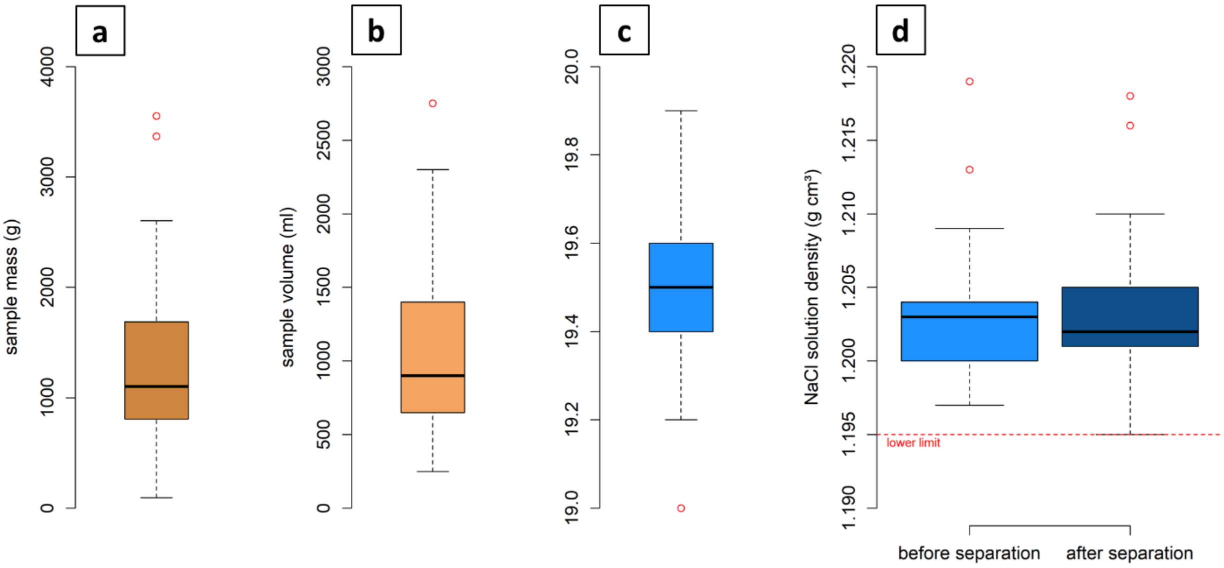


Figure A 24: Sample and density separation parameters. a: Sample mass g which was separated (fine soil fraction <2 mm); b: Sample volume ml (fine soil fraction <2 mm); c. Density (NaCl) solution temperature before separation (°C); d: Density of NaCl solution (g/cm³) before and after separation. [Original part of the supplementary material of chapter 3.5]

