OPUR : Observatoire d'hydrologie urbaine en Île de France
Thème de recherche - R2 : Diagnostic et optimisation des systèmes d'assainissement vis-à-vis des polluants et des micropolluants

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EVALUATION DE L'IMPACT DES ACTIVITES URBAINES SUR LE TRANSFERT DE MICROPLASTIQUES DANS L'ATMOSPHERE ET LEUR INFILTATION DANS LES SOLS

Rapport final
Thèse de doctorat de Max Beaurepaire
Avril, 2024

- *Thèse réalisée au sein du laboratoire Leesu sous la direction de Rachid Dris, Johnny Gasperi et Bruno Tassin*

École des Ponts ParisTech

THÈSE DE DOCTORAT
de l'École des Ponts ParisTech

Contributing to the assessment of the impact of urban activities on microplastic transport through air and runoff infiltration

École doctorale N° 531, Science et Ingénierie de l'Environnement (SIE)

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Scientific contributions associated with the PhD

Scientific publications

Microplastics in bulk atmospheric deposition of a French urban centre and its rural surroundings – Max Beaurepaire, Mathieu Goriaux, Ngoc-Nam Phuong, Sophie Ricordel , Rachid Dris, Bruno Tassin, Johnny Gasperi – 2024, manuscript in preparation

Microplastics and tyre and road wear particles infiltration in the soils of a roadside biofiltration swale – Max Beaurepaire, Tiago de Oliveira, Bruno Tassin, Johnny Gasperi, Rachid Dris – 2024, manuscript in preparation

Covid lockdown significantly impacted microplastic bulk atmospheric deposition rates – Max Beaurepaire, Johnny Gasperi, Bruno Tassin, Rachid Dris– Environmental Pollution *(*2024, https://doi.org/10.1016/j.envpol.2024.123354*)*

Sampling and analyzing microplastics in rivers: What methods are being used after a decade of research? – Rachid Dris, Max Beaurepaire, Nadia Bouzid, Cleo Stratmann, Minh Trang Nguyen, Frederique Bordignon, Johnny Gasperi, Bruno Tassin – Chapter in Microplastic Contamination in Aquatic Environments (Second Edition) (2024; https://doi.org/10.1016/B978-0-443-15332-7.00013-2)

Microplastics in the atmospheric compartment: a comprehensive review on methods, results on their occurrence and determining factors – Max Beaurepaire, Rachid Dris, Johnny Gasperi, Bruno Tassin – Current Opinion in Food Science (2021, *https://doi.org/10.1016/j.cofs.2021.04.010*)

Scientific communications

Oral communications:

- 4 presentations at international conferences
- 9 communications at national conferences including 2 as presenter

Poster presentations:

- 3 posters at international conferences
- 1 poster at a national conference

Contributing to the assessment of the impact of urban activities on microplastic transport through air and runoff infiltration

Max Beaurepaire

Abstract (english)

Plastics have permeated society and are used in all sectors of industry, from packaging to construction to the automotive industry. One consequence of this extensive, unregulated use is the now ubiquitous presence of plastic debris of all sizes in ecosystems. Plastic pollution, and in particular the presence and effects of microplastics in the environment, has been studied since 1972 and has been the focus of increasing scientific interest over the last two decades. Microplastics have been identified in virtually all environments, from marine sediments to mountaintops. While it is considered to be a dominant source of microplastics, the impact of local urban activities on the fate of microplastics in the environment remains poorly understood. This work aims to provide new insights into the relationships between anthropic activities, specifically road traffic, atmospheric deposition of microplastics, and infiltration of microplastics into roadside soils.

Firstly, the methodological choices of this PhD are presented with an insight into the current challenges of microplastic quantification in continental environments in the literature. After collection, samples undergo a treatment consisting of density-based separations with NaI and oxidative treatments. The microplastic content of each sample is characterized and quantified using a micro-FTIR imaging analysis, followed by a post-treatment using the open software SiMPle.

The impact of urban activities on microplastics in the atmospheric compartment was then addressed. Microplastic bulk atmospheric deposition was measured over 5 campaigns in 4 different sites of interest, with variable levels of urban pressure, including rural and urban sites. Key results were observed, including significantly lower deposition rates in an urban site during a Covid-related national lockdown (median 5.3 MP m^{-2} d^{-1}) than in a period of normal activity (median 29.2 MP m^{-2} d^{-1}). When comparing different sites in similar campaigns, higher deposition rates were observed in urban areas than in rural, agricultural sites, suggesting an effect of local activity on depositions. The characteristics of the deposited microplastics also varied with the level and type of activity. Different dominant polymers, and differences in size distribution, were observed.

Thirdly, the infiltration of microplastics and tyre and road wear particles into the soil of a biofiltration swale located on the side of a high-traffic highway was quantified. After manually coring soil samples from the biofiltration swale, both microplastics and tyre and road wear particles were quantified using two specialized analytical methodologies. Significantly higher

concentrations were measured on the surface than in the deeper samples, with a clear decrease in number of particles and concentration. This suggests the majority of particles were filtered by the soil and remained close to the surface. Despite consisting in different particles with different sources, similar vertical profiles were for tyre wear particles and microplastics, albeit tyre wear particles had significantly higher concentrations than other microplastics (median 2.32 mg g^{-1} for SBR, against a median of 0.05 mg g^{-1} for other microplastics in the surface samples).

This PhD contributed to the overall understanding of microplastic transfer mechanics and the role of less-studies microplastic transport vectors and reservoirs in urban environments. In particular, it helped highlighting an immediate impact of traffic on microplastic contamination and accumulation.

Evaluation de l’impact des activités urbaines sur le transfert de microplastiques dans le l’atmosphère et leur infiltration dans les sols

Max Beaurepaire

Résumé (français)

Les matières plastiques sont utilisées dans tous les domaines industriels de l'emballage à la construction, en passant par l'industrie automobile ou l'agriculture. Une conséquence de cette utilisation extensive et non réglementée est la présence ubiquitaire de déchets plastiques de toutes tailles dans les écosystèmes. La pollution plastique, en particulier la présence et les effets des microplastiques dans l'environnement, est étudiée depuis 1972 et suscite un intérêt scientifique croissant depuis les deux dernières décennies. Des microplastiques ont été décrit dans pratiquement tous les environnements, des sédiments marins aux sommets de montagnes. Si l'activité urbaine est suspectée d'affecter la production et le devenir des microplastiques dans l'environnement, ses effets exacts restent mal établis. Cette thèse vise à apporter de nouvelles informations sur les relations entre les activités anthropiques, en particulier le trafic routier, et la déposition atmosphérique de microplastiques, ainsi que leur infiltration dans les sols en bordure de route.

Tout d'abord, les choix méthodologiques de cette thèse sont présentés au regard de leur ancrage dans la littérature, avec un aperçu des défis actuels pour la quantification des microplastiques dans les environnements continentaux. Après une étape de collecte, les échantillons sont traités par séparation densimétrique à l'aide de NaI, et par digestion oxydative. Les microplastiques de chaque échantillon sont ensuite caractérisés et quantifiés à l'aide d'une analyse par imagerie cartographique micro-IRTF suivie d'un post-traitement par le logiciel SiMPle.

L'impact des activités urbaines sur le transfert de microplastiques dans le compartiment atmosphérique est ensuite abordé. 5 campagnes de suivies des retombées atmosphériques globales ont été réalisées sur 4 sites d'intérêt comprenant des zones urbaines et rurales. Des résultats majeurs ont pu être notés. Tout particulièrement, des taux de déposition significativement plus faibles ont été mesurées dans un site urbain pendant un confinement lié à la covid-19 (médiane de 5,3 MP m^{-2} j^{-1}) par rapport à une période d'activités normales sur le même site (médiane de 29,2 MP m^{-2} j^{-1}). Lors de la comparaison de différents sites au cours de campagnes similaires, des taux de déposition plus élevés ont été observés dans les zones urbaines que dans les zones rurales dominées par l'agriculture. Les caractéristiques des microplastiques déposés ont également changé en fonction du niveau et du type d'activité, avec notamment des différences dans les polymères dominants et la distribution des tailles de microplastiques.

Troisièmement, l'infiltration de microplastiques et de particules de pneus dans le sol d'une noue filtrante située le long d'une route à fort trafic a été quantifiée. Des échantillons de sol de la noue filtrante ont été manuellement prélevé par carottage, puis leur teneur en microplastiques et en particules de pneus ont été quantifiés à l'aide de deux méthodologies spécialisées. Des concentrations significativement plus élevées ont été mesurées en surface par rapport aux échantillons plus profonds, avec une diminution nette de la concentration suggérant que la majorité des particules ont été filtrées par le sol et sont restées près de la surface. Malgré des particules différentes avec des sources différentes, des profils verticaux similaires ont été observés pour les particules d'usure des pneus et les microplastiques, bien que les particules d'usure des pneus aient des concentrations significativement plus élevées que les autres microplastiques (médiane de 2,32 mg g^{-1} pour le SBR en surface, contre une médiane de 0,05 mg g^{-1} pour les autres microplastiques).

Ces travaux contribuent à une meilleure compréhension des mécanismes de transfert des microplastiques et du rôle des vecteurs de transport et des réservoirs moins étudiés dans la contamination et l'accumulation des microplastiques dans les environnements urbains.

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List of abbreviations and chemical formulae

Acronym	Definition
ABS	Acrylonitrile Butadiene Styrene
AMP	atmospheric microplastics
ATR	attenuated total reflectance
BDOH	Base de Donnée pour les Observatoires en Hydrologie
BFS	biofiltration swale
BMP	Best Management Practice
BR	Butadiene rubber
CD77	Conseil départemental du 77
FTIR	Fourier Transform InfraRed Spectroscopy
GC	Gas Chromatography
HDPE	High Density Polyethylene
IR	Infrared
ISO	Internal Organization for Standardization
JAMMS	JAMSTEC Microplastics Separator
LDPE	Low Density Polyethylene
LEE	Laboratoire Eau & Environnement
LEESU	Laboratoire Eau, Environnement et systèmes urbains
LID	Low Impact Development/Low Impact Drainage
LOQ	Limit of Quantification
MCT	Mercury-Cadmium-Telluride
MP	Microplastic
MS	Mass Spectrometry
MSFD	Marine Strategy Framework Directive
NHAPS	National Human Activity Pattern Survey
NILU	Norwegian Institute for Air research
NOAA	National Oceanic and Atmospheric Administration
OPUR	Observatoire des Polluants Urbains

OSPAR	Convention for the Protection of the Marine Environment of the North-East Atlantic (Oslo-Paris Convention)
PA	Polyamide
PA66	Polyamide 6-6
PAH	Polycyclic Aromatic Hydrocarbon
PAN	Polyacrylonitrile
PC	Polycarbonate
PE	Polyethylene
PET	Polyethylene Terephthalate
PM	Particular Matter
PM10	Particular Matter <10 µm
PM2.5	Particular Matter <2.5 µm
PMMA	Polymethylmethacrylate
PP	Polypropylene
PRAMMICS	Plateforme Régionale d'Analyse Multi-Milieux des Micro Contaminants
PS	Polystyrene
PTFE	Polytetrafluoroethylene
PU	Polyurethane
PVA	Polyvynilacetate
PVC	Polyvinylchloride
Py	Pyrolysis
QA	Quality Assurance
QC	Quality Control
SBR	Styrene-Butadiene Rubber
SD	Standard Deviation
SEM	Scanning Electron Microscope
SUDS	Sustainable Urban Drainage system
TRWP	Tyre and Road Wear Particles
TWAP	Tyre Wear Airstrip Particles
TWL	Tyre Weight Loss

Introduction

Contextualization

Since the start of their industrial production, the yearly production of synthetic polymers has consistently increased from 2 megatons (Mt) in 1950 to over 400 Mt in 2021 (Plastics Europe, 2023). Plastics have become ubiquitous in society and are used in all industrial fields, ranging from packaging, to construction, to the automotive industry. A consequence of this unregulated and extensive use is the now widespread presence of plastic litter of all sizes in the environment.

The first scientific description of plastic debris in the environment dates back to the 1970s when Carpenter *et al.* observed the presence of plastic litter on the surface of the Sargasso Sea (Carpenter et al., 1972; Carpenter and Smith, 1972). The authors highlighted potential consequences such as the accumulation of plasticizers in marine organisms. However, the study did not immediately attract the attention of the scientific community. Scientific interest in plastic pollution grew later, particularly at the beginning of the 21st century. The term "microplastics" was coined by Thompson *et al.* in 2004 to describe sub-millimetric plastic debris, leading to increased focus by the scientific community (Thompson et al., 2004).

Since these first studies, plastic litter and microplastics have been documented in a diversity of environments, including both marine and continental areas, urban and remote sites. (Abeynayaka et al., 2020 ; T. Bujaczek et al., 2021; Collignon et al., 2012; Dris, 2016; F. Liu et al., 2019a; MSFD Technical Subgroup on Marine Litter., 2013; Napper et al., 2020a; L. Yang et al., 2021).

Over the past two decades, the topic of microplastic pollution has become a hotspot of scientific interest, leaving the exclusivity of marine pollution sciences to attract research groups from multiple fields, including exposure assessments, ecotoxicology, and environmental modelling (Besseling et al., 2017; Bläsing and Amelung, 2018; Wang et al., 2019). Consequently, a wealth of knowledge was produced on the topic. Microplastics are a common form of pollution that affects both humans and wildlife. They have established direct and indirect ecotoxic effects. However, studies have also revealed significant knowledge gaps on the topic. The transfer dynamics from microplastic sources to their fate in the environment are poorly understood, as are their interactions with other pollutants. Implementing the systemic policy changes necessary to address this pervasive contamination remains challenging to envision and execute.

The LEESU (Water, Environment and Urban Systems Laboratory) focuses on environmental sciences from an urban or peri-urban perspective. The laboratory began studying microplastics in 2013, making it one of the first research teams to focus on the subject in urban environments

(Dris, 2016). Since then, several projects and PhDs have been conducted to better understand the sources and fate of microplastics in urban and peri-urban environments (Nguyen, 2023; Treilles, 2021).

Guiding question and objectives of the PhD

Though scientific interest on the topic is steadily increasing, microplastics remain understudied in urban environments. In order to better understand the major microplastic transport pathways, multiple urban environments must be assessed. These are the atmospheric compartment and urban runoff as potential microplastic transport agents, and soils as a potential major sink of microplastics.

The presence of microplastics in the atmosphere has only been recently described. Microplastics in total atmospheric fallout have been observed for the first time during Rachid Dris's PhD in 2015 (Dris et al., 2015). Since then, over 30 papers and a dozen reviews have been published on the topic. Recent studies suggest that microplastics can be transported over long distances by wind and contribute to deposition in remote environments (Allen et al., 2019; Evangeliou et al., 2020; Napper et al., 2020a). In several studies monitoring microplastic content in atmospheric fallout, precipitation events were suggested to influence atmospheric deposition (Allen et al., 2019; Cai et al., 2017a; Dris et al., 2015, 2017). Rain events may also cause a washout of suspended particles. However, a direct correlation between daily rainfall and microplastic deposition has not yet been observed. Similarly, while microplastic deposition is suspected to be affected by human activity, a direct correlation between the level of activity and deposition rates remains to be measured.

Microplastics have been described in soil environments even more recently than in the atmospheric compartment, with the first studies on the topic dating from 2018 (Liu et al., 2018; Zhang and Liu, 2018; Zhou et al., 2018). In the studies conducted on the topic, microplastics have largely been identified in agricultural soils, with wastewater sludge as a major source of microplastics (Corradini et al., 2019; Kumar et al., 2020), along with the direct use of plastic films (Y. Li et al., 2023). Because of the limited number of studies on the topic, major knowledge gaps remain. Microplastic vertical migration and potential infiltration into soils remain poorly understood, and some of the major potential sources of microplastics into soils have received little attention.

In particular, the first descriptions of microplastics in stormwater and urban runoff only date back from 2019. In a study by Hitchcock *et al.*, microplastic concentrations were noted to be significantly higher in a harbour's water after a rain event than before (Hitchcock, 2020). The author suggests that rain has a washout effect that transports all microplastics deposited on urban ground towards the harbour. In 2019, F. Liu et al. quantified microplastics in several urban stormwater retention ponds in Denmark (F. Liu et al., 2019a). Runoff waters have also been shown to be enriched with microplastics (Cho et al., 2023; Treilles et al., 2021). However, the origin of these particles remains to be determined. While the traditional principles of stormwater management consisted in the quick removal of urban runoff through general sewage systems, ideas of alternative methods to deal with stormwater runoff were developed in the 70s. The terms Best Management Practices (BMP) coined in the 1970s or Sustainable Urban Drainage Systems (SUDS) formalized at the end of the 90s broadly encompass several practices and techniques that aim at reducing sewage load during rain events (Fletcher et al., 2015). By temporarily storing, promoting the direct infiltration or evapotranspiration of stormwater, these techniques reduce the maximal flowrates during storm events and the total stormwater volumes susceptible to join sewer systems.

Overall, microplastics have seldom been studied in urban runoff and stormwater. Directly sampling stormwater is a hard process, and sampling drainage after it has joined sewer systems cannot give an indication of their origin. In particular, in the case of combined sewer systems, the fraction of microplastics that comes from stormwater cannot be separated from the fraction that comes from sewage. However, sampling soil or water from a SUDS is an easier process. Some experimental sites are already equiped with systems allowing direct stormwater sampling. Besides, one can hypothesize that a large fraction of the microplastics transported by urban runoff into an infiltration site should stay in that infiltration site. As a result, one may expect to observe an accumulation of microplastics in SUDS.

In light of these major gaps in the general understanding of microplastic transport in urban environments, the studies conducted within the frame of this PhD are focused on the interaction between urban activity, particularly road traffic, and microplastic pollution. As a whole, this work aims to address the following question:

How does urban activity affect the transfer of microplastics between environments?

As a way to address this overarching question, two specific elements of these microplastic transfer mechanics were specifically studied:

- Microplastic transport and deposition from the atmospheric compartment, and the comparative role of human activity and precipitations in atmospheric microplastic deposition rates
- Microplastic transport and infiltration into a receiving environment, specifically the soils of a roadside biofiltration swale, through urban runoff.

General outline

This manuscript is structured in 4 chapters organized as follow:

Chapter 1: Definitions, choices and methodological strategy

This first chapter summarizes the discussions and decisions that structured the scientific strategy of this PhD. The study of microplastics is a rapidly evolving field that has gained traction in recent years from research groups of various scientific disciplines. As a result, the methods used for sampling, preparation, and analysis of microplastics in the environment are not yet standardized in the literature (Dris et al., 2024). To develop a scientific strategy that is tailored to a specific problem, it is essential to identify, evaluate and select appropriate methods from the literature.

First, the notion of microplastics, its use in the literature and the discrepancies in the definitions used are highlighted. A clear definition of the way the term “microplastics” and the targeted contaminants of this PhD are provided.

After this discussion, the sampling, treatment, and analytical methods used in this work are presented and discussed in regards to the dominant methods identified in the literature. While some elements of treatment and the sites of interests vary between the subsequent chapters of this work, all methods followed the same logic and are thus only detailed once.

Finally, each section is concluded with general recommendations regarding the methods to use and the need for the clarification of methodological choices in future publications.

Chapter 2: Microplastics transfer through atmospheric deposition

In this second chapter, the roles of human activities and precipitations on microplastic atmospheric deposition are compared. After a literature review of the current major results on microplastics in the atmospheric compartment, a total of five atmospheric deposition monitoring campaigns are described and compared. In particular, the impact of the reduction of

activity caused by the 2020 national spring lockdown on microplastic atmospheric deposition in an urban site is highlighted and compared to the differences between atmospheric deposition of microplastics in urban and rural settings.

Chapter 3: Spatial and vertical distribution of microplastics and TRWP in a roadside soil

This third chapter focuses on the spatial and vertical distribution of microplastics in the soils of a single site of interest located on the side of a highway.

Soil and sediment samples were collected by manual coring and analysed for microplastics and Tyre and Road Wear Particles (TRWP). The concentration profile of microplastics is compared with that of tyre and road wear particles. These results are then used to provide an estimate of the overall stock of microplastics and TRWP particles on site and their spatial distributions.

Chapter 4: Mass balance of microplastics and TRWP accumulation in a sustainable urban drainage system

The fourth chapter of this manuscripts builds upon the results detailed in the previous chapter to conduct a first-order mass balance of microplastics and TRWP in the site of interest of chapter 3.

First, the potential sources and sinks of microplastics and TRWP in the site are presented and discussed. Using additional sampling campaigns and the results of the previous chapters, orders of magnitude of fluxes from the atmospheric compartment, urban runoff and macrolitter accumulating on the site are compared to the overall stock of microplastics and TRWP.

Chapter 1 – Definitions, choices and methodological strategy

1 Contents

2 Introduction

The study of microplastic contamination of the environment is a relatively recent topic, with only two decades of scientific development and a sudden and still increasing scientific interest. After the domain emerged from marine pollution research, scientific communities from an array of fields ranging from ecotoxicology to environmental chemistry to atmospheric computational modelling embraced the topic. These communities adapted more or less directly their own vocabulary and methodologies to the emerging field of microplastic pollution.

Since then, the number of studies mentioning the word microplastics in their title or keywords has continuously increased. Using the Web of Science search engine, the evolution of the number of publications per year that include the words microplastics or nanoplastics in their title, abstract or keywords list was estimated from 2006 to late **December 2023**. A total of **16,238** research articles were found by the search engine, with a steady increase over the years (Figure 1a). In particular, around 51% of all publications ever produced on the topic of microplastics or nanoplastics pollution were produced in 2022 and 2023. While the production rate of scientific manuscripts tends to increase in nearly every topic, the interest in microplastic pollution leads to a clearly faster increase than the overall trend, as shown Figure 1b. Topics like ecotoxicology or global warming saw a steady increase in yearly publications, with the number multiplied by 3 to 4 between 2010 and 2022. In contrast, yearly publications in the topic of microplastics in the environment were multiplied by 1,000 in the same time span. Interest in the topic is growing exponentially, with a median increase of 70% per year in the number of annual publications from 2009 to 2022.

A consequence of this Cambrian explosion of publications is that methodologies and terminologies vary greatly across the microplastic community. In particular, the methods used to collect, prepare and analyse environmental samples are subject to a high degree of variability. In this context of quickly evolving methodology, it is necessary to have an understanding of the global methodological trends before starting new research projects.

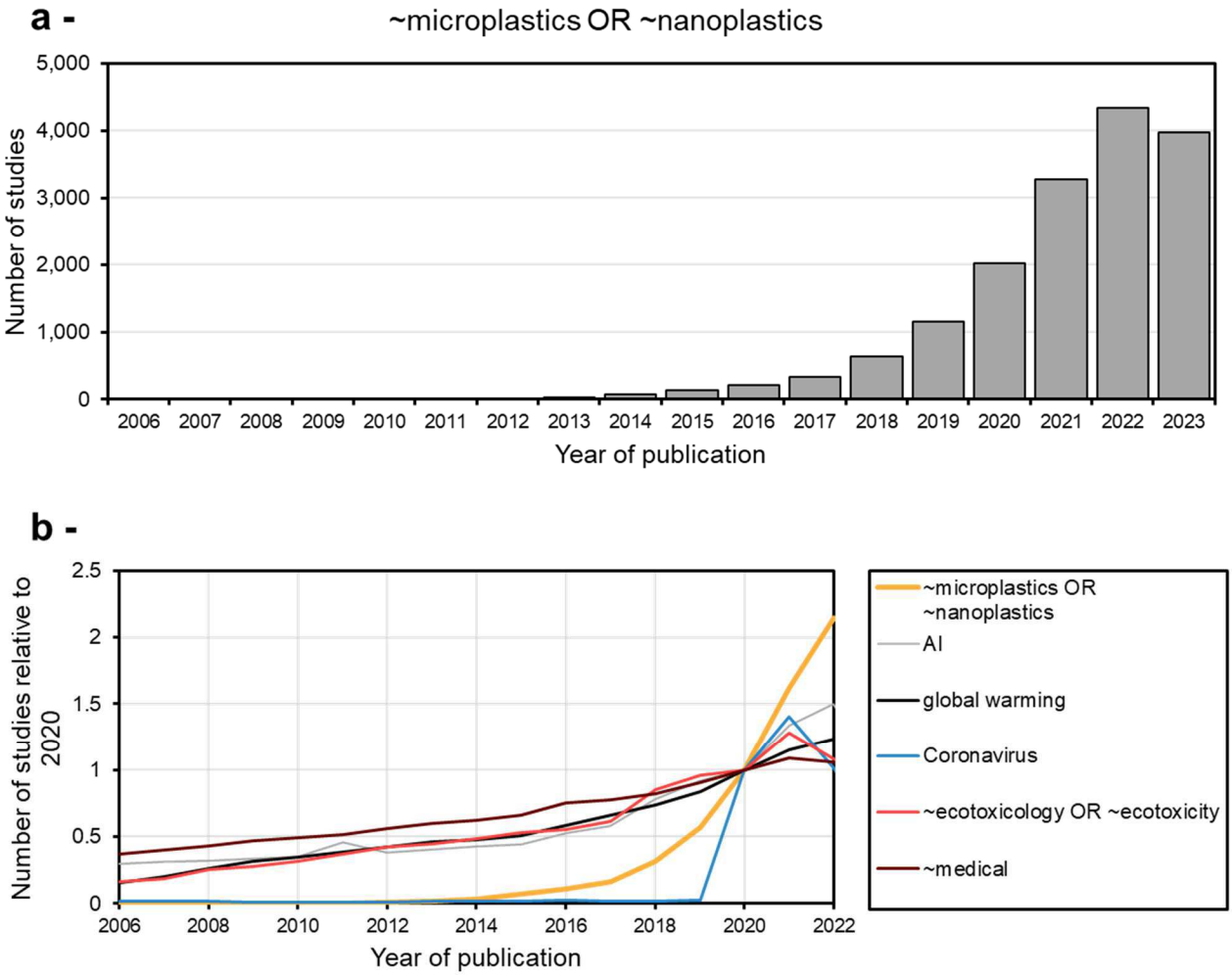

FIGURE 1A – EVOLUTION OF THE NUMBER OF PUBLICATIONS PRODUCED PER YEAR FROM 2006 TO THE END OF DECEMBER 2023, IDENTIFIED BY THE WEB OF SCIENCE SEARCH ENGINE USING THE REQUEST ~MICROPLASTICS OR ~NANOPLASTICS. EARLY STUDIES ON UNRELATED TOPICS USING THE SAME KEYWORDS WERE NOT INCLUDED; B – COMPARATIVE EVOLUTION OF THE NUMBER OF PUBLICATIONS PRODUCED PER YEAR FROM 2006 TO 2022 FOR MICROPLASTIC STUDIES AND OTHER KEY RESEARCH TOPICS

This chapter aims to **i)** identify the methodological trends on microplastic sampling, treatment and analysis across the literature, **ii)** provide a commentary on the benefits and limits of these methods, and some possible insights for future improvements, and **iii)** position the methods used throughout this PhD in relation to the dominant methodologies observed in the literature.

While this chapter consists in a discussion based on the literature, it should not be considered an exhaustive representation of the methodologies used in the literature for microplastic studies. In December 2020, the number of published articles about microplastics was equal to **4,642.** That number increased further and reached **16,238** in December 2023. Even the number of studies on the topic of microplastics in continental environments (soils, freshwater, the

atmospheric compartment, or urban environments) is now superior to **4,700**, which is too many to be entirely detailed here.

Additionally, the methodological choices made for this work were not always made to be the best available. They were also constrained by the existing materials available to the laboratory. The objective of this chapter is not to justify the methods used as the best possible, but rather to clearly position them.

A fraction of this chapter is developed from a review article published in 2021 on the topic of atmospheric microplastic pollution (Beaurepaire et al., 2021). Another fraction was inspired by a book chapter co-written during this PhD and published in 2024 (Dris et al., 2024). Finally, additional literature researches using the Web of Science and Google Scholar search engines were conducted to complete the literature insight.

3 Targeted particles – complex and changing definitions

3.1 Microplastics, a difficult definition

As mentioned above, the study of microplastic contamination is a recent topic. The term microplastics was first coined in 2004 in a now historical paper by Thompson *et al.* (Thompson et al., 2004).

In spite of, or rather as a consequence of this heightened interest and influx of researchers from different scientific communities, the scope of particles included in the term "microplastic" and microplastic studies underwent a dynamic evolution over time, struggling to reach a fully consensual definition among researchers. A definition of the term "microplastics" was adopted by researchers in 2009, following the publication of the proceedings of the international research workshop on the occurrence, effects, and fate of microplastic marine debris (Arthur et al., 2009). The definition agreed on was as follows: *"The Workshop participants defined microplastics as plastic particles smaller than 5 mm."*

This definition determined two elements of the scope of particles included in microplastic studies. First, a definition was made for an upper bound of particles considered as microplastics. This upper bound was largely followed by subsequent studies. No lower bound for microplastics was defined, as the authors of the proceedings noted that this lower bound

depends on the sampling procedures, particularly the 333 µm mesh of the nets used to sample marine waters.

As the potential existence of nanoplastics, plastic debris smaller than 1 µm, emerged in 2014 in a study by Besseling *et al.* (Besseling et al., 2014), the scope of particles considered as microplastics was fixed as ranging from 5 mm to 1 µm. In practice however, the size range targeted varies between studies, as it remains highly dependent on the sampling and analytical procedures.

In addition to this physical definition of what constitutes a microplastic, an implicit chemical definition remains, that is less clear and has not reached a clear consensus: microplastics are plastic particles. According to the International Organisation for Standardization("ISO 472:2013(en), Plastics — Vocabulary," 2013), a plastic follows the definition:

Material which contains as an essential ingredient a high polymer and which, at some stage in its processing into finished products, can be shaped by flow

Note 1 to entry: Elastomeric materials, which are also shaped by flow, are not considered to be plastics.

Note 2 to entry: In some countries, particularly the United Kingdom, the term "plastics" is used as the singular form as well as the plural form.

This definition contains several terms that need to be defined as well. First, polymers are a class of materials formed of macromolecules, which are themselves high-molecular weight

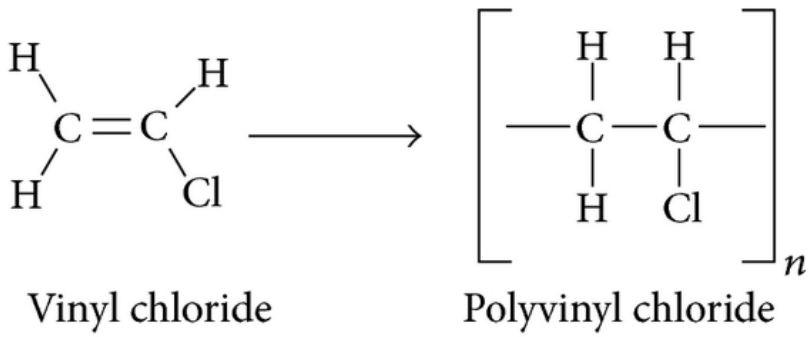

FIGURE 2: POLYVINYL CHLORIDE, AN EXAMPLE OF A POLYMER

assemblages of low-mass molecules. Figure 2 illustrates this definition of a polymer. Secondly, at some step in the processing or manufacturing of a plastic product, the product can be shaped by flow. This means the material is, for a moment, sufficiently malleable that it can be deformed into a shape before it hardens and retains this shape.

As noted in the definition, plastics are not exclusively composed of a polymer. A fraction typically ranging from 5 to 50% of their total mass is composed of charges and additives used to alter the physical or chemical properties of the material: elasticity, resistance to oxidation, flame retardants, etc.

While the ISO standard definition clarifies the materials that may be classified as plastics, it does not represent a specific guidance for microplastics. Though not mentioned, many study implicitly focus on products of petrochemistry. This can be noted from results, where exclusively petrochemical polymers are considered. Some studies consider cellulose-based semi-synthetic materials, such as viscose and cellophane (Lusher et al., 2013) (Dehaut et al., 2016). While their dominant polymer is cellulose, these consist in man-made products with a higher durability than naturally occurring cellulose that adhere to the ISO standard definition of plastics. It is reasonable to consider in first approximation that they are susceptible to the same transport dynamics as microplastics, and might cause similar ecotoxicological concerns as microplastics, and thus should be included in microplastic studies. (Lusher et al., 2013) (Dehaut et al., 2016).

This is particularly the case in studies focused on the quantification and fate of microfibres in the environment (T. Bujaczek et al., 2021; Stanton et al., 2019; Treilles et al., 2021). A wide diversity of anthropogenic materials can be eroded and produce small-sized fibres. While some of these microfibres are strictly petrochemicals such as polyamides and polypropylene, a large amount of fibres produced by human activities are cellulose-based, such as viscose or cotton, and may represent similar environmental concerns as synthetic microfibres (Stanton et al., 2019). The ISO/TR 11827 :2012 norm defines fibres as either natural, that is to say fibres which occur in nature, or man-made: fibres that are obtained by a manufacturing process. These man-made fibres can either be obtained by the transformation of natural materials (artificial fibres) or entirely made from synthetic materials (synthetic fibres) (“ISO/TR 11827,” 2012; Treilles, 2021). Several studies focused on the occurrence of microfibres in the environment include all forms of man-made fibres, as they all represent a form of anthropogenic pollution (T. Bujaczek et al., 2021; Dris et al., 2016a; Prata et al., 2020).

Another category of particles that is adjacent to microplastics yet not always included in microplastic studies are tyre and road wear particles (TRWP). These are complex particles with a highly varying composition. A tyre is composed of a mix of natural and synthetic elastomeric rubber polymers, which are explicitly excluded from the ISO standard definition of plastics (“ISO 472:2013(en), Plastics — Vocabulary,” 2013). The two main synthetic elastomers used

in tire manufacturing are butadiene rubber and butadiene styrene rubber. Their proportion relative to the rest of the tyre, and the natural rubber, depends on the use of the tyre. Typically, a heavy-duty vehicle tyre contains 34% of natural rubber for 11% of synthetic polymers, while a passenger vehicle contains 24% of synthetic rubber and 19% of natural rubber. The rest of a tyre's composition consists in steel, fillers, and an array of additives such as antioxidants and antiozonants (U.S. Tire Manufacturers Association, 2020).

TRWP are formed from the abrasion of tyres on the road. While they are formed throughout the entirety of a tyre's use, more TRWP are formed in areas of high friction such as zones of acceleration or braking. Because of their formation process, road mineral incrustations are present in TRWP alongside the general composition of a tyre. The relative proportion of these road mineral incrustations varies, and could reach up to 50 or 60% of a tyre wear particle's volume (Eisentraut et al., 2018; Spanheimer and Katrakova-Krüger, 2022).

Although elastomers are specifically excluded from the ISO definition of a plastic ("ISO 472:2013(en), Plastics — Vocabulary," 2013), TRWP are often considered as microplastics by the microplastic pollution community (Eisentraut et al., 2018; Galafassi et al., 2019; More et al., 2023) and included in the discussions of microplastic sources (Kole et al., 2017). Similar to microplastics, they form particles that are ubiquitous in the environment (Wik and Dave, 2009), are likely to follow the same transport routes and pathways albeit to different proportions (Kole et al., 2017), and may present similar ecotoxicological and health concerns (Wik and Dave, 2009).

TRWP have been studied independently and for longer than microplastics. A study from Thompson *et al.* identified tyre rubber in roadway dust in 1966, using a combination of pyrolysis and gas chromatography (Thompson et al., 1966). However, these early studies were largely contained in specific environments close to TRWP sources, and did not focus on their dissemination in the environment.

Even currently, when they are studied alongside microplastics, TRWP quantification requires specific adaptations that are partly incompatible with spectroscopic analyses, the dominant methods used for microplastic characterization and quantification. Due to their significant road mineral content (Eisentraut et al., 2018; Kayhanian et al., 2012), TRWP have a higher density than other microplastics, potentially reaching 1.5 to 2.2 g cm^{-3} (Kayhanian et al., 2012). As a result, an isolation from environmental samples using density-based separation procedures is compromised. Additionally, TRWP are composite particles that contain significant amounts of

carbon black, which prevents the use of spectroscopic techniques such as FTIR or Raman and leads to the use of techniques like Pyr-GC/MS for characterization (Mattonai et al., 2022).

3.2 Definitions – Recommendations

The definition and categorization of notions and objects of interest is central to the scientific process. As seen earlier, the theoretical physical range of particles included in microplastics studies is relatively agreed on, ranging from 1 µm to 5 mm. In practice, both the upper and the lower range of studied particles vary based on the sampling and analytical methods. The chemical scope of studied particles is more implicit, and less clear. Few studies explicitly detail what they consider plastics, while some particles that do not fit the standard definition of plastic represent a similar environmental concern to that of microplastics, with separate sources yet a similar fate in the environment.

The absence of a clear, fully consensual scope of what constitutes microplastics may not necessarily represent an issue by itself. The study of microplastics is a recent and increasingly attractive research topic, and it is normal that research progresses in an array of different directions. Different and innovative analytical methodologies remain to be explored for the overall quantification of microplastics in environments to evolve.

However, in order to assess the comparability of results from different studies as well as in order to properly communicate the implications of studies to the broader study of microplastic pollution, it is particularly important for authors to clearly redefine the terms used in each study. Both the upper and the lower bound of the size range assessed should be explicitly mentioned, as well as a description of the chemical scope of particles considered for the research. As both these descriptions are heavily dependent on the analytical methodology of the study, such a description needs to be anchored in the presentation of the materials and methods section of research papers.

3.3 Definitions selected for this PhD

Several choices were made for this PhD regarding the scope of targeted particles. In light of the previous discussions, these choices need to be highlighted and justified. Firstly, when discussing general sources and transports of microplastics, this work considers microplastics as including all plastic and elastomeric particles with a major dimension larger than 1 µm and

smaller than 5,000 µm. This theoretical definition follows early guidelines and agreements regarding the size range definition of plastics (Arthur et al., 2009).

The practical range of plastics analysed is however different from this theoretical definition. Firstly, because of analytical limitations, only particles larger than 25 µm were considered during quantification of microplastics in samples. As will be discussed later in this chapter (6.2.4), the analytical method available represented a relatively hard limit on the lower size of particles. On the other end of the size spectrum, while particles larger than 500 µm were characterized, their abundance was less than one particle per sample, making their quantification unreliable. In addition, this PhD focuses on microplastics in the atmospheric compartment, and microplastic infiltration into soils. The particles susceptible to be transported into the atmosphere or to be infiltrated in soils are expected to be smaller than 500 µm.

Secondly, while it is likely that fibres are present in the results of the different studies included in this PhD, they were not specifically quantified or separated from other microplastic shapes. Microfibres are a likely major component of microplastic contamination in soils (Liu et al., 2018; Zhang and Liu, 2018) and in the atmospheric compartment(Cai et al., 2017a; Stanton et al., 2019). However, the analytical method selected for this work (micro-FTIR imaging, section 6.2.4) did not facilitate the clear distinction between fibres and other particles. More details will be provided later in this chapter.

When this PhD project was first conceived, Tyre and Road Wear (TRWP) were not included, as they require specific methodologies for isolation and analysis that were not developed in this research group. Over the course of this PhD, two factors changed this initial decision. First, the main site of interest selected for the work presented in Chapter 3 of this manuscript was located on the side of a highway, a few hundred meters past a zone of braking and acceleration. It appeared likely that TRWP concentrations would be extremely high in soil samples from that site, which would facilitate their quantification. Secondly, a method for the quantification of TRWP was developed at the LEE in Nantes. Consequently, TRWP were included in sampling campaigns and discussions related to Chapter 3. However, as they are not included in all campaigns TRWP are explicitly mentioned when studied. The use of the term “microplastics” thus exclusively refers to polymers quantified by micro-FTIR, ranging from 25 µm to 500 µm.