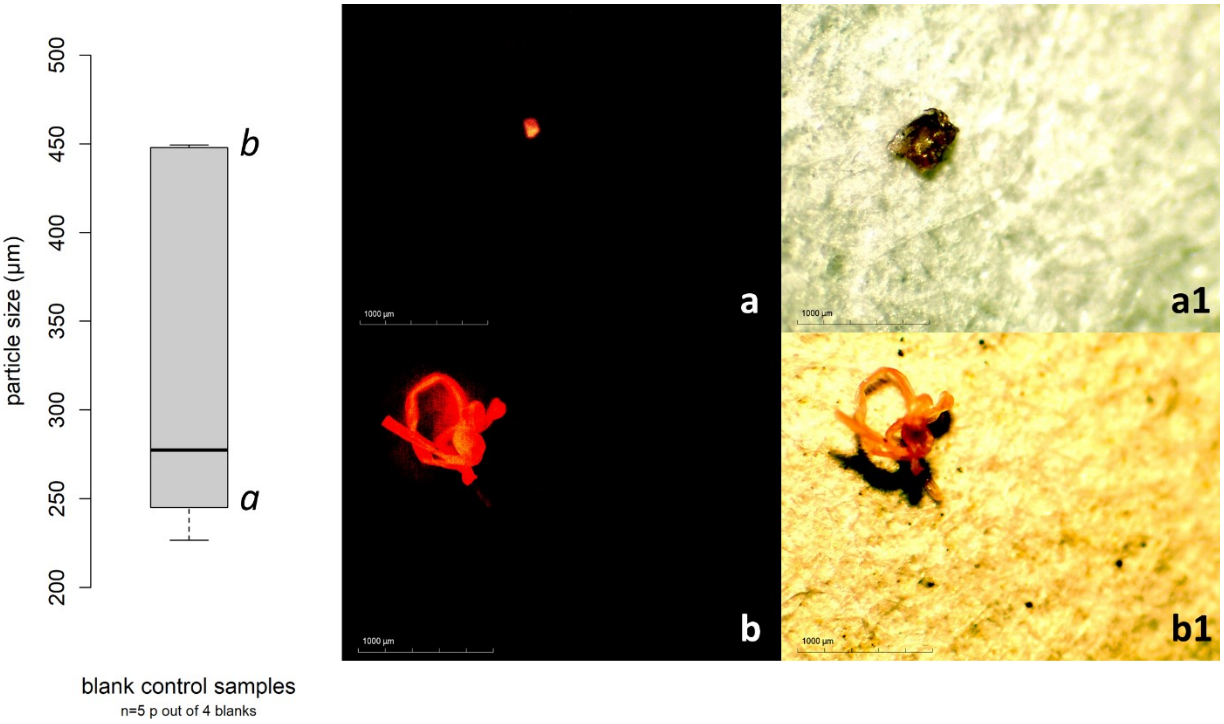


Figure A 25: Particle sizes of particles extracted from blank samples (B1-B4, B5 clean) and examples for identified particles. a/a1: Fragment with a size of 245.0 µm; b/b1: Filament with a length of 449.4 µm. [Original part of the supplementary material of chapter 3.5]

Figure A 26: Macroplastic particles collected from soil surfaces on sampling sites OKA-2 and OKA-3 (agricultural field). a: Primose shield, DIY store; b: Fork, c: Bottle cap part, d: Lollipop stick, e: Component, b1: Fries fork on soil surface, b2: Component on soil surface. [Original part of the supplementary material of chapter 3.5]

Table A 5: Average contents of plastic abundance, selected elements, pollution indices and soil conditions within studied soil profiles. [Original part of the supplementary material of chapter 3.5]

Transect ***(river km)***	**Sampling point**	**Average plastic load (p kg^{-1})**	**Elemental contents (mg kg^{-1})**[a]						**Pollution indices**		**Soil conditions**				
			Cr	Ni	Cu	Zn	Cd	Pb	EF[b]	PLI[c]	Clay[d]	Silt[d]	Sand[d]	OM[e]	pH
NID *(62.5 km)*	NID-1	3.92	21.77	24.73	14.00	45.47	0.26	24.22	2.54	0.99	41.0	52.9	6.1	10.1	5.8
	NID-2	3.92	29.54	29.50	16.66	50.76	0.21	21.11	2.30	1.01	33.3	62.0	4.7	9.3	6.0
MOK *(55.0 km)*	MOK-1	4.19	32.38	31.50	18.34	68.39	0.43	29.19	2.54	1.29	47.9	47.0	5.1	14.5	6.4
	MOK-2	1.06	37.61	42.73	24.24	83.01	0.45	34.46	2.56	1.54	46.7	45.1	8.2	11.5	5.5
	MOK-3	1.78	26.66	28.71	14.77	55.83	0.32	24.07	2.23	0.87	22.1	67.8	10.1	6.2	5.9
OKA *(35.5 km)*	OKA-1	1.73	27.39	28.41	15.20	49.74	0.22	19.79	2.05	0.98	28.3	49.7	22.0	7.6	6.9
	OKA-2	6.44	33.88	33.03	16.52	55.41	0.25	20.93	2.27	1.11	30.6	58.7	10.7	7.7	7.3
	OKA-3	2.22	32.72	36.64	18.36	55.38	0.25	22.74	1.86	1.28	31.5	58.9	9.6	6.5	6.7
FRA *(2.0 km)*	FRA-2	2.85	28.98	26.76	13.21	42.41	0.17	19.82	1.91	0.89	19.1	50.4	30.5	4.6	6.1
	FRA-1	4.19	28.02	30.85	15.29	50.66	0.27	22.50	2.03	1.01	19.5	59.7	20.8	5.4	6.9

[a] Average values of selected elements according to existing precautionary values in the German Federal Soil Protection Ordinance; [b] Enrichment factor (>2 = moderate enrichment); [c] Pollution load index (> 1 = significant pollution); [d] Grain size composition given in mass percent (wt%); [e] Organic matter given in mass percent (wt%).