In addition, TRWP were quantified by Pyrolysis coupled with Gas Chromatography and Mass Spectrometry (Py-GC-MS), as will be presented in more details later in this chapter. This analytical process is destructive, and retrieves the mass of specific molecules used as marker for the targeted materials. As a result, this analytical method is not dependent on size, but on a

sufficiently high concentration for the markers to be quantified in a sample. While samples analysed for TRWP are sieved with a 500 µm mesh before quantification, no lower dimension of targeted particles was determined. In order to compare their concentration to that of polymeric microplastics, the microplastics mass concentration in samples is extrapolated from their abundance.

Finally, larger plastic debris, which could potentially serve as sources of microplastics, are also examined in some sections of this PhD. As these are not microplastics and were characterized and quantified using different methodologies from microplastic samples, they are explicitly mentioned and addressed independently from other samples.

In order to facilitate the readability of the manuscript, the decisions taken regarding the scientific strategy and the methods of sampling, treatment and analysis of the results presented in this PhD will be represented as a figure throughout this chapter. Figure 3 indicates the types of particles targeted in the following chapters. Chapter 2 is dedicated to microplastic deposition from the atmospheric compartment, and microplastics ranging from 25 to 500 µm were the main target of the study. Chapter 3 targets both microplastics, and TRWP with different analytical methodologies. Finally, chapter 4 completes these studies and collects macrolitter accumulating on a site of interest.

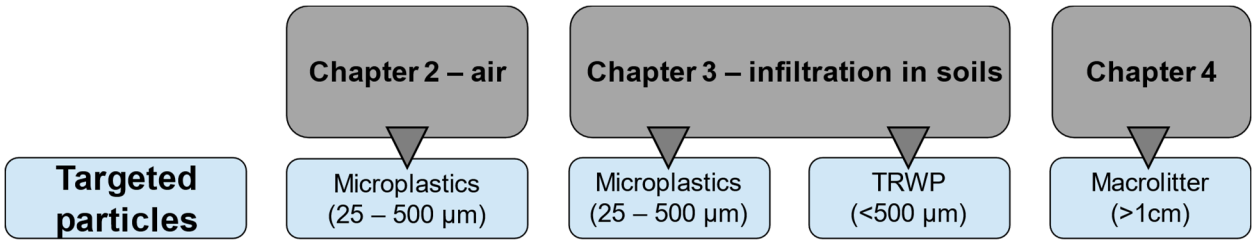

FIGURE 3: SUMMARY OF THE TARGETED PARTICLES FOR THE FOLLOWING CHAPTER OF THIS PHD

4 Sampling strategies

4.1 Introduction

The development of specific practices dedicated to the collection and analysis of relevant samples from specific environments is at the centre of experimental environmental sciences. As microplastic studies remain a relatively recent research field, sampling procedures are still largely inspired by methodologies from other fields.

The field of microplastic contamination in the environment first emerged from marine studies (Ng and Obbard, 2006; Thompson et al., 2004). As a result, sampling procedures were directly adapted, in particular from marine biology studies (H. and W., 2002; Wurl and Obbard, 2005). Oceanic sampling campaigns consist in large expeditions, during which samples are collected by filtering a volume of water through trawls with mesh sizes of a few hundred micrometres.

As microplastic particles differ both from plankton and from other marine pollutants, sampling procedures evolved and were progressively adapted to the specific challenges posed by microplastics. (Andrady, 2011; Hidalgo-Ruz et al., 2012). Plastic materials were removed from the sampling and laboratory equipment so as to avoid contamination, and filters were adapted to collect particles of smaller sizes based on the available analytical equipment.

In addition, sampling procedures were developed for an array of different environments. Samples were collected in freshwater for the first time in 2011 (Moore et al., 2011), which required a limited adaptation from oceanic samples. However, the study of sediments, continental environments, or the atmosphere required the development of different methodologies.

Several different environmental matrices were collected over the course of this PhD. In particular, monitoring campaigns targeting the atmospheric compartment were conducted in urban and rural sites. One larger sampling campaign was conducted to collect samples of soil from a biofiltration swale collecting runoff from a high traffic highway.

This section aims at providing a discussion on the factors taken into consideration when preparing for the sampling phase of an environmental campaign. A comment is made on the methods identified in the literature to sample the atmospheric compartment and the soils, and the sampling strategies selected for this work are presented and discussed, as well as the ways they are anchored in or divert from other methods identified in the literature. However, the

exact details of sampling procedures are largely dependent on the exact context of a campaign. Thus, further precisions on the sampling procedures are disclosed in later chapters dedicated to the findings of this PhD.

4.2 Sampling the atmosphere

The content of this section is inspired from the following review: Microplastics in the atmospheric compartment: a comprehensive review on methods, results on their occurrence and determining factors – Max Beaurepaire, Rachid Dris, Johnny Gasperi, Bruno Tassin – 2021 – https://doi.org/10.1016/j.cofs.2021.04.010

4.2.1 Sampling the atmosphere – Literature insight

The atmospheric compartment is among the most recent environments where microplastic contamination was identified and quantified. The first study identified in the literature that detected microplastics in atmospheric deposition dates back to 2015 (Dris et al., 2015), with a more detailed publication in 2016 (Dris et al., 2016a). Since then, the number of studies increased quickly. In order to review the literature on the topic, documents were gathered using the Web of Science® and Google Scholar® search engines. Papers were sorted both by relevance and by date in order to ensure all relevant studies were found. Different keywords were used to ensure no major paper was missed. The exact research query was as follows:

TI = (microplastics AND (~air OR ~airborne OR ~atmosphere OR ~atmospheric)) OR KA = (microplastics AND (~air OR ~airborne OR ~atmosphere OR ~atmospheric)).

In that query, the elements following TI relate to the title of the papers. The elements following KA relate to the author keywords of the papers. Studies collecting already deposited snow were excluded from the corpus of this review. By December 2020, 45 published articles were found on the subject of microplastics in the atmosphere. This number includes a high fraction of bibliographical reviews: a fifth (10 out of 45) of the papers identified were review articles. That number greatly increased over the course of this PhD, and by December 2023, **239** studies were found using the same query. 49 of these studies are identified as review articles.

The content presented here is largely based on a document that was published in early 2021, at the beginning of this PhD. While the number of studies dramatically increased since the publication of the review, there was no drastic evolution of the dominant methodological trends on sampling in that period. As a result, the majority of studies that are cited and discussed in this section were published before 2021.

The present review specifically aims at providing a comprehensive and comparative overview of methods and results used. Twenty-six articles include samples of microplastics from the atmospheric compartment. Other articles include physical models of microplastic transport by the atmosphere, ecotoxicity assessments, methodology presentations and opinion papers. Excluding reviews and opinion papers, 77% (24 out of 32) of all studies found date from 2019 or later, while only 9% (3 out of 32) date from 2015.

Just as the methodologies used to sample microplastic in water samples were first derived from other fields of environmental studies, the sampling of microplastics in the atmospheric compartment was first adapted from other fields of atmospheric studies. In particular, the first studies on the topic used a sampling approach and materials derived from earlier works within the same research group, on atmospheric micropollutants (Bressy, 2010).

In order to study the microplastic contamination of the atmospheric compartment, two broad categories of sampling strategies can be noted, as described on Figure 4.

The first sampling method consists in collecting suspended atmospheric microplastics, either in indoor air or outdoor air. The objective of these studies is to measure the abundance of microplastics in the air, in number or mass of microplastics per volume unit. Such abundances represent crucial information to assess the atmospheric compartment as a microplastic reservoir, as well as to assess human or ecosystems exposure to atmospheric microplastics. Information on this exposure is in in turn necessary to assess the ecotoxicological risk of atmospheric

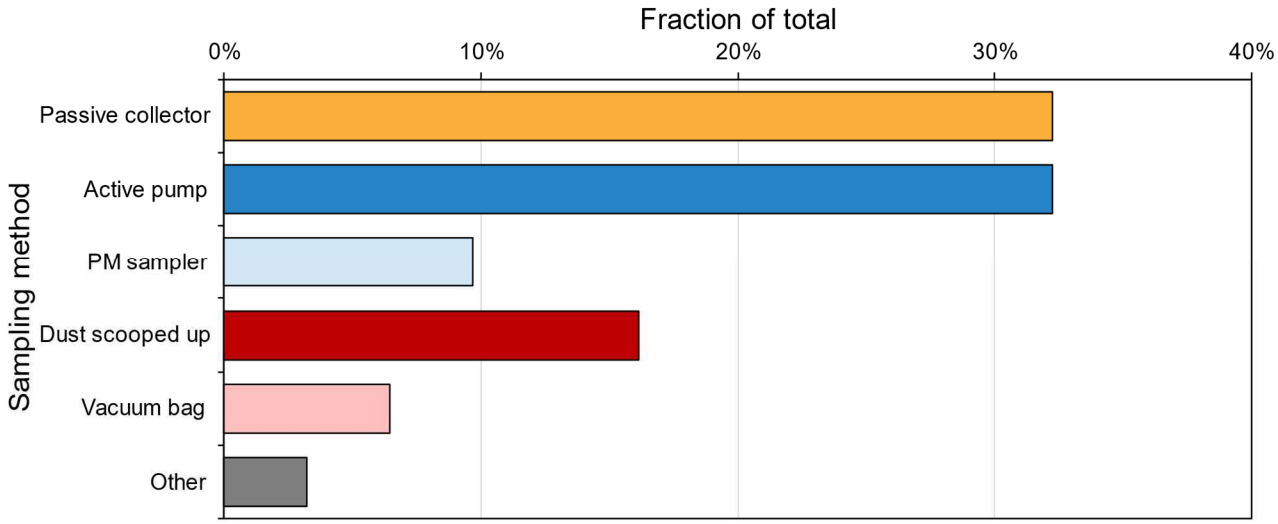

FIGURE 4: DISTRIBUTION OF TARGETED SAMPLE TYPES AMONG STUDIES FOUND ON MICROPLASTICS IN THE ATMOSPHERIC COMPARTMENT (N=26 STUDIES).

microplastics. A second way to assess microplastic contamination in the atmospheric compartment is to collect deposited particles such as atmospheric deposition and settled street dust. These studies are a means to indirectly assess atmospheric microplastic contamination and evaluate the role of the atmosphere in microplastic transfer over short or long distances.

Suspended particles are obtained by actively pumping and filtering the air from a given environment. In studies sampling air, the volume of filtered air is necessary to calculate the microplastic concentration. To estimate this volume, the filtering speed of the sample is necessary, along with the sampling time. Sampled volumes are highly varying, from a few cubic meters sampled in 1 hour, to several thousand over 45 hours. Sampling larger volumes of air allows for a better averaging of the microplastic concentration. However, it also requires to characterize a higher number of particles and prevents from assessing small variations.

In three studies, specialized particulate matter samplers typically used to assess air quality for suspended matter smaller than 2.5 µm or 10 µm were used (Abbasi et al., 2019; Akhbarizadeh et al., 2020; Prata et al., 2020). Such sampler heads have long been used to assess air quality and human inhalation of particulate matter (Davidson et al., 2005). Actively sampling air in order to collect suspended atmospheric microplastics poses several major challenges. Firstly, depending on the targeted size, suspended atmospheric microplastic abundances are in the orders of 1 – 10 MP m^{-3} of air. As a result, a volume of air in the order of the cubic meter, or dozens of cubic meters needs to be collected for each sample in order to obtain a sufficiently high number of particles. Additionally, most studies, in any sampling matrix including air, appear to measure a higher concentration of smaller microplastics than of larger particles. Consequently, the larger the particles being measured, the higher air volume to filter for a representative sample.

In addition to the need to collect a high volume of air, an uncertainty remains as to whether the collected air passes through the pump only once. In studies focused on outdoor air, a strategy can be to orient the sampling system according to the prevailing wind, and to filter air sufficiently slowly so as to avoid turbulences.

Two major sampling strategies emerge from the literature to collect microplastic atmospheric deposition samples. The first consists in conducting atmospheric deposition monitoring campaigns. In particular, 10 studies used a passive bulk atmospheric deposition collector to that avail. Such passive samplers consist in a collecting surface, typically a funnel of a certain geometry and surface area, collecting settling atmospheric dust. In a bulk atmospheric deposition collector, rain and dry settling dust are indiscriminately collected, and pooled

together as one sampler. However, some atmospheric pollution studies separate dry atmospheric deposition from rain by preventing particles from settling during rain events. Separated dry and wet atmospheric deposition can then be compared and summed into what is considered total atmospheric deposition.

The geometric characteristics of atmospheric deposition samplers vary greatly between studies. Some studies use square collectors, others use circular funnels. The surface area also varies from one study to another. For instance, in their founding studies, (Dris et al., 2015, 2016a), Dris *et al.* used a passive bulk atmospheric deposition collector. The sampler consisted in a square metallic funnel with a total surface area of 0.3 m², connected to a 10L-collection bottle. In multiple other studies, the sampler is smaller and closer to 0.0314 m^2 (Allen et al., 2019; Klein et al., 2023). It is likely a decision made for practical reasons, such as a widely available commercial sampling device (NILU, n.d.). Using a smaller surface area has benefits regarding the cost and transportability of a system. However, it also constrains the sampling period, as less particles will deposit on a smaller surface and the sampling period needs in turn to be increased.

This high degree of variability between sampling methods in studies represents an issue for the comparability of results. It is likely that the geometry of a sampler directly affects atmospheric deposition rates.

Another major characteristic of passive atmospheric deposition monitoring is that the sampling necessarily occurs over time. Monitoring campaigns are typically continuous, and last from a few months to a full year. Each sample must be collected over a sufficiently long period to contain a quantifiable number of microplastics. This means the sampling period of a monitoring campaign is selected based on the expected microplastic deposition rates in the area, as well as the dimensions of the atmospheric deposition collector. In the literature, samples were collected at frequencies ranging from twice a week (Wright et al., 2020; Zhang et al., 2020) to once a month (Cai et al., 2017a; Stanton et al., 2019). In several studies, the sampling frequency varied with the precipitation intensity for technical reasons such as meteorological constraints or the difficulty to access the sampler (Allen et al., 2019; Dris et al., 2016b, 2015).

In addition, the variability in sampling time periods means meteorological events affect results differently from study to study. The effects of individual rain event or small-scale changes in meteorological parameters such as wind speed or direction cannot be assessed with monthly sampling. Similarly, the effects of small-scale changes in human activity, such as daily traffic or weekday-weekend requires adapted methodology. In one study by Zhang *et al.* (Zhang et al.,

2020), indoor deposition was collected over 24h periods in two sites, on Tuesdays and Saturdays. This allowed the researchers to directly measure a difference between week-day samples and weekend samples, as well as a difference between a home environment and a workplace.

In some studies, microplastic atmospheric deposition is evaluated using a different form of passive sampler: instead of a funnel regularly washed, particles are collected by a large dish filled with a layer of water (Song et al., 2020). There is no consensus on whether such samplers are better than bulk atmospheric deposition collectors. Water-mirror samplers prevent the remobilization of settled particles. This allows to quantify the entirety of microplastics that deposit on the sampler, but is less representative of the transfer of microplastics from the atmospheric compartment to the ground.

The other major method to indirectly sample atmospheric microplastics consists in dust collection (Abbasi et al., 2019; Dehghani et al., 2017; Dris et al., 2017; C. Liu et al., 2019a). In such sampling campaigns, the temporal aspect of atmospheric deposition is harder to measure. A qualitative description of the deposited microplastics is however entirely possible. In these studies, a well-measured area of floor or road dust is swept with an anti-static brush and a metallic pan (Abbasi et al., 2019; Dehghani et al., 2017). The content of vacuum bag content can also be collected as a proxy for indoor air deposition (Dris et al., 2017; C. Liu et al., 2019a).

Finally, one study was focused on atmospheric deposition of microplastics as a form of contamination for other samples (Song et al., 2020). In that work, deposition samples were collected by leaving dust to settle on laboratory glassware.

4.2.2 Sampling the atmosphere – recommendations

The atmospheric compartment is a variable environment, determined by a number of meteorological parameters. Because of this high degree of variability, it is impossible to fully reproduce samples from different times or environments.

In order to improve the comparability of future atmospheric studies, the monitoring of meteorological conditions that may affect microplastic transport in the atmosphere appears crucial. In this preliminary review, only 4 studies specifically mentioned that the meteorological conditions were followed during sampling (Allen et al., 2019; Dris et al., 2015, 2016b; K. Liu et al., 2019b). For these authors, the precipitation rates were measured nearby the sampling sites either by independent organizations or by the authors. However, in addition, several other studies mentioned that the volume of atmospheric deposition varied based on the precipitations.

In studies focused on atmospheric deposition, passive sampling is typically conducted over several days to ensure a sufficient number of particles. However, this limits the capacity of studies to assess the effects of parameters that act on small temporal scales. Further discussions in that regard will be provided on chapter 2 of this manuscript.

The study of microplastic in the atmospheric compartment is subject to similar issues as the study of other atmospheric contaminants, some of which have been studied for longer. To address some of these challenges, future studies should be conducted in collaboration with atmospheric scientists dedicated to other pollutions.

4.2.3 Sampling the atmosphere – strategy chosen for this PhD

In this PhD, the atmospheric compartment is not considered as a microplastic reservoir but as a potentially major secondary source of microplastics and a vector for microplastic transport to other environments. As a result, the objectives are not to assess microplastic concentrations in the atmospheric compartment, but rather to assess the microplastic flux from the atmospheric compartment to the surface and how this flux may vary depending on the level and type of surrounding human activity. Passive monitoring was therefore the sampling method chosen for this work. ***While this sampling method does not allow to assess the influence of small-scale factors, it allows to estimate an average deposition flux***.

Bulk atmospheric deposition monitoring campaigns were carried out between April 2020 and December 2022 at four different sites: two sites dominated by agriculture and two urban environments. As the nature of each of these campaigns is directly related to the nature of the sampling sites, the details of the sampling procedures are further discussed in the dedicated chapter.

4.3 Sampling solid matrices

4.3.1 Sampling solid matrices – literature insight

Similar to the atmospheric compartment, the study of microplastic contamination in soil environments is recent in the domain of microplastic studies. The first mention of the potential presence of microplastics in soils was in 2012 by M. Rillig (Rillig, 2012). However, this first publication was an opinion paper, and microplastics were not quantified in soils. On the contrary, the author notes that soil matrices are a complex that is significantly harder to collect and extract microplastics from than water.

The first study that actually collected soil samples and quantified their microplastic content was published in 2005 (Zubris and Richards, 2005). However, that initial work did not lead to an increase in scientific focus. Interest in microplastic contamination in soils started again in 2017 (*Microplastic in Danish wastewater*, 2017), and exploded in 2018 with multiple studies published in the same year (Liu et al., 2018; Piehl et al., 2018; Zhang and Liu, 2018; Zhou et al., 2018). In two of these first studies, the targeted samples were agricultural soil (Liu et al., 2018; Zhou et al., 2018). In another, beach soils from different coastal environments were targeted and collected (Zhang and Liu, 2018).

After these founding studies, the topic of microplastics contamination in soil environments progressively gained traction, with the number of published documents increasing rapidly. A literature search was conducted in December 2023 using the Web of Science search engine with the following query:

TI =((microplastic OR microplastics) AND ~soil) OR AK =((microplastic OR microplastics) AND ~soil)

This survey was aimed at retrieving all studies dedicated to the topic of microplastics in soil environments, and identified a total of **995** published papers, **165** of which were review papers. However, it seems that in the majority of these studies, environmental samples are not collected.

In 2021, a review by Yang *et al.* only identified **29** published papers dedicated to the quantification of microplastic in soils (Ling Yang et al., 2021). The objective of this work is not to conduct an extensive review of the literature on soils but rather to provide an insight of the methodological practices and the choices of this PhD in regards to the literature practices. As a result, only a fraction of these studies is fully detailed here.

Soil is a matrix rich in particles and marked by a high degree of heterogeneity. In some studies, microplastic concentrations vary greatly even in similar samples of the same site (Chen et al., 2024; Ling Yang et al., 2021). This spatial heterogeneity may be a subject worth investigating as itself. However, the objective of the majority of studies published on microplastics in soils seems to be the quantification of the microplastic concentrations in different sites, and the comparison of these concentrations between sites (Corradini et al., 2019; J. Li et al., 2023; Zhang and Liu, 2018; Zhou et al., 2018). Thus, there is a need to produce representative soil samples.

To that avail, studies typically collect several subsamples at randomized locations in a given site, and mix these subsamples together into one larger sample. The resulting samples reach masses of 500 g to 4 kg and is variable from study to study.

Table 1 summarizes the strategies selected in the first studies conducted and in several more recent studies. The level of details provided varies from study to study, and is often lacking in clarity.

Unfortunately, a consequence of collecting large masses for a sample is that it often is impossible to analyse the entirety of the sample. Thus, the heterogeneity problem arises again. As shown on

Table 1, in all studies, a small fraction of the collected sample is treated and analysed. The pre-selection of this small fraction can be conducted by combining multiple subsamples. It remains a source of heterogeneity in the sample that is often unassessed.

Several studies describe the vertical distribution of microplastic across soils. In two of the first 2018 studies on the topic, a separation was made between surface and deeper soils (Liu et al., 2018; Zhang and Liu, 2018). However, the sampled depths are highly variables between studies, ranging from the 2 cm of top soil (Zhou et al., 2018) to a complete 60 cm soil profile (J. Li et al., 2023; Wahl et al., 2024). This variability can be expected, as the depth of the soil is a parameter highly site-dependent. In addition, the depth at which samples are collected is expected to be determined by the objectives of a study.

TABLE 1: DESCRIPTION OF SOIL SAMPLING STRATEGY IN A FEW SELECTED ARTICLES

Location	Sampling strategy	Sample depth	Sampled mass (g)	Treated mass (g)	Treated/sampled mass ratio	Source
Bohai Sea and Yellow Sea	Multipoint mixed sampling	0-2 cm	4,000	---	---	(Zhou et al., 2018)
Dian lake, Southwest china	6 subsamples collected and mixed for each sample	0-5 cm; 5-10 cm	400	30	7.5%	(Zhang and Liu, 2018)
Shanghai China	Undescribed, triplicates	0-3 cm; 3-6 cm	1,000	50	5%	(Liu et al., 2018)
Mellipilla county, Chile	Undescribed, randomly selected on sites	0-25 cm	500	5	1%	(Corradini et al., 2019)
Spain	Manual collection with hand shovel	0-5 cm; 5-10 cm; 10-15 cm	50-100; 500	75	~100%; 15%	(Schell et al., 2022)
Shandong province, China	5 subsamples collected and mixed for each sample	0-10 cm; 10-20 cm; 20-30 cm	2,000	50	2.5%	(J. Zhang et al., 2023)
Shouguang, China	5 subsamples collected and mixed for each sample	0-20 cm; 20-40 cm; 40-60 cm	2,000	50	2.5%	(J. Li et al., 2023)
Ontario, Canada	*undescribed*	---	50; 750; 2,500	150	100%; 20%; 6%	(Chen et al., 2024)
Central France	8 subsamples collected and mixed for each sample	5 cm sections for 0-60 cm	--	---	---	(Wahl et al., 2024)

4.3.2 Sampling solid matrices – recommendations

In light of this preliminary insight on the literature, two recommendations can be made for further studies.

The study of microplastics in soil environments is a very new domain. As a result, methodologies are still highly variable, and likely not optimized yet. While the standardization of sampling practices is not expected, authors should provide as detailed information on their practices as possible, in order for subsequent studies to either imitate or improve on existing practices rather than develop entirely new sampling methods. If such details take too much space to be provided directly on the papers, they should be properly explained on the supplementary materials of the studies.

Additionally, the topic of the representativity of samples should probably be tackled with more details in future studies. In order to obtain representative samples of large soil sections, authors homogenise several subsamples randomly selected, similar to practices that were first developed in pedology. However, because of this sampling method, only a small fraction of a sample is typically treated and analysed.

In order to better assess the heterogeneity in a sample or across samples in a sampling site, the ideal practice should be to collect multiple duplicates of samples and subsamples, and directly treat each sample as a statistical population. However, such a practice would likely increase the total analytical time by an order of magnitude, and thus reduce the total number of samples that can be analysed.

4.3.3 Sampling solid matrices – strategy chosen for this PhD

In this work, the primary objective is to assess the vertical migration of microplastics into soils. This requires not only the collection of samples at several different depths, but also to preserve the structural integrity of the soil layers. In order to ensure this, the sampling strategy that was selected was manual coring. A 5 cm diameter hand drill was used to collect cores at a depth of down to 35 cm. After each core was collected, it was separated into 4 subsamples by depth. Samples were not mixed either by depth or by core, in order to retain both the spatial heterogeneity of the samples, and the structural relation between the surface and the deeper soil of each core sample.

As the precise details of the sampling strategy are directly related to the characteristics of the sampling site and the objectives of the work, further information is provided on chapter 3.

4.4 Sampling strategies selected

As a continuation to the end of the section 3: Targeted particles – complex and changing definitions, Figure 5 summarizes the main sampling strategies selected for the following chapters of this PhD. The atmospheric compartment was targeted indirectly. Passive collectors were used to monitor bulk atmospheric deposition over periods ranging from 4 to 12 months in 4 distinct sites. In order to assess microplastics and TRWP infiltration in the soils of a roadside biofiltration swale, a hand drill was used to manually collect cores, which were separated into subsamples by depth.

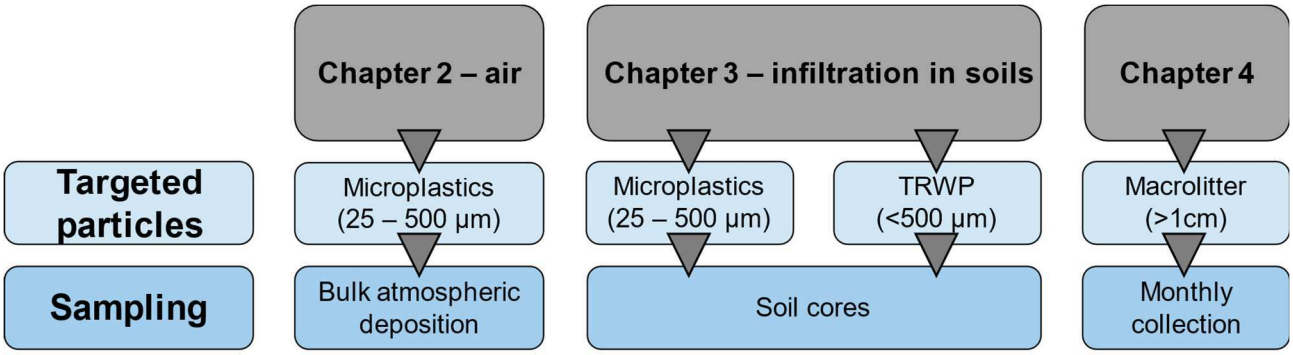

FIGURE 5: SUMMARY OF THE SAMPLING PRACTICES SELECTED FOR THIS PHD

5 Concentration treatment of microplastics

5.1 Introduction – necessity of a laboratory treatment

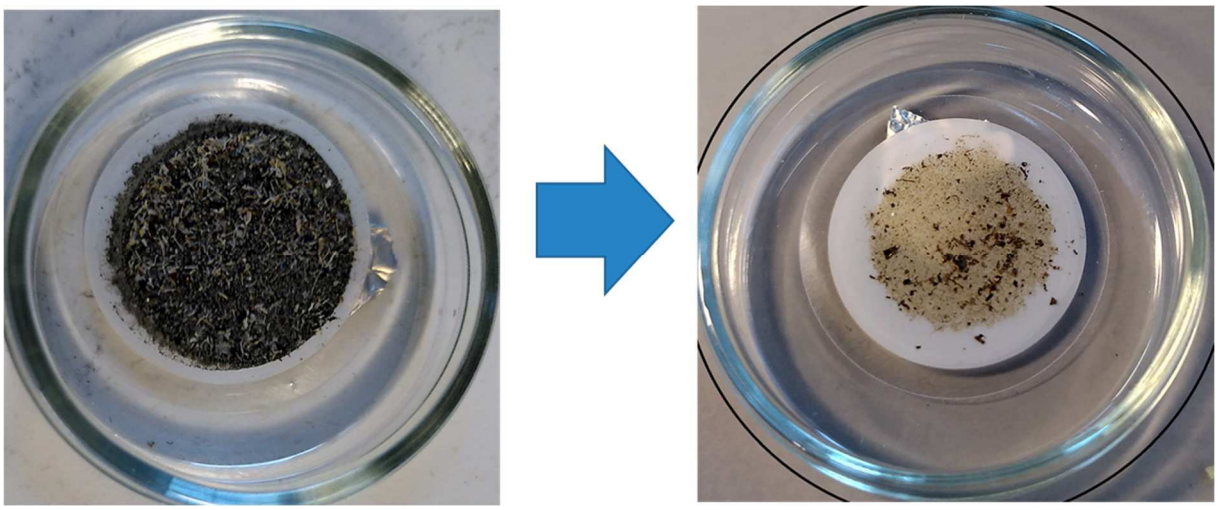

FIGURE 6: COMPARISON BETWEEN AN UNTREATED AND TREATED SAMPLE AFTER DEPOSITION ONTO AN ALUMINE FILTER

While microplastics are ubiquitous in the environment, the microplastic content of any sample is low in regard to the rest of its matrix. Even studies that reported particularly high microplastic abundances and concentrations reach concentrations lower than 1‰ in mass (Dierkes et al., 2019). In number of particles, this fraction is even lower.

Because of this relatively low concentration, the removal of the mineral and organic particles that compose an environmental sample matrix are necessary for chemical analyses to be conducted. While a preliminary treatment may not be necessary for some situations, for instance in a non-quantitative study, characterization methods based on spectroscopy require such a treatment: any chemical identification of a sample may be undermined by organic or mineral particles present in the sample. Figure 6 shows, as an example, an untreated sample deposited on a filter.

An environmental sample is composed of an array of particles, including organic debris, mineral particles, and fluids. The nature, distribution, and concentration of these particles is highly variable and depends on the targeted matrix. For example, a soil or sediment sample contains a significantly higher mass of minerals than a bulk atmospheric deposition sample. This composition can also vary over time and be affected by external factors. A bulk atmospheric deposition sample collected in spring contains a high fraction of pollens, while a sample collected in winter contains more black carbon particles formed from combustion.

The selection of a preliminary treatment is constrained by several partially contradictory factors, as shown in Figure 7. These factors are as follow:

- The treatment must isolate microplastics efficiently from the matrix so that the analysis can be conducted.
- The treatment must not remove or damage the microplastics, as this would impede on the quantification.
- The treatment needs to limit the contamination of the samples with external microplastics.
- The process must be time-efficient enough to allow for the analysis of a significant number of samples.
- The treatment should be standardized enough to allow for the comparison between samples. Ideally, the treatment process should be comparable to that of other studies found in the literature. However, in the current state of microplastic research, very few studies are fully comparable to one another. At the very least, the selected protocol must remain the same throughout the campaign. As the composition of the sample's matrix can vary a lot from sample to sample, this requires the selection of a broad-spectrum treatment process.

Sample treatment can be divided into two major categories. First, the removal of organic matter from the matrix which relies on the relative resistance of plastic materials to chemical treatment. Specific reagents such as enzymes, diluted acids or oxidizers are used to dissolve or eliminate organic matter without damaging microplastics. Secondly, treatment steps aimed at removing the mineral matter from the sample rely on the lower density of plastic materials when compared to minerals.

The following subsections aim at presenting the microplastic treatment processes, respectively organic chemical treatments and density-based mineral separation treatments used in the literature to isolate microplastics from air and soil samples. The practices selected to prepare samples in this PhD are detailed and justified in regards to the literature. Finally, the differences in practices between the two main matrices studied in this PhD, namely deposited atmospheric particles and soil substrate, are discussed.

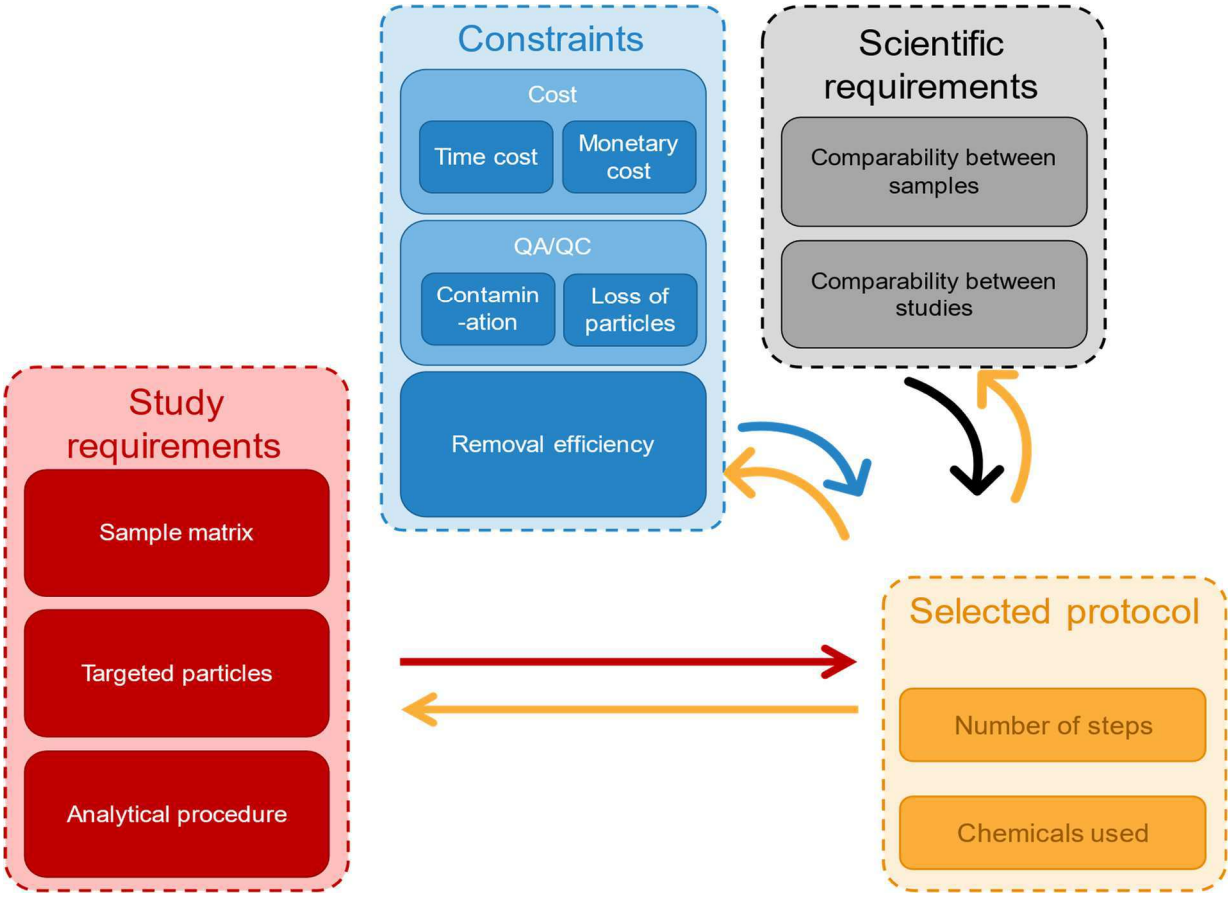

Figure 7: factors affecting the selection of a treatment protocol

5.2 Chemical dissolution of organic matter

5.2.1 Chemical treatment – literature insight

In most environmental samples, a large fraction of the matrix consists in dead plant matter, algae, and other biological materials. This organic matter represents a limit to microplastic identification in numerous ways. First, some organic debris may have a similar aspect as microplastics, and may be misidentified as plastics in visual-based analyses. Secondly, as will be detailed later, the dominant microplastic identification strategies are based on infrared

spectroscopy. Organic materials absorb IR light in a similar way as microplastics, and thus can hide or falsify spectroscopic analyses. Figure 8 highlights this similarity: the infrared spectra of polyethylene and polyamide 6-6 are compared to that of a common protein and cellulose, which is a very common composition of organic material found in samples. Both organic materials present multiple absorption bands at 3,800 – 2,800 cm^{-1} and 1,800 – 1,200 cm^{-1}, which are susceptible to hide the absorption bands of polymers and prevent their identification.

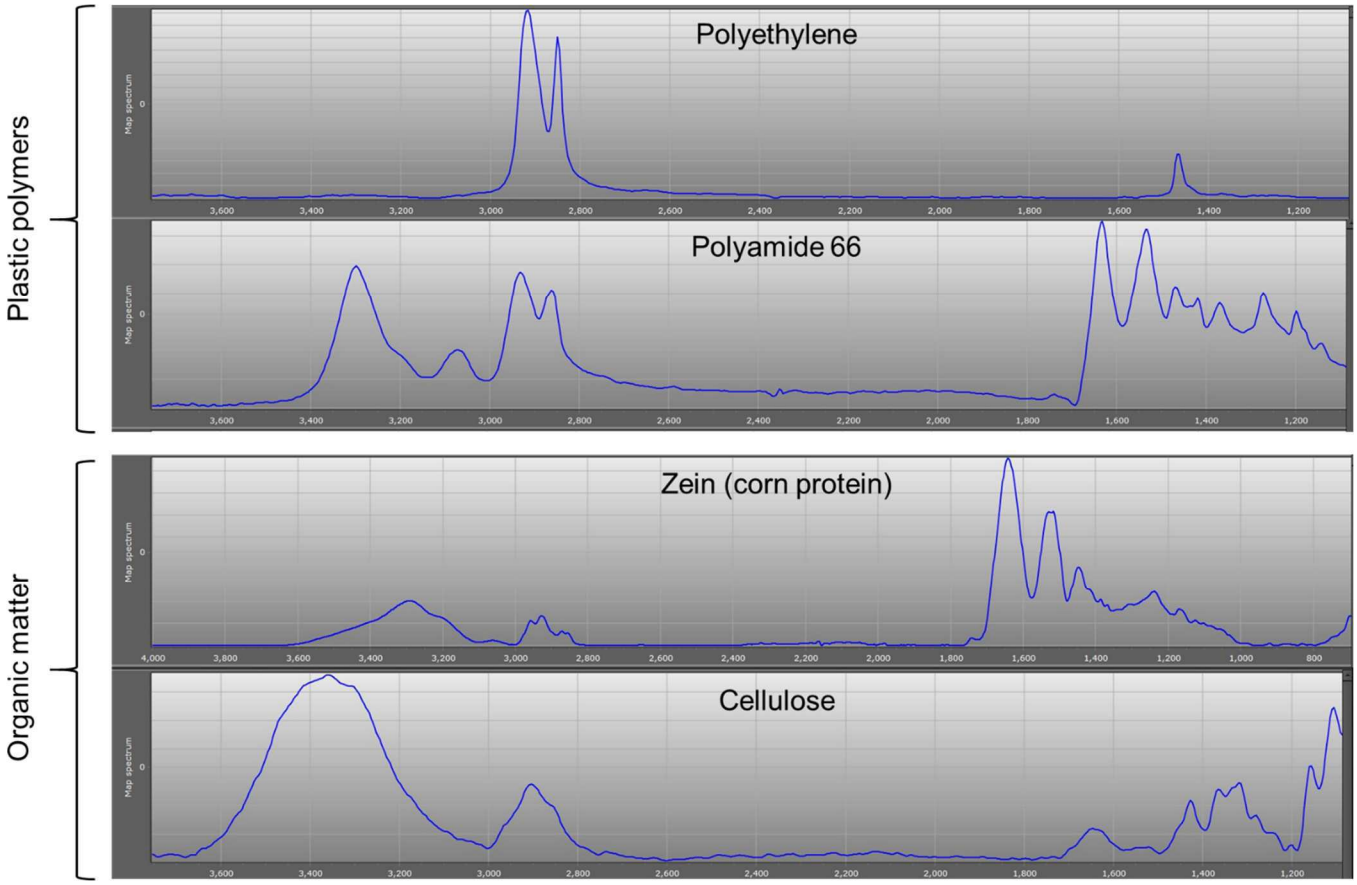

FIGURE 8: EXAMPLE OF IR SPECTRA OF KEY POLYMERS AND ORGANIC MATERIALS THAT DISPLAY ABSORPTION PEAKS SUSCEPTIBLE TO PREVENT THE DETECTION OF PLASTICS

The majority of treatment practices aimed at separating microplastics from the organic fraction of their matrix rely on differences in chemical reactivity between the two classes of particles to selectively remove organic matter while sparing the plastics. Indeed, microplastics, in particular the synthetic polymers that constitutes their structure, can resist to oxidative, acidic or alkaline treatments that remove the majority of organic debris.