Table A 6: Macroplastics and their features from surface sampling at sampling site OKA (agricultural field). [Original part of the supplementary material of chapter 3.5]

FID	Site	Type	Shape*	Degradation state	Color	Size (mm)	Polymer	Identification	Picture
1	OKA-2	fragment	regular	weathered	colored	55	PMMA	Primose shield, DIY store	***a***
2		fragment	broken	weathered	blue	74	PS	Fries fork	***b***
3		fragment	regular	weathered	white	25	LD-PE	Bottle cap part	***c***
4		fragment	regular	weathered	green	75	PP	Lollipop stick	***d***
5		fragment	broken	weathered	grey	46	PP	Pen part	
6		fragment	broken	weathered	grey	100	PVC		
7		fragment	broken	weathered	grey	76	PVC		
8		film	irregular	weathered	black	100	HD-PE		
9		film	irregular	weathered	black	72	LD-PE		
10		film	irregular	weathered	blue	45	HD-PE		
11		film	regular	fresh	blue	14	PVC		
12		film	irregular	weathered	green	40	HD-PE		
13		film	irregular	weathered	black	36	HD-PE		
14		film	regular	incipient alteration	white	32	PP		
15		film	irregular	weathered	white	74	LD-PE		
16		film	irregular	weathered	white	60	HD-PE		
17		film	irregular	weathered	white	69	LD-PE		
18		fragment	irregular	weathered	silver	58	Phenoxy resin	Wrap	
19		film	irregular	weathered	transparent	52	PET	Bonbon wrap	
20		film	irregular	weathered	transparent	35	HD-PE		
21		film	irregular	weathered	transparent	80	HD-PE		
22	OKA-3	fragment	regular	incipient alteration	black	150	HD-PE	Component vehicle	
23		fragment	irregular	incipient alteration	grey	65	PET	Component	***e, e1***
24		fragment	regular	fresh	green	95	PP		
25		fragment	regular	fresh	red	103	LD-PE	Bottle cap part	
26		film	regular	fresh	white_red	84	PET	Food wrap	
27		film	irregular	incipient alteration	white	58	HD-PE		
28		film	irregular	incipient alteration	white	99	HD-PE		
29		film	irregular	incipient alteration	white	82	HD-PE		
30		styrofoam	irregular	incipient alteration	white	55	Styrofoam		
31		styrofoam	irregular	weathered	white	45	Styrofoam		

* Shape classes: regular (regular shape, no broken or irregular edges), broken (broken edges), irregular (irregular shape with irregular edges, e.g., frayed edges)

Table A 7: Polymer types abbreviations (order following mention within Figure 43a). [Original part of the supplementary material of chapter 3.5]

Abbreviation	Polymer type
PVA	Poly(vinyl alcohol)
PVC	Polyvinyl chloride
PS	Polystyrene
HDPE	High-density polyethylene
PA	Polyamides
PUR	Polyurethane
PTFE	Polytetrafluoroethylene
ABS	Acrylonitrile butadiene styrene
LDPE	Low-density polyethylene
PP	Polypropylene
PET	Polyethylene terephthalate
CSM	Chlorosulfonated polyethylene
CPE	Chlorinated polyethylene