Several factors are considered to determine an appropriate removal protocol, in an example of a multi-factorial optimization problem. Firstly, the treatment must be efficient at removing the organic matrix of the sample. Secondly, it must not alter the targeted particles. Finally, the

treatment must be cost-effective and time-effective enough that a high number of samples can be collected and prepared for analysis. For example, while a high-temperature treatment with a concentrated strong acid would efficiently remove the majority of organic matter in a matter of hours, it would also significantly damage the microplastic content of the samples, thus making it inappropriate for quantitative analyses.

A wide array of processes exists in the literature to isolate microplastics from natural organic debris. A summary of these processes and their effects is provided on Table 2, inspired from two studies that compared the effects of multiple treatment strategies (Hurley et al., 2018; Treilles et al., 2020). A first category of processes relies on the use of enzymes such as cellulase, lipase and protease (Chen et al., 2024; Hidalgo-Ruz et al., 2012; Löder et al., 2017). These enzymatic treatments present several benefits. Enzymes are non-toxic, highly specific to their target molecules and present no risk of altering the microplastic in the sample. In addition, as they are catalysers, low concentrations are required which facilitates the management of waste liquids. However, they are costly, and often require several successive steps. As mentioned at the beginning of the section, a higher number of steps used to prepare samples increases the risk of contamination or loss of particles.

TABLE 2: SUMMARIZED REPRESENTATION OF THE IMPACT OF THE MAJOR TYPES OF ORGANIC REMOVAL TREATMENTS

Type of treatment	Temperature	Removal efficiency	Damage to microplastics	Toxicity	Environmental concern	Cost
Enzymatic		++	-	-	-	+++
Acidic	*High T*	+++	++	++	+	+
	Low T	++	+	+	+	+
Alkaline	*High T*	+++	++	++	+	+
	Low T	++	+	+	+	+
Oxidative	*High T*	+++	+	++	+	+
	Low T	++	-	+	+	+
Fenton		++	-	+	+	++

A second category of treatments rely on the use of strong acid such as chlorohydric or sulfuric acid, or strong bases such as sodium or potassium hydroxide to remove organics. These processes are less costly than enzymes, and can be accelerated by increasing the reaction temperature. However, strong acids and bases are significantly more toxic than enzymes, especially at a high temperature, and raise environmental concerns. They require laboratory organization, the use of protective equipment, and adapted waste management. In addition, recent studies increasingly suggest that the use of acids or bases at high temperatures is

susceptible to alter the microplastics in the samples. In particular, (Hurley et al., 2018) suggests that Polyamide 6-6 (PA66), Polycarbonate (PC) and Poly Ethylene Terephthalate (PET) are susceptible to degradation by NaOH, KOH, especially at temperatures >60 °C. In a 2020 study comparing the effect of an array of treatment protocols on microfibres, Treilles *et al.* found that high temperature KOH treatment was degrading PET fibres, while lower temperature did not (Treilles et al., 2020).

Finally, an array of treatments is based on the use of strong oxidants to dissolve organic debris. In particular, hydrogen peroxide (H_2O_2) is frequently used in the microplastic community, at varying concentrations and temperatures. Similar to acidic and alkaline treatments, oxidative removal of organic matter presents environmental concerns and necessitates specialized waste management and protective equipment. In addition, when conducted at temperatures of 60 or 70°C, oxidative treatments also appear to damage the integrity of some polymers (Hurley et al., 2018). However, it is possible to conduct these treatments at a sufficiently low temperature not to alter the microplastics. It seems that the use of strong oxidants is increasingly common in the literature. For instance, in a 2024 book chapter focused on the methodology used for microplastics collection, treatment and identification for microplastics in river environments, 53% of all studies used H_2O_2 for the preparation of samples.

The Fenton reagent is an emerging treatment strategy among the oxidative treatment methods used in the literature. It is an advanced oxidation process, an aqueous phase oxidation method that relies on the use of highly reactive oxidizers such as hydroxyl radicals (HO•) to destroy the target organic matter (Sirés et al., 2014). Advanced oxidation processes are often used to remove organic pollutants from wastewater (Deng and Englehardt, 2006; Lin and Lo, 1997). They are non-selective, and are capable of completely mineralizing a wide array of organic pollutants. The Fenton reaction in particular is an advanced oxidation process first described in 1934 (Haber et al., 1934). It consists in a catalytic decomposition of hydrogen peroxide H_2O_2 into hydroxyl radicals HO• and HO_2• by iron II. The iron is typically introduced in the form of iron sulfate salts $FeSO_4$. The following equations sum up the reaction:

$$\mathbf{Fe^{2+} + H_2O_2 = Fe^{3+} + HO^- + HO\bullet}$$

$$\mathbf{Fe^{3+} + H_2O_2 = Fe^{2+} + H^+ + HO_2\bullet}$$

The net equation of the catalysed reaction is represented as follows:

$$\mathbf{2\ H_2O_2 = HO\bullet + HO_2\bullet + H_2O}$$

This catalysed reaction works most efficiently in acidic conditions, with an optimum at pH = 3.0 (Babuponnusami and Muthukumar, 2014). Above that pH, ferric iron forms precipitates with hydroxides ions ($Fe(OH)_3$) that are harder to reduce back to ferrous ions (Boonrattanakij et al., 2011; Grundl and Delwiche, 1993).

The Fenton process is applied to microplastic isolation treatment in several studies. The first use of the process is mentioned in an early review by Hidalgo-Ruz *et al.* (Hidalgo-Ruz et al., 2012), where it is called Wet Peroxide Oxidation. It was more recently suggested as a potentially viable microplastic organics removal treatment (Free et al., 2014; Masura et al., 2015). Finally, three recent studies conducted comparison of the use of the Fenton reagent to other oxidative and acidic treatment processes. While high-temperature oxidative treatments and acidic treatments damage some specific polymers, the Fenton doesn't (Hurley et al., 2018; S. Tagg et al., 2017; Treilles et al., 2020).

5.2.2 Chemical treatment – recommendations

Chemical treatments to dissolve the organic matter are necessary for the concentration of microplastics in samples. These treatments present clear limitations and their optimization is challenging. As mentioned above, relevant chemicals must be used to ensure not to damage the microplastics. In that regard, enzyme-based treatments are the safest available process (Löder et al., 2017). However, the treatment must also be fast and efficient enough to enable the quantification of microplastics. Enzyme-based treatments require multiple step, which each increase the overall length of the preparation of samples and the risk of contamination or loss of particles. These concerns are often as central to the selection of an adapted protocol as the risk of damaging microplastics, which can also be avoided with most other treatments available.

In regards to these limitations, it is necessary for studies to assess the efficiency of their treatment overall. Laboratory blanks and recovery tests are required, and should be clarified with as much detail as possible in published studies. More details regarding this necessity are provided in the QA/QC section of this chapter (section 7).

As of yet, the chemical processes used to remove organics from samples are not standardized in the microplastics research community. It is unlikely that a complete standardization of these processes will occur soon, as the type of treatment used is highly dependent on the targeted matrix.

5.2.3 Chemical treatment – strategy selected

Two forms of oxidative treatments were selected and used over the course of this PhD. In the first 3 atmospheric deposition sampling campaigns, samples were treated using the Fenton treatment.

The Fenton treatment used in this PhD was an adapted protocol from an earlier study conducted in the laboratory (Treilles et al., 2020). In that study, the authors used two solutions. A 30% vol/vol H_2O_2 solution was used in combination with a 20 g L^{-1}, or 0.07 mol L^{-1} iron (II) sulfate heptahydrate ($FeSO_4$, 7 H_2O). The study showed microplastics were unaffected by the treatment.

In the preliminary tests, the formation of iron precipitate was an issue frequently encountered. This deposit cannot be removed easily by subsequent treatment steps, and appeared to coat microplastics, preventing their identification. In order to avoid this, the iron catalyst concentration was decreased, and the process was carried out in highly acidic conditions (pH 1-2). Two stock solutions were created. The Fenton reagent stock solution contained iron (II) sulfate heptahydrate at a concentration of 0.1 mol/L. 6 mL of concentrated sulfuric acid was added for every 500 mL of Fenton Reagent solution, which turned the solution acidic (pH 1-2). After mixing, this solution was vacuum-filtered through a GF/D filter and stored in the dark. A hydrogen peroxide stock solution was also created by diluting a 50% vol/vol H_2O_2 solution with water to obtain a 30% vol/vol solution. This H_2O_2 solution was also vacuum-filtered through a GF/D filter, and stored in a refrigerator between uses. During the oxidative treatment, each mother solution was poured in a beaker containing the resuspended sample, and completed with GF/D-filtered water to reach a total volume of 200 mL. The resulting solution had an iron sulfate concentration of 0.05 mol/L and a hydrogen peroxide concentration of 1.5% vol/vol. The solution was kept around 30 °C for 6 hours of reaction.

The Fenton treatment worked to remove organic debris from samples, and did not appear to alter microplastics. However, it was not deemed a clear improvement from peroxide hydrogen treatments. The improvement in the amount of organic matter removal was not clear for atmospheric deposition samples, and the reduced treatment time was counterbalanced by the necessity to remain in proximity to samples at all time, which represent a net loss of time.

Consequently, both the subsequent atmospheric deposition monitoring campaigns and the soil sampling campaign of this PhD did not apply the Fenton treatment. Instead, a hydrogen peroxide treatment was applied using the following protocol. In all treatments, samples were

suspended in a 100 mL solution with a 30% vol/vol H_2O_2 content. The solution was left to agitate with a magnetic stirrer for 24h, while maintained at a temperature of 30 °C.

5.3 Density-based separation of minerals

5.3.1 Introduction

Just as organic particles, the mineral fraction of a sample matrix is a direct hindrance to microplastic identification. Minerals are often opaque to spectroscopic analysis, and can directly hide microplastics. In addition, some mineral debris can have a similar appearance to microplastics, and be misidentified in visual-based analyses.

However, unlike organic particles, minerals are typically highly resistant to dissolution via chemical treatment. Therefore, as mentioned at the beginning of this section, protocols aiming at the isolation of microplastics from the mineral fraction of the matrix typically rely on a difference in density between minerals and microplastic particles. Figure 9 represents the density ranges of an array of polymers, as well as major minerals, which shows that the majority of plastic polymers are less dense than minerals. In a density-based microplastics isolation treatment, samples are mixed in a liquid of a density comprised between that of the majority of plastics and that of minerals, and left to settle. Once all particles have settled, the supernatant can be collected and filtered, while the sunken particles are left.

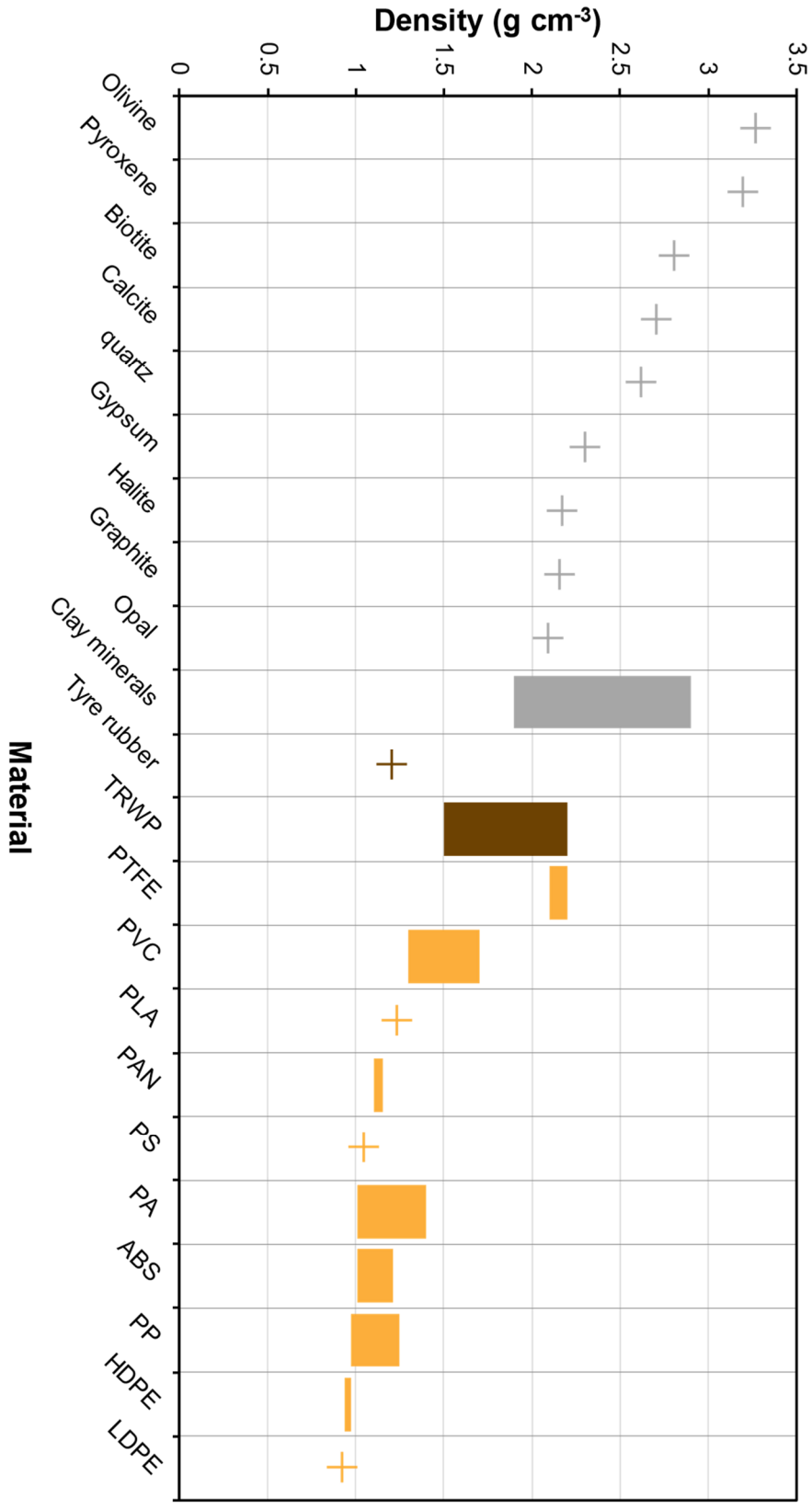

FIGURE 9: DIFFERENCES IN THE RANGES OF DENSITY BETWEEN DIFFERENT PLASTIC POLYMERS, MINERALS, AND CONCENTRATED MINERAL SALT SOLUTIONS

5.3.2 Selection of a density liquid

While the principle behind this treatment is straightforward, several of its technical aspects are more complex in practice than they first appear. In particular, the selection of an adapted density liquid is not evident. In order to be adapted to a density separation, the selected solution must be relatively chemically inert, has an easy to control density, and comes at a sufficiently low cost and environmental concern to be handled in a laboratory.

In early microplastic studies, saturated sodium chloride (NaCl) solutions were used to that avail (Hidalgo-Ruz et al., 2012), reaching a density of 1.2 g cm^{-3}. NaCl solutions were used to isolate microplastics from marine sediments in the founding paper by Thompson, which likely led to the ulterior reproduction of that method (Thompson et al., 2004). Additionally, NaCl solutions are the cheapest option available and their use has no environmental consequence.

As shown on Figure 9, a density of 1.2 g cm^{-3} is above that of many of the most commonly produced polymers, including PE, PP, PS However, denser polymers like PVC or fluorinated polymers are not separated from minerals. In particular, some fluorinated polymers such as PTFE can reach densities above that of some clay minerals. Additionally, while pristine tyre rubber has a density of 1.2 g cm^{-3} (U.S. Tire Manufacturers Association, 2020), TRWP are composite particles and contain a significant fraction of mineral, meaning their density are variable and can be above 2 g cm^{-3} (Spanheimer and Katrakova-Krüger, 2022).

As a result, in more recent studies, other forms of mineral salt solutions are used, so as to reach higher densities. In the majority of studies conducting such treatment, density ranges of 1.4 to 1.8 g cm^{-3} are used. This ensures the removal of minerals, and the retrieval of the majority of polymers. Examples of widely used density solutions are represented Table 3, and include saturated Sodium Chloride (NaCl), Sodium Iodide (NaI), Zinc Chloride ($ZnCl_2$), and Polytungstate ($Na_6[H_2W_{12}O_{40}]$).

Currently, no density liquid appears to have reached a clear dominant position in the literature. All solutions widely used in the literature present clear limits that remain to be addressed. In practice, NaI and $ZnCl_2$ can reach high densities, but they are not chemically inert. In NaI solutions, Iodide I^- is part of the I_2/I^- redox couple, which has a redox potential of 0.536 V. This means it can react with trace oxidants present in the reaction material. In particular, it can react with hydrogen peroxide H_2O_2 if some remains after the organic removal treatment of the sample. Similarly, aqueous $ZnCl_2$ is highly reactive with aluminium and oxidants. In addition

to the chemical reactivity of these density liquids, both represent environmental hazards, and require specialized waste management procedures.

Density liquids based on sodium polytungstate ($Na_6[H_2W_{12}O_{40}]$) are significantly easier to handle in a laboratory environment. They are chemically inert, non-toxic, and present little to no environmental concern. However, sodium polytungstate is much more expensive to acquire than other mineral salts.

TABLE 3: COMPARATIVE DESCRIPTION OF THE MAJOR DENSITY SOLUTIONS USED IN THE LITERATURE. THE COST ESTIMATE MAY VARY BETWEEN REGIONS, AND WAS ASSESSED IN FRANCE.

Salt used	Formula	saturation density (g cm^{-3})	chemical reactivity	toxicity	environmental concern	cost
Sodium Chloride	NaCl	1.2	-	-	-	-
Sodium Iodide	NaI	1.9	+	+	++	+
Zinc Chloride	$ZnCl_2$	2.1	++	++	++	+
Sodium polytungstate	$Na_6[H_2W_{12}O_{40}]$	3.1	-	-	-	+++

5.3.3 Selection of the appropriate glassware and laboratory protocol

In addition to the need for an adequate density liquid, the efficiency of density-based microplastic separation protocols is limited by the procedure and the materials used. While exact details of the material used are rarely disclosed in the literature, several types of laboratory glassware can be used for this purpose.

The first element that may be used for a separation is a regular beaker. However, while the suspension of a sample in the density liquid and the following settling is easy, the actual separation is not effective in such a glassware. In order to retrieve the supernatant, the beaker must be tilted to pour the top, which break downs the stratification that formed during the settling process.

Another material that may be used is the separatory funnel. Separatory funnels are initially designed to separate two immiscible phases with separate density. They are used in liquid-liquid extraction processes, where one phase is usually a hydrophobic organic solvent while the other is aqueous. This makes them adapted for the settling of particles according to density. However, they are initially designed for the collection or removal of liquid material settled at the bottom

of the funnel. As the bottom of a density-based separation of environmental samples is usually rich in mineral particles of varying sizes, the stopcock is susceptible to clogging.