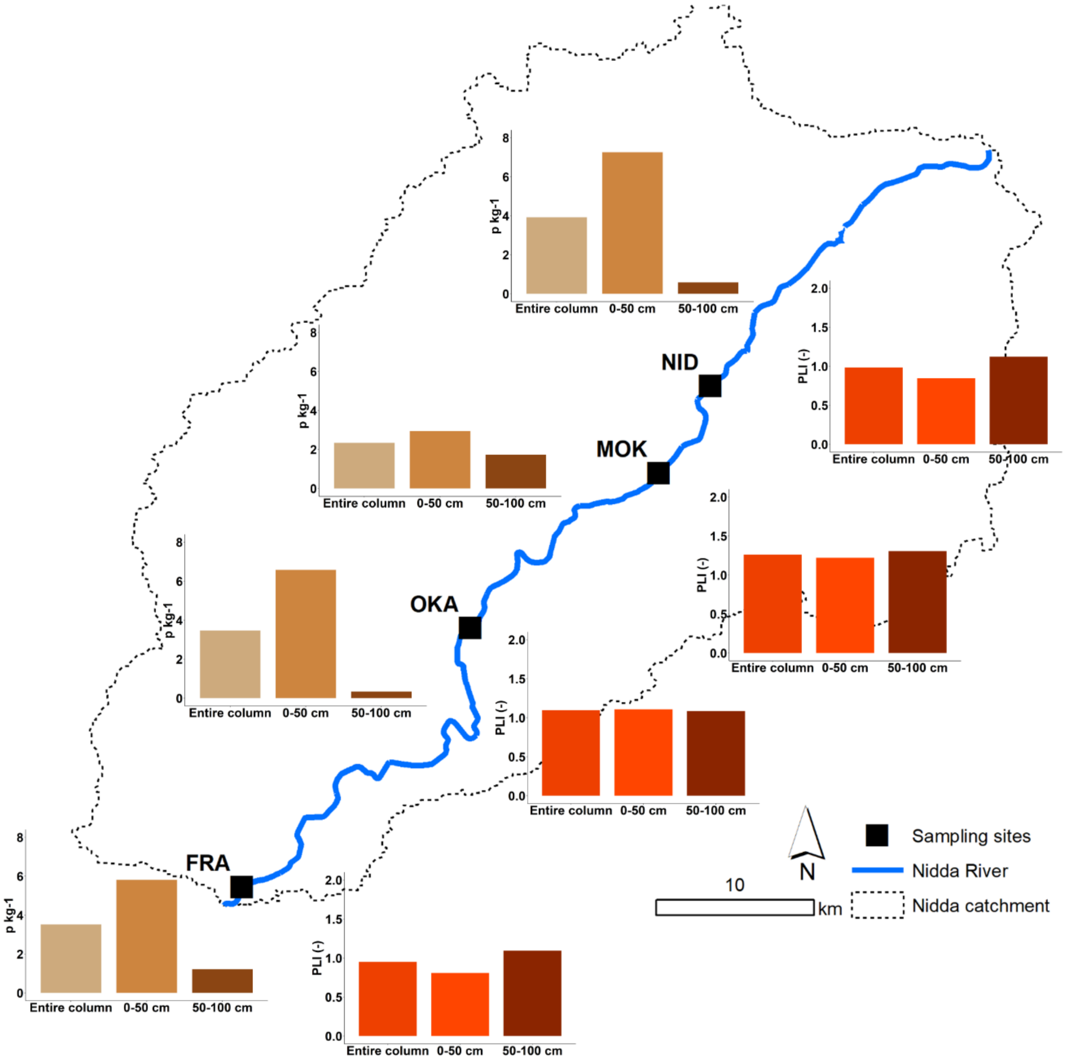


Figure A 27: Plastic loads (p kg^{-1}) and Pollution load index (PLI) along the Nidda River course. [Original part of the supplementary material of chapter 3.5]

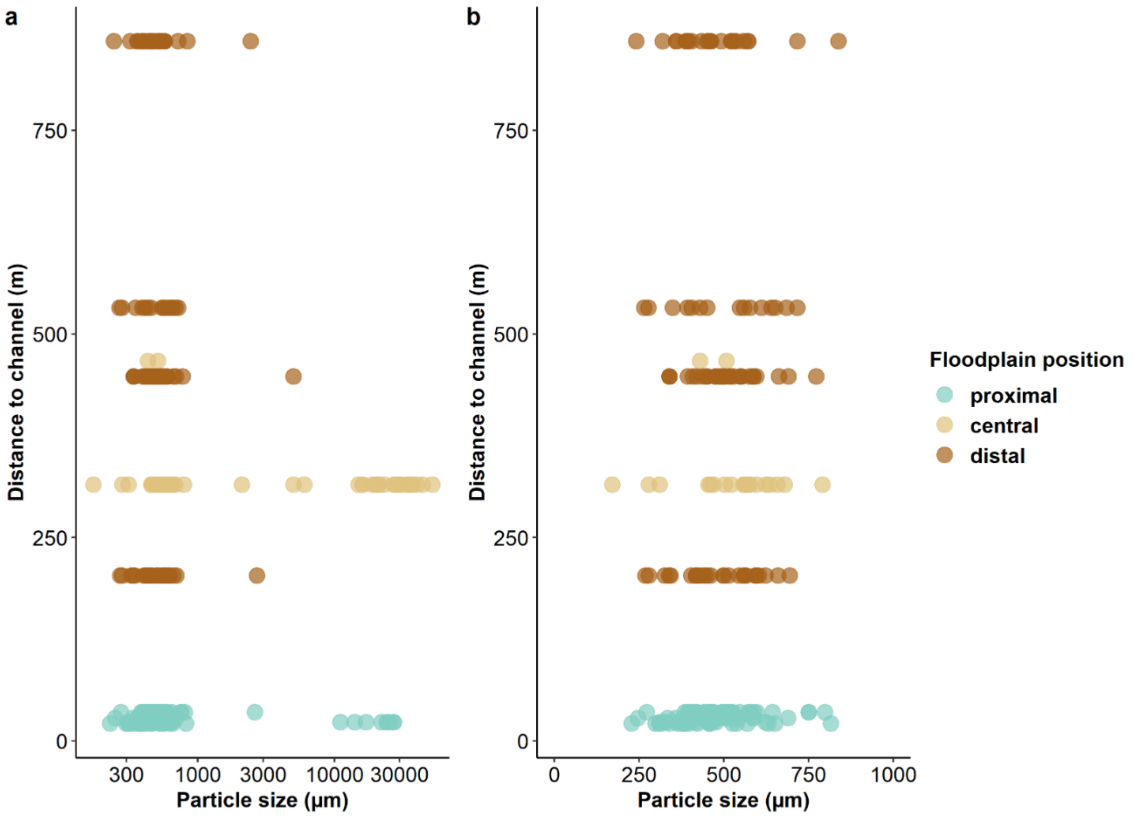


Figure A 28: Plastic particle sizes in dependence of distance to channel (m) classified according to floodplain position with a: entire plastic particle size range and b: excerpt of sizes between 0 and 1000 µm. [Original part of the supplementary material of chapter 3.5]