In an attempt to overcome these limitations, specialized glassware has been developed by multiple laboratories for the treatment of microplastics. Some were developed using a ball valve. The first one, developed in 2012 by Imhof *et al.* was a large metallic funnel adapted to the separation of microplastics from high volumes of sediments (Imhof et al., 2012). Recovery tests conducted during the initial study reported that the equipment recovered close to 100% of particles from a sample. However, it was cumbersome, took a long time to settle, and was hard to handle. Smaller, more portable models were developed using the same ball valve system that allowed to separate the supernatant from the settled sediment without creating turbulence that may resuspend some particles (Coppock et al., 2017)

Another piece of equipment was proposed by Nakajima *et al.* (Nakajima et al., 2019). The glassware, consists in two separate pieces placed on top of one another. When the two pieces are adjusted, they produce a single, water-tight cylindrical tube. After the sample has settled, the two pieces can be separated, enabling the retrieval of the supernatant without mixing it with the settled sediments. In the study showing this proof-of-concept, the authors recovered 94 to 98% of all microplastics spiked prior to a density separation. Five different polymers were used in the recovery test, including PE, PP, PVC, PET and PS.

5.3.4 Limits of the process and recommendations

While they are necessary for the concentration of microplastics in samples, density-based separation of minerals from samples present clear limitations. As mentioned above, adapted chemicals must be used to ensure not to lose plastics. Adapted glassware must be used to ensure the stratification remains until the supernatant is collected.

Even so, the treatments are not perfectly effective and are likely to cause the loss of particles in the settled fraction. In particular, mineral particles may remain stuck to microplastics, which increase the density of the plastics, sinking them. Microplastics may also stick to the walls of the glassware used and be lost.

In regards to these limitations, it is necessary for studies to assess the efficiency of their treatment overall. Laboratory blanks and recovery tests are required, and should be clarified with as much detail as possible in published studies.

More details regarding this necessity are provided in the QA/QC section of this chapter (section 7).

5.3.5 Strategy selected

Density-based separation treatments were conducted during all sampling campaigns of this PhD. In the light of the previous discussions, NaI was used as a density solution. While Sodium Polytungstate would have been a less toxic choice, it was above the budget of the laboratory. In order to reduce both the costs and the environmental pollution of the treatment, the density liquid was reused throughout the entire PhD. NaI appears easier to recycle than $ZnCl_2$, which is why it was ultimately selected as a density liquid.

In all treatments, a density solution of 1.7 g cm^{-3} was produced. Glass-fibre vacuum filtered ultrapure water was used as a solvent, and was used with analytical grade NaI powder. The solution's density was measured by weighing 10 times 1 mL of density solution before usage.

The density solution was recycled after all treatments. After samples were filtered out of the solution, the solution itself was vacuum-filtered on glass-fibre filters. The filtered solution's density was measured. It was then re-adjusted with filtered water if the density was too high, or with the addition of NaI powder or evaporation of the excess water if the density was too low. The solution was filtered again before it was re-used.

The JAMMS developed by Nakajima *et al*. was considered the best material to use for density separation (Nakajima et al., 2019). It can be entirely built out of glass and can be cleaned using the same process as all other glassware. It was therefore selected and used in all density separations of this PhD. A total of 16 separation units were ordered in a Parisian glass workshop and used for that process. 8 units have a total volume of 500 mL, the other 8 have a total volume of 250 mL. Figure 10 represents both a schematic representation and a photograph of this piece of equipment.

In order to maintain the glassware watertight, a drop of mineral silicone gel as well as ethanol was used on the flat surfaces. Screw clamps were used to ensure the two pieces remained pressed together throughout the treatment.

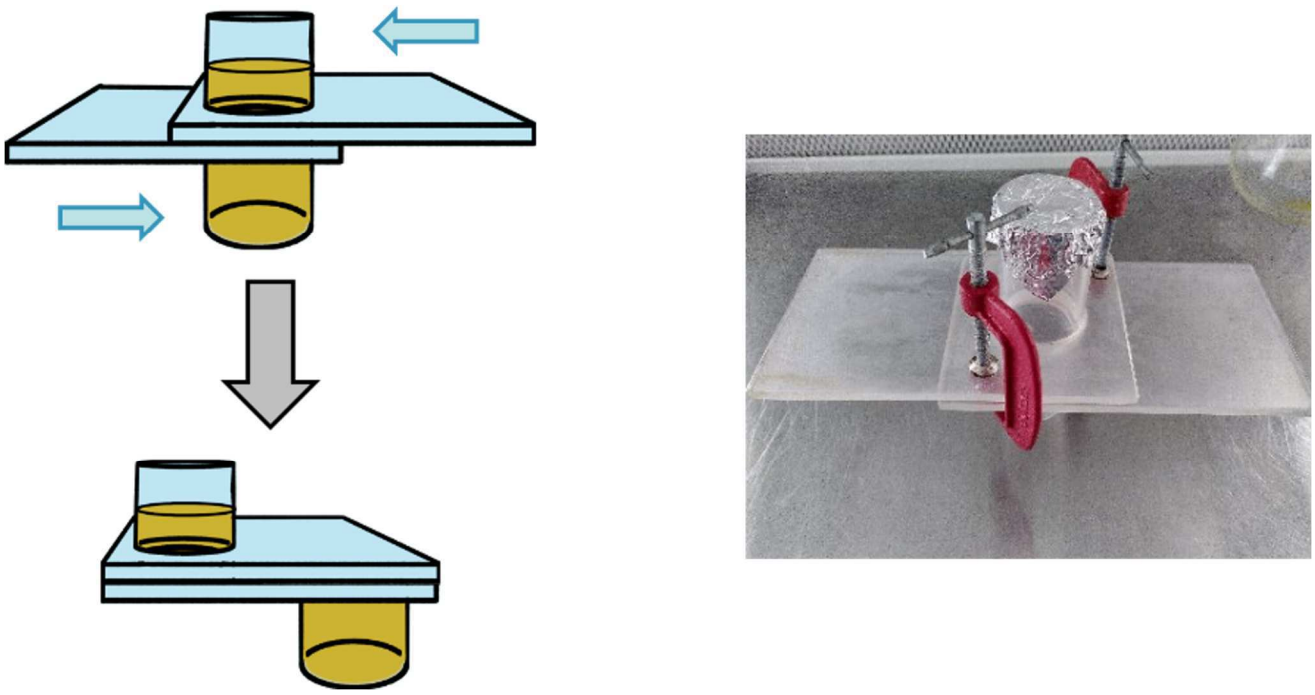

FIGURE 10: SCHEMATIC REPRESENTATION AND PHOTOGRAPH OF THE SPECIALIZED GLASSWARE USED FOR DENSITY SEPARATION

5.4 Microplastics concentration treatment – differences between targeted matrices

As previously stated, the two primary matrices examined in this PhD, namely deposited atmospheric particles and soil substrate, exhibit significant differences in microplastic concentrations and particle content. Dense minerals are not concentrated or absent from air or atmospheric deposition samples, and organic materials are less concentrated than in other matrices.

As a result, as shown on Figure 11, the majority of studies found in the review conducted at the beginning of the PhD (17 out of 26) did not apply any treatment to the samples. While the absence of treatment poses challenges for the identification of particles, it also presents some benefits. In particular, as discussed on Figure 7 in section 5.1, the absence of treatment reduces the probability of losing particles or, on the contrary, of contaminating samples with external particles

Treatment was particularly limited for suspended particles. Among the reviewed documents, only one by Allen *et al.* sampled air from the ocean and chemically treated its samples before

analysis (Allen et al., 2020). In that work, samples underwent an organic removal treatment during which samples were flushed in a vial and 30% volume/volume hydrogen peroxide (H_2O_2) was added for 7 days.

The targeted particle size, as well as the analytical methods selected, are likely to determine whether a treatment is necessary or not. Non-plastic particles found in the atmospheric compartment are mostly smaller than a few dozens of micrometres, in the range of PM 10 or PM 2.5. As a result, large microplastics >200 µm are likely less hidden by that fine matrix and do not require any major treatment prior to analysis. In order to quantify smaller microplastics however, a treatment remains necessary.

It should be noted that while no treatment was conducted in older studies (Cai et al., 2017a; Dris et al., 2015, 2016b, 2017), sample treatment is more common among recent studies(Allen et al., 2019; Klein and Fischer, 2019; K. Liu et al., 2019c). This trend appears to be maintained, with the majority of recent studies on microplastics in the atmospheric compartment carrying out a sample treatment protocol before analysis (Chang et al., 2023; Jenner et al., 2022; Klein et al., 2023).

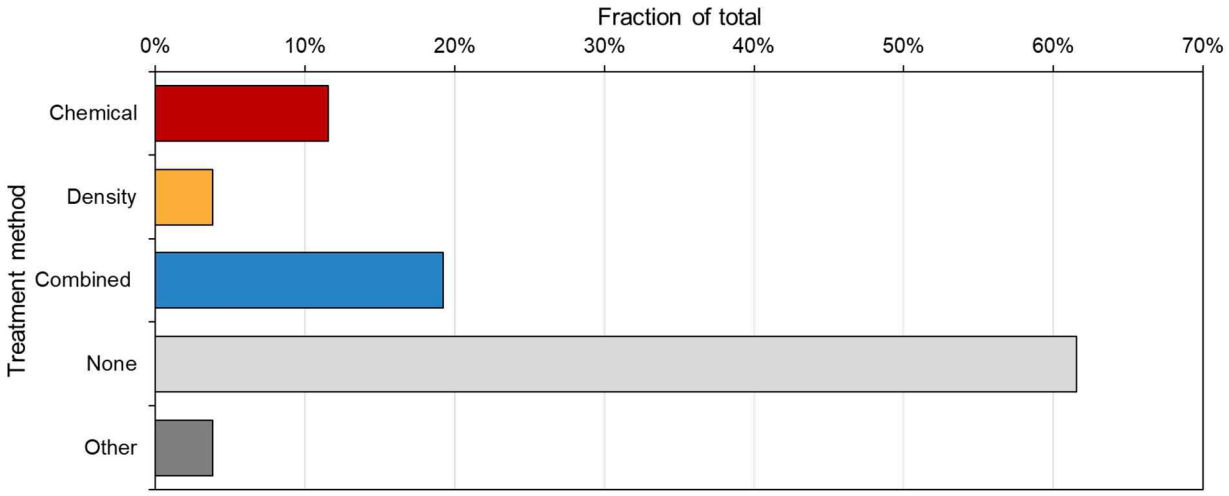

FIGURE 11: DISTRIBUTION OF THE TREATMENT PROCESSES CARRIED OUT IN THE LITERATURE FOR ATMOSPHERIC SAMPLES (N=26 STUDIES)

Soil samples are at the opposite end of the matrix concentration range from air samples. They are concentrated in diverse organic and mineral particles, and highly heterogeneous. Any quantification of microplastics is impossible without a preliminary concentration treatment.

The first studies that focused on microplastics in soils conducted concentration treatments on all samples, using density separation and H_2O_2 digestion (Liu et al., 2018; Zhang and Liu, 2018; Zhou et al., 2018). A concentration treatment is also conducted in all subsequent studies. The

majority of identified studies are applying at least one form of density-based separation, with several studies conducting multiple density-based separations.

5.5 Microplastics concentration treatment – summary and selected practices

Figure 12 summarizes the treatment practices employed throughout this PhD. In the second chapter, atmospheric deposition samples undergo both a density-based separation and an oxidative treatment. In the third chapter, soil samples prepared for the quantification of microplastics undergo an oxidative treatment, followed by a density-based separation and a second oxidative treatment. Samples prepared for the quantification of TRWP do not undergo this treatment, and are only sieved and dried. Indeed, the TRWP concentration in highway soil samples is particularly high, which allowed to detect TRWP without a concentration treatment prior to analysis. Finally, macrolitter samples are rinsed and dried before they are analysed.

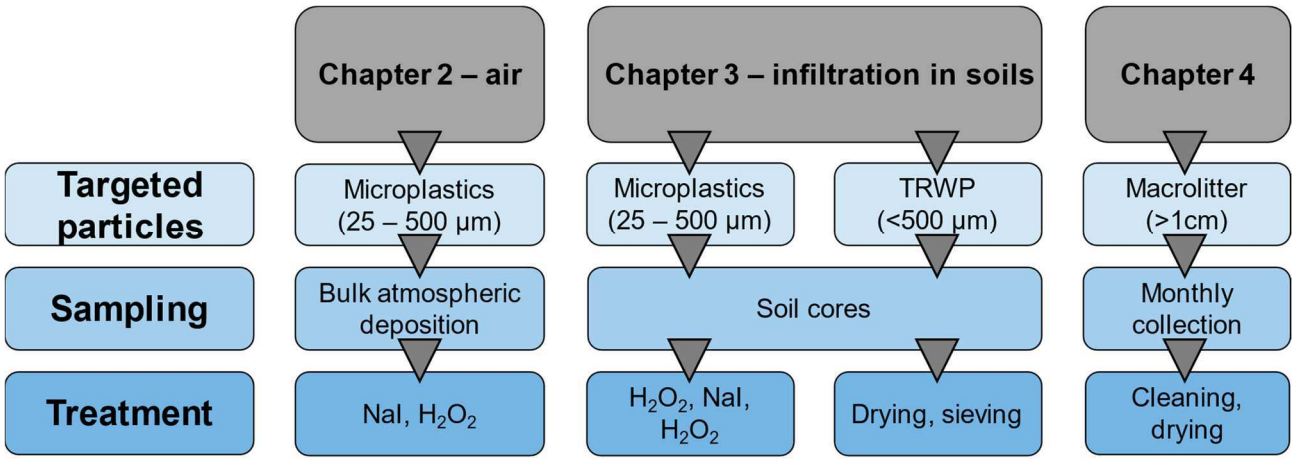

FIGURE 12: SUMMARY OF THE TREATMENT PRACTICES SELECTED FOR THE FOLLOWING CHAPTERS OF THIS PHD

6 Chemical characterization and quantification of microplastics

6.1 Introduction

After they are collected and isolated from their environmental matrix, the microplastic content of all samples remains to be analysed. The objective of such an analysis is double. The microplastics of the samples are characterized by shape, sizes, and polymers. They are also quantified, by mass or by number.

Microplastic identification practices evolved a lot over time. In the earliest studies, microplastics were identified using spectroscopic analytical methods like FTIR (Thompson et al., 2004) or Raman (Imhof et al., 2012). As the scientific interest for microplastics increased, an array of analytical methods developed. Some of these methods were based on purely visual identification of microplastics in samples. In these cases, stereomicroscopes are used to observe the microplastics and characterize them using parameters such as their shape, their colours and their texture. (Collignon et al., 2012; Costa et al., 2010; McDermid and McMullen, 2004).

Analyses based on visual identification are relatively quick, and require very little cost or material to be conducted, which is likely the reason why they were often carried out in early studies. However, these methods present numerous biases (Lenz et al., 2015; Martin et al., 2018; Prata et al., 2019a; Song et al., 2015). Purely visual identification methods have no way to chemically confirm the nature of the particles observed, and thus present a high rate of both false positives and false negatives. In addition, the polymer distribution of the particles cannot be assessed, which makes it impossible to discuss the potential sources of microplastics from the sample. Secondly, visual identification of microplastics is very experimenter-dependent, Results from a same sample can vary based on the person conducing the analysis, which severely hampers the possibility of comparison between studies. Because of these biases, purely is more and more criticized in the literature, and is not recommended unless it is combined with some form of chemical identification of microplastics (Lenz et al., 2015; Prata et al., 2019a).

The current section aims to detail some of the dominant microplastic identification and quantification methods currently employed in the literature to analyse soil and air samples, and to present the chosen analytical methodology of this PhD.

6.2 Spectroscopic characterization of particles

6.2.1 General principles

Two main forms of spectroscopic methods are widely used for the characterization or quantification of microplastics in samples. These two methods are Fourier-Transform Infrared (FTIR) spectroscopy, and Raman spectroscopy.

FTIR spectroscopy

Fourier-Transform infrared spectroscopy (FTIR) is a form of infrared spectra acquisition method. While dispersive spectroscopy acquires spectral data over narrow wavelengths successively, FTIR spectroscopy allows the simultaneous collection of spectral data over a wide range, through the use of a beam splitter and differential interferences. Figure 13 is a schematic representation of the process of spectrum acquisition in an FTIR spectroscope.

FTIR spectroscopy provides the absorption spectrum of a given material over wavenumbers ranging from 4000 to 500 cm^{-1} (wavelengths of 2.5 to 20 µm) which corresponds to the near infrared. This absorption spectrum is specific to the material, as absorption bands are caused by shifts in vibration modes of certain covalent bonds in a given material. Each obtained infrared spectra can be analyzed in depths: each absorption peak can be related to a certain energy level and to the associated shift in vibration mode, until the detailed chemical environment that produced the spectrum is completely uncovered.

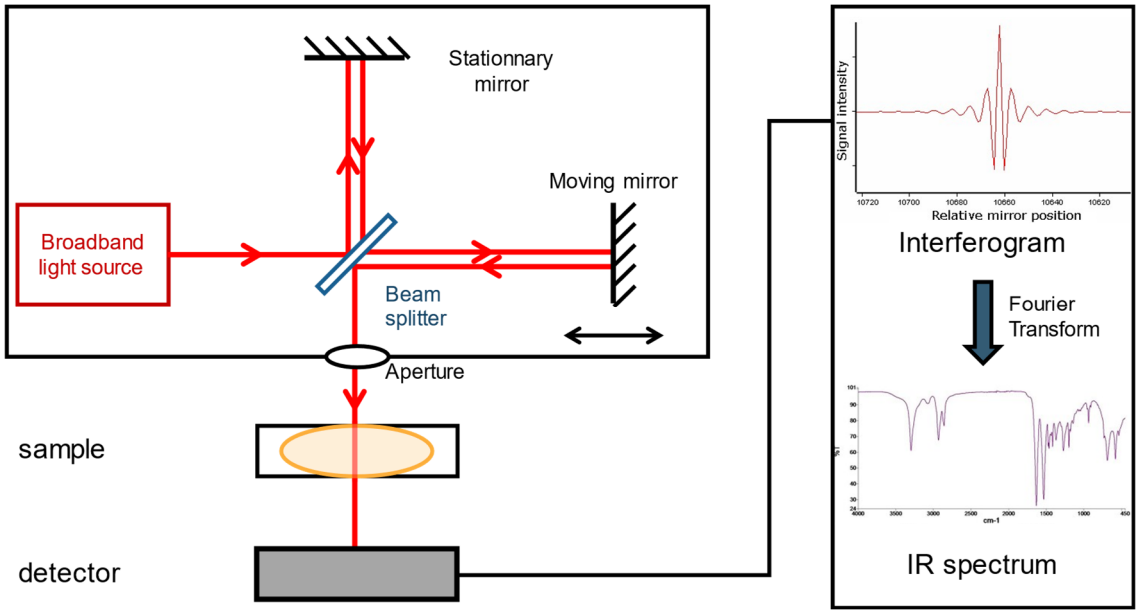

FIGURE 13: REPRESENTATION OF A FTIR SPECTRUM ACQUISITION IN TRANSMISSION MODE

Such a detailed analysis, however, is not compatible with the imperatives and issues of microplastics quantification from environmental samples. Environmental samples are often altered, complex, and thus present spectra that can prove hard to directly correlate. Besides, an in-depth analysis of a single infrared spectrum is time-consuming, and would significantly increase the time required for microplastic quantification in a sample. Instead, a surface comparison with a library of already identified spectra is typically conducted. A Pearson's correlation coefficient between the obtained spectrum and each spectrum of a library is calculated. Based on its similarity score, the acquired spectrum is confirmed or infirmed as being microplastics (Chen et al., 2020; Primpke et al., 2017; Xu et al., 2019).

ATR-FTIR spectroscopy

Attenuated Total Reflectance (ATR) spectroscopy is an acquisition mode for FTIR spectroscopy that is regularly used for the identification of larger microplastics. During an ATR-FTIR acquisition, the beam of infrared light passes through an ATR crystal in direct contact with the sample, at such an angle that it immediately reflects to the interface surface between the crystal and the sample. The resulting infrared spectrum is the absorption spectrum of the surface of the analysed material, as the infrared beam typically only penetrates between 0.5 and 2 µm into the material. A wide array of ATR spectroscopes exists in the market, ranging from high resolution micro spectroscopy to less expensive instruments adapted to the analysis of particles large enough to be seen and manipulated without binoculars. Figure 14 represents the general principle of ATR-FTIR spectroscopy.