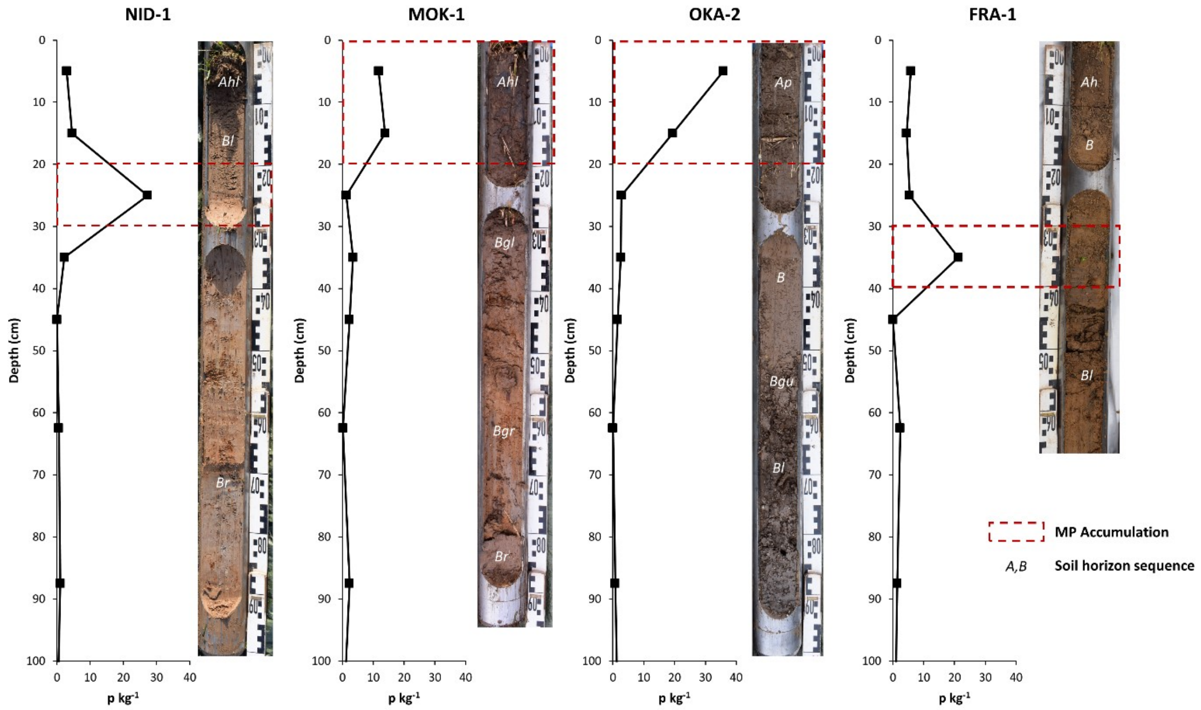


Figure A 29: Plastic accumulations in four different floodplain soils. Plastic loads (p kg^{-1}) and drill core pictures for upper soil layers. [Original part of the supplementary material of chapter 3.5]

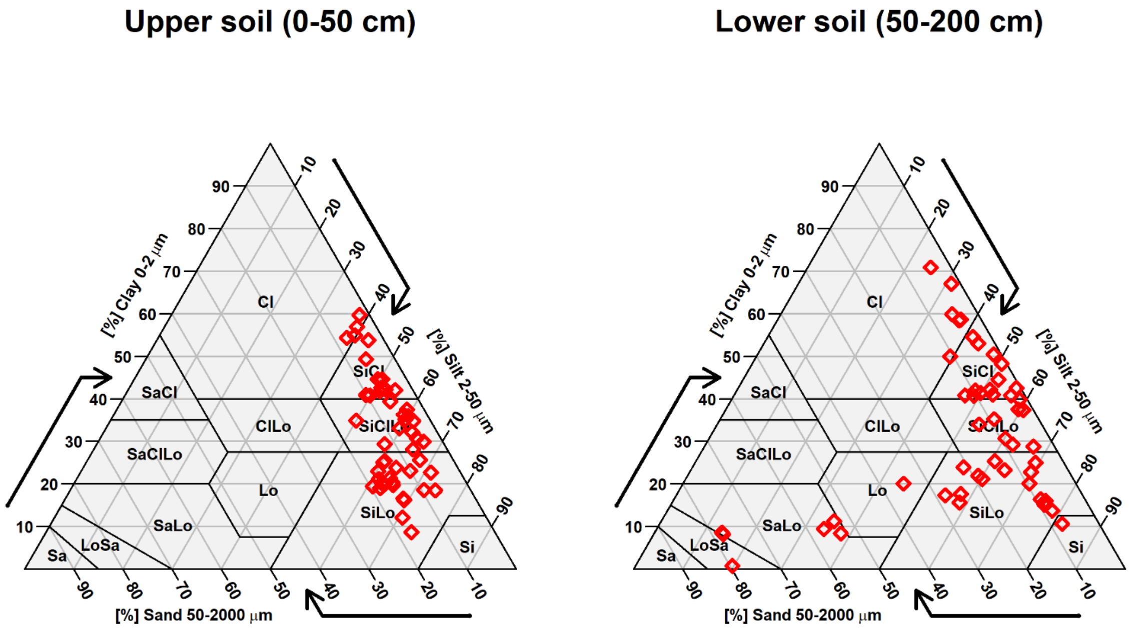


Figure A 30: Soil textures according USDA soil texture classification for upper soil layers (left) and lower soil layers (right). [Original part of the supplementary material of chapter 3.5]