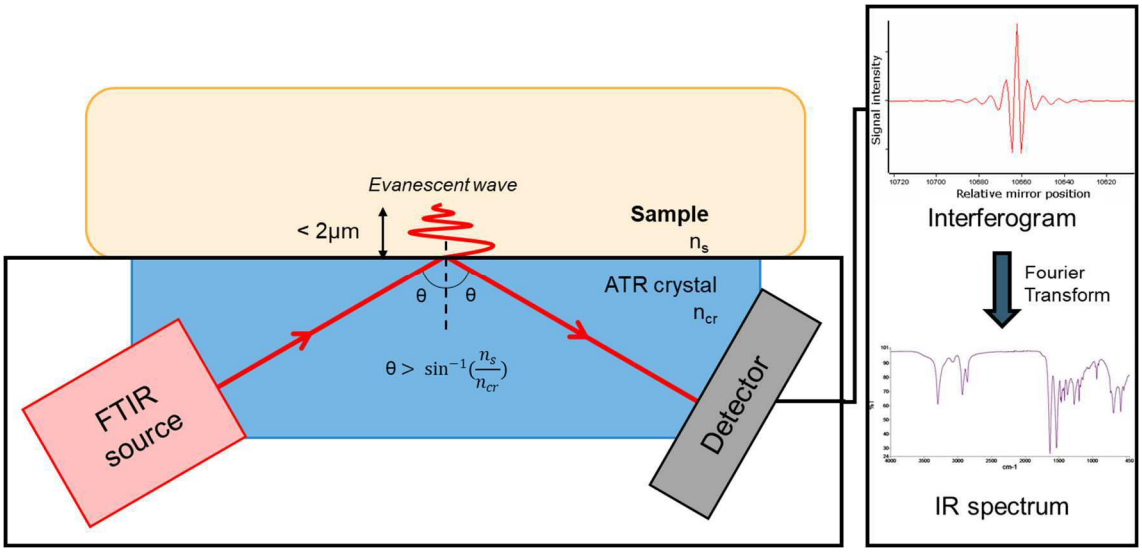

FIGURE 14: SCHEMATIC REPRESENTATION OF AN ATR-FTIR SPECTRUM ACQUISITION

Raman spectroscopy

Raman spectroscopy is another form of widely practiced spectroscopic method. Although Raman spectra are represented with a wavenumber in the same ranges as infrared spectra for the x-axis, they are not infrared spectra. Where infrared spectra directly show the absorption of infrared light by molecules based on their vibrational modes, Raman spectroscopy relies on the inelastic scattering of higher-energy light when interacting with molecular vibration, called Raman scattering. Typically, a laser is used to interact with a sample. As the light interacts with molecular vibration, its energy level (and thus wavelength) is shifted. After it interacted with a sample, the laser passes through a monochromator, and is then detected. The resulting Raman spectrum represents the intensity of light over the shifted wavenumber, or Raman shift. Figure 15 represents the process of a Raman spectrum acquisition.

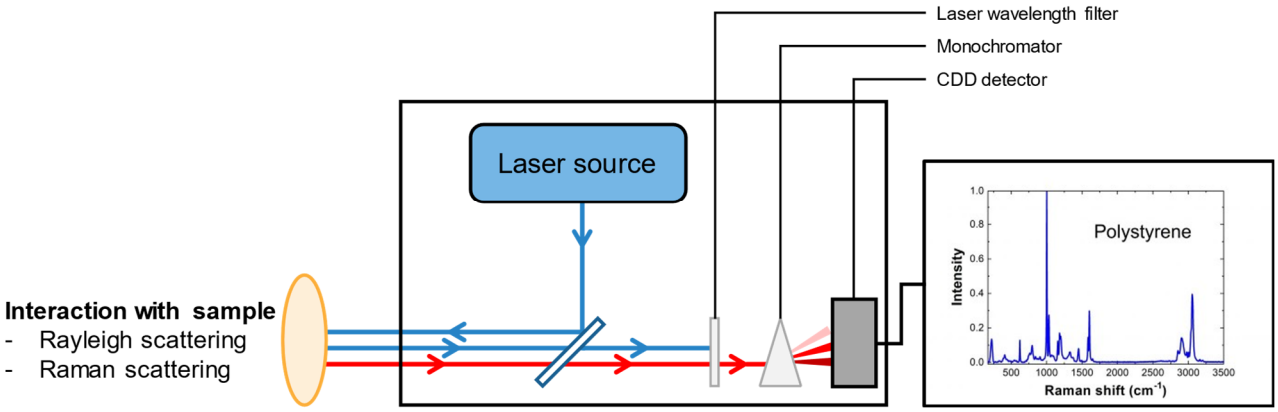

FIGURE 15: SCHEMATIC REPRESENTATION OF A RAMAN SPECTRUM ACQUISITION

6.2.2 Spectroscopic characterization procedures used in the literature

Methods used to identify and characterize microplastics in the air are presented in Figure 16. While these methods vary, some trends can be observed. In the majority of studies, a combination of visual identification and spectral analysis is used (Dris et al., 2016b, 2015; Klein and Fischer, 2019; Zhou et al., 2017). In these studies, samples are first observed and sorted under stereomicroscope. Authors use some visual characteristics of particles such as their colour, texture and shape to estimate whether some particles are likely to be microplastics (Hanvey et al., 2017; Hidalgo-Ruz et al., 2012; Mai et al., 2018). A subsample of these suspected microplastics are then randomly selected and analysed using spectroscopic methods.

Fourier-Transformed Infrared spectroscopy (FTIR) is the dominant identification method. Raman spectroscopy is another viable method of chemical identification (Akhbarizadeh et al., 2020; Allen et al., 2020, 2019; Gaston et al., 2020; Klein and Fischer, 2019). In these studies,

atmospheric microplastic abundances were proven to be overestimated as many natural particles were mistakenly considered of synthetic origin.

A limited fraction of studies is exclusively based on visual methods to identify and characterize microplastics (Abbasi et al., 2019; Dris et al., 2015; Prata et al., 2020). While visual identification used to represent a major aspect of microplastic characterization (Hidalgo-Ruz et al., 2012), this method is less used by newer studies.

In the case of the atmospheric compartment, purely visual identification is not frequently used. Only 2 studies by Prata *et al.* (Prata et al., 2020) and Abbasi *et al.* (Abbasi et al., 2019) exclusively analyse samples through visual analysis.

Some techniques are used to improve the process of visual identification. One of these techniques is the "hot needle test" (Hidalgo-Ruz et al., 2012; Postma, 2022). In this test, a hot metallic point is used to probe the deformation behaviour of particles: plastics are susceptible to deform and melt when subjected to a pointed head, while natural particles stay in place. This test is particularly useful to identify fibres. In a 2023 study by Beckingham *et al.*, a blind trial of researchers showed synthetic and natural fibres were correctly identified >70% of the time (Beckingham et al., 2023).

Fluorescence microscopy is used in some studies to improve visual identification. In particular, Nile Red staining techniques were used in four studies to help distinguish synthetic from natural particles. Nile Red has shown in earlier studies to make microplastics fluorescent (Erni-Cassola et al., 2017; Maes et al., 2017). However, the selectivity of Nile Red is imperfect. In their report, Gaston *et al.* mention that some plant materials were stained by Nile Red (Gaston et al., 2020).

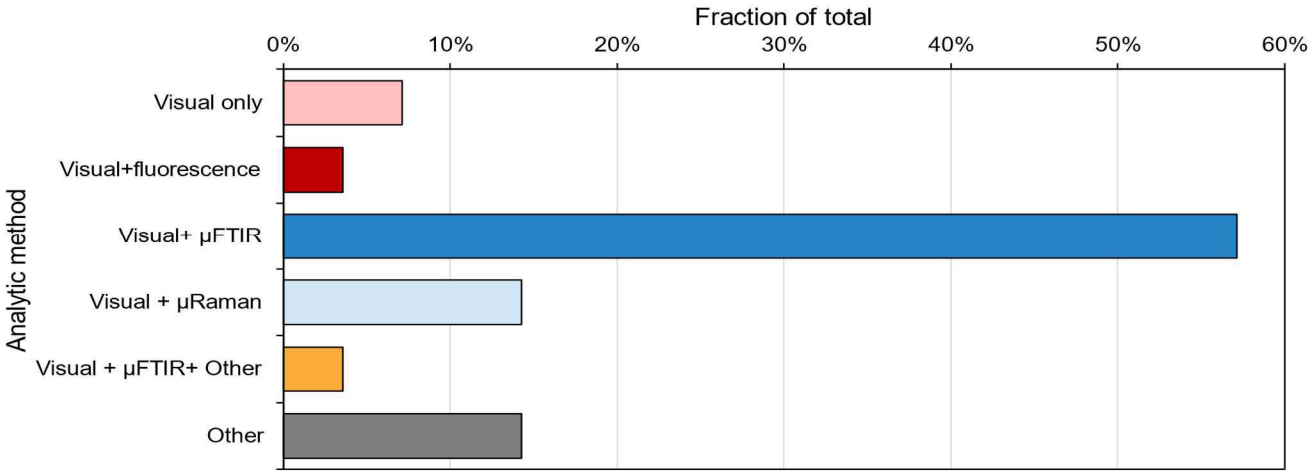

FIGURE 16: ANALYTICAL METHODS USED FOR MICROPLASTIC IDENTIFICATION IN THE ATMOSPHERIC COMPARTMENT (N=26 STUDIES)

On the opposite, plastic polymers are not all stained at the same strength. PP and unaltered PE are strongly stained, for example, while PET or weathered PE are less fluorescent after the staining. While the authors mentioned this could be used as a way to further identify polymer types, it may also cause mistakes in identification.

In more recent studies, the development of imaging analyses has allowed to analyse all particles of one sample with spectroscopic methods. Figure 17 provides an example of the process of an imaging analysis for microplastic quantification. In such a process, samples are typically deposited on a filter or solid surface after their isolation treatment. Spectroscopic acquisition is then conducted on the entirety of the sample. This produces an infrared pixel map of the entirety of the analysed region. Finally, the pixel map undergoes post-treatment using a third-party software.

While automated imaging analyses are not frequently used in the analysis of atmospheric microplastics, these methods are developing and are increasingly used to quantify the microplastic content of waters or soils (Johnson et al., 2020a; Mintenig et al., 2020; Park et al., 2020). In several studies, only a fraction of all identified particles are analysed by FTIR or Raman spectroscopy (Klein et al., 2023; Purwiyanto et al., 2022; Welsh et al., 2022). This adds a systematic human bias to all analyses, which is avoided in an imaging analysis, as it allows to indiscriminately acquire the IR spectra of all elements on the analysed area (F. Liu et al., 2019a; Primpke et al., 2017).

In addition to visual and spectroscopic techniques, a few studies used other analysing methods: Scanning Electron Microscope (Abbasi et al., 2019; Dehghani et al., 2017) and Pyrolysis – Gas

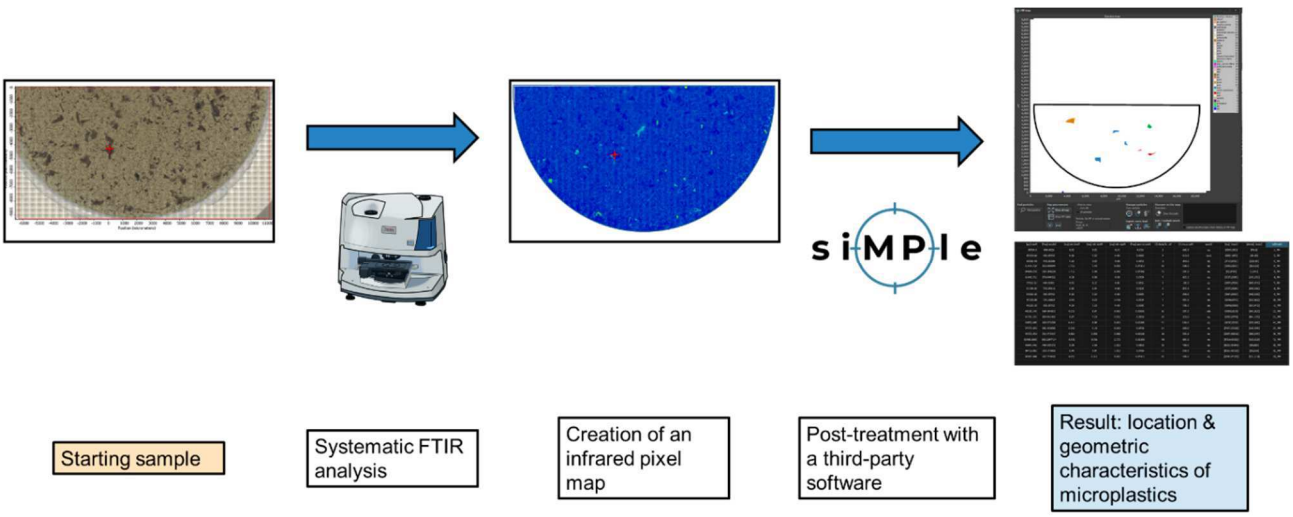

FIGURE 17: SCHEMATIC REPRESENTATION OF THE PRINCIPLE OF IMAGING ANALYSES

Chromatography coupled with Mass Spectroscopy (O'Brien et al., 2020). These methods are also used in other microplastic studies.

The methods used to characterize and quantify microplastics in soil environments are similar to the methods used in the atmospheric compartment. In a 2020 review by Büks and Kaupenjohann, the majority of identified studies used a combination of visual identification with stereomicroscopy, and FTIR analyses (Büks and Kaupenjohann, 2020). This trend continued in more recent studies, with the majority of studies using micro-FTIR or ATR-FTIR to characterize suspected microplastics (J. Li et al., 2023; Schell et al., 2022; Wahl et al., 2024). One 2019 study was noted to use Pyr-GC-MS to quantify multiple polymers in soil samples (Dierkes et al., 2019). In another, more recent study, visual and FTIR analyses were coupled with thermo-gravimetric analysis to identify microplastics in agricultural soils (Chen et al., 2024). However, the authors did not find the method reproducible enough when applying this method to field samples.

6.2.3 Limits and recommendations

The objective of a microplastic analysis is to quantify and characterize the microplastic contamination in a sample with as much representativity as possible and as little random bias as possible.

Studies that do not perform any chemical identification of samples are the most flawed in that regard. In particular, studies exclusively based on the visual identification of suspected microplastics cannot reliably distinguish plastic particles from natural debris.

While better than a purely visual identification of microplastics, methods based on a subsampling of the suspected particles still present some human bias. The way particles are actually selected is rarely precisely described. This is likely to cause representativity issues. For example, the use of ATR-FTIR not coupled to a microscope to characterize microplastics means only the larger particles can be reliably analysed.

The manual characterization of all suspected microplastics with a micro-FTIR or a micro-Raman reduces the problems of representativity caused by the selection of a subsample. However, it is still subject to experimenter-related human biases. Different users analysing the same sample may select different particles as suspected microplastics, leading to differences in results. Manual characterization of all suspected microplastics is also significantly more time-costly than the analysis of a subsample of particles.

Automated analyses are a way to avoid this human bias. The majority of experimenter biases are replaced by constant, reproducible machine biases. Additonally, fully automated systematic imaging analyses remove all representativity issues, and are even better than analyses based on an automatic detection of particles based on visual contrast. By analysing the entirety of a sample, the likelihood of missing missing a microplastic present is removed entirely. While such automated analyses are necessarily significantly longer due to the high number of spectra collected, the automatization means this is not a loss of active time.

Though they are less biased than other analytical methods, the generalized used of automated imaging analyses in the community is likely to be slowed by the increased investment cost, as micro-FTIR or micro-Raman spectroscopes are expensive and a specialized detector is typically required for analysis.

6.2.4 Spectroscopic identification strategy selected

In light of these discussions, automated imaging analyses were deemed the least biased micro-FTIR identification methods and were used throughout this PhD. In all sampling campaigns, samples were vacuum-filtered to be deposited onto 25 mm diameter, 0.2 µm pore size Whatman Anodisc® aluminium oxide filters for micro-Fourier Transform InfraRed (FTIR) spectroscopic analysis. 1 to 4 filters were required to successfully deposit the entirety of each sample

The Anodisc filters were then analysed via micro-FTIR using a Nicolet™ iN10 (Thermo Scientific, USA) FTIR in transmission mode, equipped with a linear array of MCT cooled imaging detectors. The detector had a spectral range of 4000-500 cm^{-1}, however the use of the Anodisc filters limited the detection to a spectral range of 4,000 – 1200 cm^{-1}. 8 scans were acquired to produce each spectrum. The imaging detectors have a 25 µm pixel resolution. 25 µm was hence considered the observable size limit of this study. A photograph of the FTIR is provided on Figure 18a.

Each filter underwent complete imaging to obtain infrared maps of the entire filter. While an Anodisc has an overall diameter of 25 mm, each filter is surrounded by a 3.5 mm wide plastic ring where no filtration occurs. As a result, the collection of 9x18 mm maps allowed to process the entire filter. All subsamples were analysed leading to a full characterisation of collected

a

b

FIGURE 18A – PHOTOGRAPH OF THE NICOLET IN10 USED FOR MICROPLASTIC ANALYSIS; B – PHOTOGRAPH OF THE NICOLET IS5 USED FOR THE CHARACTERIZATION OF MACROLITTER.

particles. As the size of the raw data file had to remain below 900 Mb to be successfully exported, it was necessary to analyse the filter in two runs focused each on one half of the filter.

After acquisition, chemical identification of microplastics was conducted using the open software for Systematic Identification of MicroPlastics in the Environment (siMPle, (https://simple-plastics.eu/), developed at Aalborg university, Denmark and the Alfred Wegener Institute, Germany (F. Liu et al., 2019a; Primpke et al., 2020). The microplastic spectra library directly provided with the download of the freeware was used for post-treatment.

SiMPle was developed from the combination of the software MPhunter first developed at the Aalborg University (F. Liu et al., 2019a) and the automated analysis developed by Primpke *et al.* at the Alfred Wegener Institute (Primpke et al., 2017). During the post-treatment, each pixel of the analysed region is compared with a library of polymers and natural particles. For each spectrum, Pearson correlation coefficients r_0, r_1 and r_2 are respectively obtained for the raw spectrum and its first and second derivatives. Global weights for each of these correlation coefficients are selected by the user: k_0, k_1 and k_2 respectively for r_0, r_1 and r_2. Using these coefficients and their weight, a score $S_{d(i,j)}$ can be calculated, with d the number of the reference spectrum, and (i,j) the pixel coordinate of the collected spectrum.

$$S_{d(i,j)} = \frac{k_0 r_0^2 + k_1 r_1^2 + k_2 r_2^2}{k_0 + k_1 + k_2}$$

By default, k_0, k_1 and k_2 are respectively set to 0, 1 and 1, meaning the software focuses on the coefficient correlation between the spectrum's first and second derivatives.

For each material, three thresholds $t_1>t_2>t_3$ are used to determine the composition of a spectrum. According to the detailed study, a particle is considered as belonging to a material if for at least one pixel, $S_{d(i,j)}\geq t_1$. If this condition is filled for several different reference materials, the pixel is considered of the same material as the highest score. This pixel is then considered as the nucleus for a particle. The algorithm then evaluates the score of the adjacent pixels. If for any adjacent pixel, a score $S_{d(i,j)}\geq t_2$ is observed, that pixel is considered part of the same particle. Further details regarding the algorithms and its limitations are provided in the original papers (F. Liu et al., 2019a; Primpke et al., 2020).

SiMPle uses as input the raw data file exported from OMNIC Picta, the Thermo Scientific FTIR software. Its main output includes the list of all identified microplastics as well as geometric and spatial parameters such as their location on the map, their polymer type, their best match with spectra from the SiMPle library, and their dimensions

In addition to the micro-FTIR imaging analyses, ATR FTIR analyses were conducted to characterize macro-litter samples. A Nicolet is5 (Thermo Scientific, US) was used to perform these analyses. Each item was cleaned, described and weighed prior to analyses, while the ATR crystal was cleaned with ethanol between each acquisition. 16 scans were acquired to produce each spectrum. The obtained spectra were then compared to a combination of the instrument's internal libraries and a small library of item analysed by the LEESU. In order to confirm the nature of a polymer, the confirmed spectra were visually compared with their best match from the library. Figure 18b is a photograph of the is5 used for that purpose.