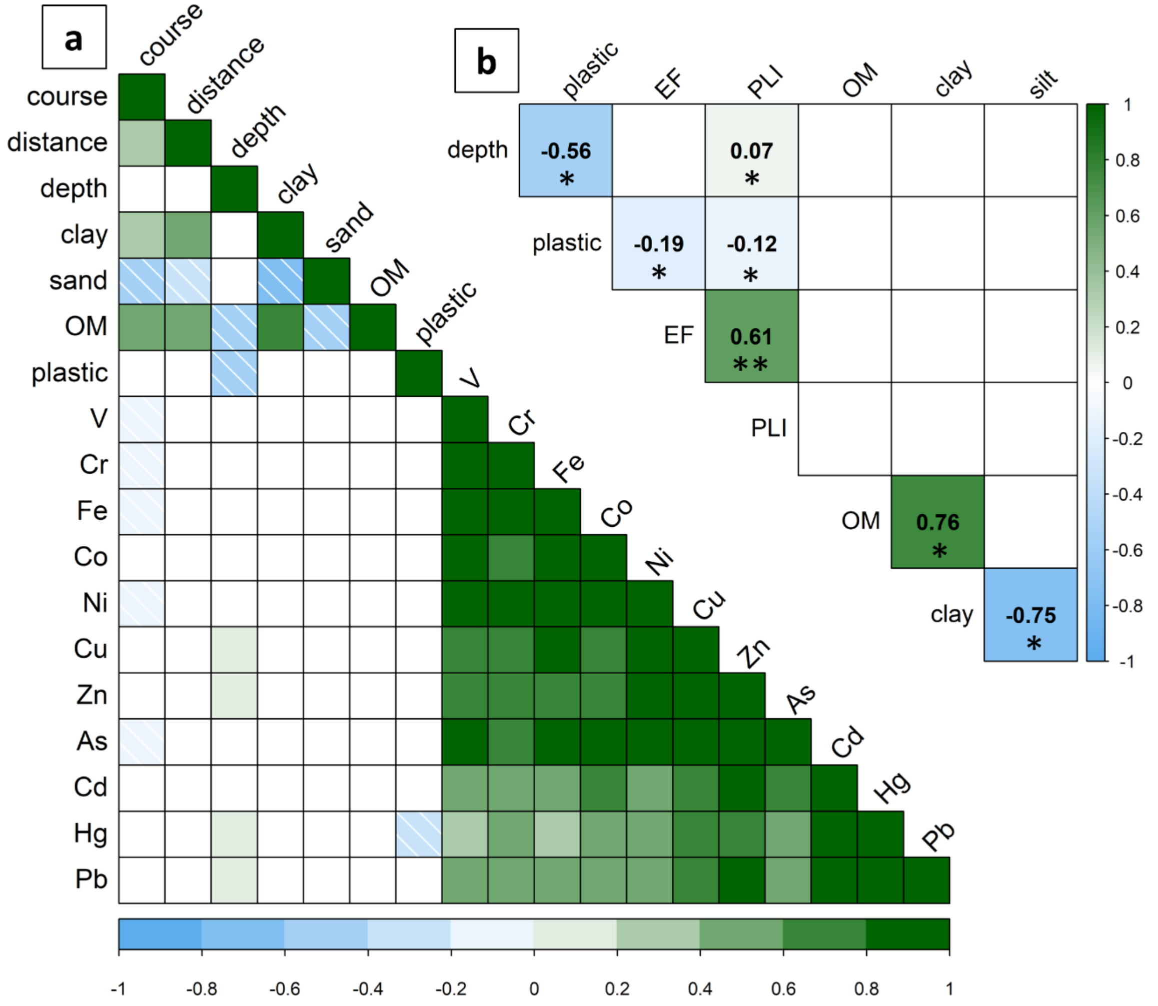


Figure A 31: Spearman correlation coefficients of spatial features, soil properties, metals, pollution indices and plastic loads. a: Spearman correlation coefficients expressed through color scale for spatial features (course: River km, distance: distance to channel, depth: soil depth), soil properties (clay content, sand content, OM: organic matter content), plastic loads (p kg^{-1}) and metal loads (mg kg^{-1}) ($p > 0.05$ = blank grid section); b: Spearman correlation coefficients for plastic loads (p kg^{-1}), Enrichment factor (EF), Pollution load index (PLI), soil depth (cm), clay content, sand content and organic matter (OM) content. Significance levels: $p \leq 0.01$ (**); $p \leq 0.05$ (*); $p > 0.05$ (blank grid section). [Original part of the supplementary material of chapter 3.5]

Erklärung

Ich erkläre an Eides statt, dass ich meine Dissertation

Spatial Distribution of Meso- and Microplastics in Floodplain Soilscapes:
Novel Insights from Rural to Urban Floodplains in Central Germany

selbstständig und ohne unerlaubte Hilfe angefertigt und mich dabei keinerlei anderer als der von mir ausdrücklich bezeichneten Quellen und Hilfen bedient habe.

Die Dissertation wurde in der jetzigen oder einer ähnlichen Form noch an keiner anderen Hochschule eingereicht und hat noch keinen sonstigen Prüfungszwecken gedient.

Marburg, 13.06.2022

Collin Joel Weber