6.3 Mass characterization of microplastics with Py-GC-MS

6.3.1 General principle

Pyrolysis coupled with Gas Chromatography and Mass Spectrometry (Py-GC-MS) is a destructive, targeted method of chemical quantification. In an analysis, samples are pyrolyzed and degraded into low-molecular weight molecules. In particular, polymers or elastomers composing microplastics and tyre-weight particles are turned into a diversity of molecules, some of which are highly specific of a polymer and can be quantified by calibration.

Figure 19 summarizes the process of a Py-GC-MS analysis. First, a sample is thermally decomposed through a process known as pyrolysis. The sample is placed in a pyrolizer, which can rapidly reach temperatures of more than 500 °C. As it is heated, the weaker molecular bonds in the sample are broken. In particular, the polymeric component of microplastics is decomposed into several repeatable volatile molecules. These organic compounds are then separated by gas chromatography and mass spectrometry (Bouzid et al., 2022; Fries et al., 2013).

In order for specific polymers to be quantified, a calibration curve must typically be produced using known polymers. Samples are then quantified using this calibration curve.

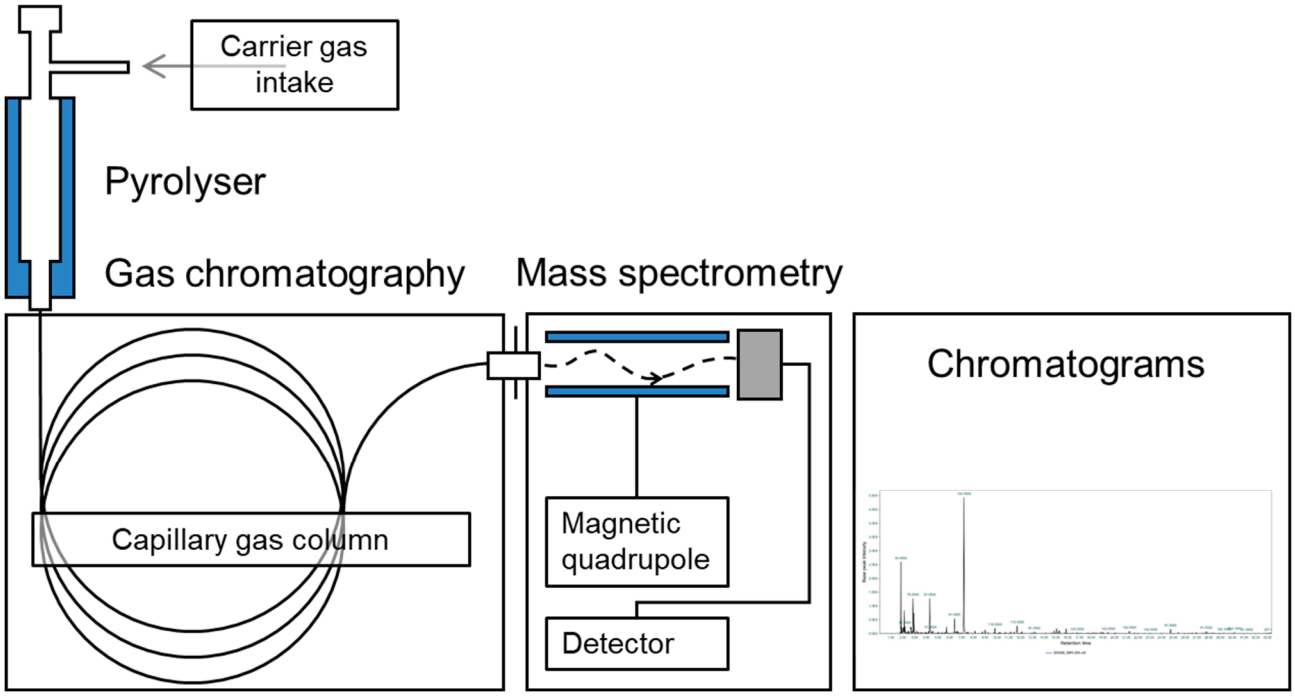

FIGURE 19: SCHEMATIC DIAGRAM OF A PY-GC-MS ANALYSIS (CHROMATOGRAM ILLUSTRATION FROM RØDLAND *ET AL.*, 2022)

6.3.2 Py-GC-MS practices in microplastic studies

Py-GC-MS was used to characterize the presence of plastic contamination in soil and sediment samples as early as 1986 (De Leeuw et al., 1986). However, the use of Py-GC-MS in microplastic studies started later, in the 2010s. Early studies mainly used the method to confirm observations made using visual microscopy (Fries et al., 2013; Nuelle et al., 2014). A method was first developed in 2017 by Fischer and Scholz-Böttcher to quantitatively analyse 8 specific polymers in environmental samples, without preliminary sorting using a stereomicroscope (Fischer and Scholz-Böttcher, 2017).

Since the development of this method, studies have used Py-GC-MS to quantify microplastics in multiple environmental matrices, including atmospheric deposition (Luo et al., 2023) and soil and sediment samples (Dierkes et al., 2019; Fischer and Scholz-Böttcher, 2019). In a recently published book chapter reviewing the methodologies used for the sampling, preparation and identification/quantification of microplastic in river samples, 6 out of the 175 studies analysed used Py-GC-MS for the qualitative (Campanale et al., 2020; McCormick et al., 2016; Pojar et al., 2021) or quantitative (Käppler et al., 2018; Laermanns et al., 2021) analysis of microplastics (Dris et al., 2024).

6.3.3 Limits and recommendations

Py-GC-MS analyses present specific advantages and limitations that differ from FTIR and Raman analysis, making the two approaches complementary and beneficial to use in tandem.

First, Py-GC-MS is a destructive and targeted analytical method. While chromatograms obtained can still be scanned for unintended polymers, the absence of an initial calibration curve prevents their quantitative analysis. As a result, only the polymers initially targeted can be quantified. This limits the possibility of reproducing analyses in different laboratories.

Secondly, this method cannot provide information on the geometric characteristics of the identified microplastics. Size or shape distributions cannot be directly measured. Conversely, the analytical method has no size-related limit of quantification. It is possible to detect any plastic size, provided they are sufficiently concentrated in the samples. A lower size limit is however still constrained by the preliminary filtration steps.

Thirdly, Py-GC-MS does not directly provide a number of microplastics. The initial result is the mass of a targeted polymer, which can be converted in a plastic concentration in the initial sample. This differs from the results obtained with spectroscopic methods. However, it is arguably more useful to model the sources and fate of microplastics in the environment. In particular, it allows to directly discuss a link between plastic production or plastic waste emission and microplastic concentrations.

Similarly to automated imaging spectroscopic analyses, the last clear limitation of methods based on Py-GC-MS for the quantification of microplastic in environmental samples is their cost. While this methodology is highly promising and complementary to spectroscopic analyses, instruments are expensive and remain costly to operate.

6.3.4 Py-GC-MS analysis selected

While the majority of the sampling, analysis and post treatment of this PhD was conducted in the LEESU, the treatment and analysis of samples by Py-GC-MS were conducted in the LEE, in Nantes. The details of the standard preparation were taken directly from a procedure described in a study published by Oliveira *et al.* (De Oliveira et al., 2024).

Standard preparation and calibration

Several procedures are required for a Py-GC-MS analysis. First, a standard solution is prepared for the creation of a calibration curve. The SBR polymer used for the preparation of the standard solution was a copolymer poly(styrene-co-1,2-butadiene-co-1,4-butadiene) (Product ID: P19147B-SBdran).

Additionally, an internal standard is added to all standards and samples, in order to assess variation in the signal intensity. Here, a deuterated SBR polymer was selected as an internal standard, as it has a similar reaction to pyrolysis as SBR and a predictable difference in reaction in gas chromatography and mass spectrometry. The d-SBR selected is a copolymer poly ([deuterated styrene-d8]-co-[deuterated butadiene-d6]) (Product ID: P19284-dPSdPBdran). All the polymers were purchased from Polymer Source, Inc. (Dorval, Quebec, Canada).

The two standards were dissolved under agitation in $CHCl_3$ purchased from Sigma-Aldrich (St. Louis, Missouri, USA) at 40°C following the method stressed out by Unice *et al.* (Unice et al., 2012). In order to obtain the calibration curve, eight different masses of SBR ranging from 19 ng to 11 µg were diluted in $CHCl_3$ to obtain different concentrations. Each concentration was analysed in triplicates. Additionally, 1.27 µg of the internal standard d-SBR was introduced into each cup. Finally, a mass of 2.50 mg of SiO_2 purchased from Sigma-Aldrich (St. Louis, Missouri, USA) was added to each standard cup. The SiO_2 acted as an inert matrix, ensuring a consistent solid state between the standard sample and the soils samples.

Analysis

Analysis was performed using a multi-shot pyrolizer EGA/PY-3030D equipped with an auto-shot sampler (AS-1020E) from FrontierLab (Fukushima, Japan) set at 600°C, associated with the 8890 gas chromatography and the 5977B mass spectrometer from Agilent Technologies, Inc. (California, USA). The gas chromatography column used for the compound elution was the Ultra ALLOY+-5 from FrontierLab (Fukushima, Japan).

Two specific pyrolysis products were selected for the detection and quantification of SBR and BR in soils samples based on an analytical method developed by More et al. (More et al., 2023). The first marker was 4-vinylcyclohexene (4-VCH), targeting m/z = 54 Da for the quantification and m/z = 79 Da for the confirmation. The second marker was 4-phenylcyclohexene (4-PCH) targeting m/z = 104 Da for the quantification and m/z = 158 Da for the confirmation. The detection and quantification of the deuterated SBR analogue was performed, targeting m/z = 60 Da for the quantification of d-4-VCH and m/z = 112 for the quantification of d-4-PCH. The quantification was achieved combining multiple markers for more accuracy as suggested by Rødland et al. (Rødland et al., 2022b) and following the specific method proposed by De Oliveira et al., (De Oliveira et al., 2024).

7 Quality assurance and quality control considerations

7.1 introduction

Quality assurance and quality control are terms regularly used in published articles relative to microplastic contamination in the environment. Broadly, quality assurance can be defined as all activities and procedures implemented within a system that can provide confidence it will fulfil its quality requirements. Quality control consists in all procedures implemented to ensure and verify that a system will fulfil its quality requirements.

In the context of the characterization and quantification of the microplastic contamination from environmental samples, a study has one clear quality requirement: the results obtained after analysis must be representative of the microplastic contamination in the environment. This has two major implications. Firstly, the number of particles identified on each sample must be a close approximation to the real number of particles in that sample. Secondly, the nature of the particles identified on each sample must be the same as the particles in the sample. In practice, these implications translate into two specific requirements. Samples must not be contaminated by outside particles before their analysis, and the loss of microplastics from the sample must be avoided.

In this section, the main QA/QC practices identified in the literature are presented and discussed. The procedures conducted in this PhD are then presented in regards to the practices observed in the literature

7.2 Literature insight

7.2.1 Contamination prevention

Contamination has been a major concern of microplastic studies since the early studies on the field. Some of the earliest studies on microplastics in marine environments detail procedures to avoid contamination of the samples, in particular by adapting the treatment procedure and laboratory equipment (Ng and Obbard, 2006; Thompson et al., 2004). In 2012, the first review article published on methods used to identify and characterize microplastics in marine environments provided several recommendations to avoid contamination of samples (Hidalgo-Ruz et al., 2012). The authors recommended to minimize sources of contamination and loss of particles, and to regularly conduct control samples.

In recent years, studies dedicated to the topic of QA/QC in microplastic studies were published (Prata et al., 2020; Song et al., 2020). Recommendations were provided to authors of studies and to the broader microplastic community, both concerning the limitation of sample contamination, the production of control samples, and the conduction of cross-laboratory collaboration projects to assess the comparability of results from different research teams and analytical methods.

7.2.2 Field and laboratory blanks

Contamination can occur at any stage of the analytical process, from sample collection to final quantification of microplastics. The most common way to evaluate this contamination is to use control, or blank samples. Control samples undergo the same treatment protocol as real samples and are analysed in the same way.

The majority of studies conducted in the atmospheric compartment report the use of control samples to verify the level of contamination of samples. The majority of studies report the use of laboratory blanks, meant to assess the contamination of samples during their treatment and analysis. In a book chapter reviewing microplastic contamination in river environments, 70% of all reviewed papers reported the use of laboratory blanks (Dris et al., 2024).

Field blanks are another category of control samples, meant to assess the level of contamination of the sampling procedure: deposition from the atmosphere, contamination by plastic materials, etc. In a 2020 study by Prata *et al.*, the presence of field blanks with concentrations similar to that of samples was reported (Prata et al., 2020). This raises a major concern for contamination

in atmospheric microplastic studies, as it largely lowers the reliability of both their and previous results.

7.2.3 Limit of quantification

The use of a limit of quantification is advised in the literature to present microplastic quantification results when a sufficiently high number of control samples are collected. A limit of quantification (LOQ) equal to the mean of the control samples plus ten times the standard deviations is expected. (Bråte et al., 2018; Johnson et al., 2020b).

Statistical limits of quantification are rarely mentioned in the literature for microplastics. In the majority of atmospheric studies, control samples retrieved no or a negligible amount of microplastics. In other studies, the number of plastics identified in the blanks is simply subtracted from the actual samples.

In their 2024 book chapter, Dris *et al.* noted a similar use of blanks for data correction. Studies that conducted control samples either detected no or negligible amounts of microplastics (Irfan et al., 2020; Ji et al., 2021), or In other studies, the contamination level is either reported independently with the results, or subtracted microplastics found in blanks from the result. In some study, this subtraction was conducted based on particle characteristics such as polymer type or morphology (Taylor Bujaczek et al., 2021; Lin et al., 2021).

7.2.4 Recovery tests

Recovery tests are a third type of procedure conducted in order to assess the fraction of particles that were lost during sample analysis. In such a test, a sample or a control sample is injected with a known number of microplastic particles before undergoing the same treatment and analytical steps all samples undergo. The quantification of the known microplastics, and its comparison with the initial number of injected microplastics can provide a recovery rate, which indicates the fraction of particles that were lost throughout the treatment and analysis.

Recovery tests are currently not conducted in a lot of studies in the literature. They were not conducted in early studies on microplastic contamination in the atmospheric compartment. In a book chapter reviewing microplastic contamination in river environments, 24 out of the 175 studies reviewed conducted some form of recovery test (Dris et al., 2024). The majority of studies used PE or PP as a spiked polymer.

In addition, the recovery tests typically conducted they are often biased. The microplastics spiked into the samples are pristine, easy to identify and with different surface properties from

the weathered particles found in an environmental sample. This means they are likely to behave differently in analyses.

7.3 Recommendations

Several elements can be highlighted regarding the communication of QA/QC concerns in the literature. First, the divulgation of laboratory practices conducted to avoid contamination is variable from study to study, but tends to be transparent and easy to understand.

However, the number and nature of blank tests conducted is rarely divulged, and is often too low. As mentioned above, the majority of studies do not produce a sufficiently high number of blanks to measure a statistical limit of quantification. Consequently, no limit of quantification can be determined, which limits the comparability of results between studies.

A major point to highlight is that authors should stop publishing results in which the number of plastics from the blank was subtracted from the total number of plastics identified in the samples, as this is a statistical error that hides the high degree of variability of microplastics quantification. Instead, studies should provide the overall microplastic abundances obtained and the number of plastics identified in blank samples and directly discuss the results.

Finally, recovery rate tests are crucial for validating and verifying the analytical methods used in microplastic analysis. They also facilitate cross-comparisons between studies. While their use is currently limited in the literature, their quality and frequency should increase in future studies.

7.4 QA/QC procedures conducted in this PhD

Several procedures were implemented throughout the works of this PhD in order to limit and control the contamination of samples and loss of particles. These procedures will be detailed below.

As the analytical process was different for the quantification of TRWP using the Py-GC-MS, the QA/QC procedures conducted for these analyses will be detailed in their own section.

7.4.1 Contamination prevention measures

The first array of procedures aimed at mitigating the risk of contamination by limiting the use of plastic materials as much as possible throughout all studies. In particular, all laboratory equipment that came into direct or indirect contact with either samples or treatment fluid was

made of either glass or metal. To limit dust accumulation, all glassware was stored in closed racks and covered with aluminium foil. To further mitigate the risk of introducing contaminants, any item that came into contact with a sample or rinsing liquid underwent at minimum thorough rinsing with filtered water and subsequent drying, which is expected to remove more than 90% of all plastic particles from the glassware (Song et al., 2020). All liquids that came into contact with samples or that were used for cleaning procedures were vacuum-filtered using 0.45 mesh size glass fibre filters.

Additionally, all material that could withstand the temperature was burned at a 400°C for two hours, a temperature at which all plastic materials are expected to burn and be removed (Song et al., 2020). In order to limit atmospheric deposition of microplastics during treatment, all laboratory treatment was conducted either under a laminar flow hood or a closed fume hood, while the top of the glassware was protected by aluminium foil.

7.4.2 Laboratory blanks and limit of quantification

The second set of procedures aimed at assessing contamination was assessed throughout the studies by collecting and analysing blanks. Control samples were collected on all campaigns by sieving 200 mL of filtered water was through a 47 mm diameter, 10 µm pore size aluminium mesh. The control samples then underwent the same treatment as the rest of the samples on the campaigns, and underwent the micro-FTIR imaging analysis as all other samples. In total, 9 control samples were analysed throughout this PhD. The detailed results of these control samples are presented in Table 4.

No limit of quantification was measured for any single sampling campaign, as the total number of blanks collected was too low. However, the control samples obtained from all analyses can be pooled together into a single control dataset to provide some theoretical limit of quantification. This represents an average ± standard deviation of $\mathbf{1 \pm 0.95}$ microplastic per control samples. In order for a sample to be above this theoretical limit of quantification, it must contain more than $\bar{\boldsymbol{x}} + \mathbf{10}\boldsymbol{\sigma} = \mathbf{11}$ particles, with $\bar{\boldsymbol{x}}$ the average number of microplastics in the blanks and $\boldsymbol{\sigma}$ the standard deviation.

However, such a limit of quantification is likely to be inaccurate. Not all sampling campaigns were conducted using the same methods. More importantly, not all campaigns underwent the same treatment protocol, which may represent major differences in deposition rates.

In the absence of a clear limit of quantification, samples may be considered as probably different from the control samples if the number of microplastics is five times above the mean number of particles in control samples from the campaign.

TABLE 4: DETAIL OF THE RESULTS OBTAINED FOR ALL BLANKS DURING THIS CAMPAIGN

Sample	Campaign	Treatment	Number of plastics	
			PP	PE
Air A20	Air, Paris (chapter 2)	Fenton, NaI	0	0
Air A21	Air, Paris (chapter 2)	Fenton, NaI	0	2
Air B21	Air, Paris (chapter 2)	Fenton, NaI	0	0
Air C22-D22 1	Air, Nantes (chapter 2)	H_2O_2, NaI	0	1
Air C22-D22 2	Air, Nantes (chapter 2)	H_2O_2, NaI	0	1
Air C22-D22 3	Air, Nantes (chapter 2)	H_2O_2, NaI	0	1
Soil 1	Soil (chapter 3)	H_2O_2, NaI, H_2O_2	3	0
Soil 2	Soil (chapter 3)	H_2O_2, NaI, H_2O_2,	0	0
Water 1	Runoff (chapter 4)	H_2O_2, NaI	0	1

7.4.3 Recovery tests

A recovery test was conducted in two campaigns of this PhD. Two samples that had already been quantified were selected. Each sample was resuspended from the alumina filters it was deposited on. The resuspended samples then underwent the entirety of the treatment process, and were deposited on new alumina filters. Both the new and the initial filters were then analysed for microplastics. The initial filter was analysed to determine the effectiveness of the resuspension. The new filter was analysed to establish how many particles had been lost in the treatment process.

No particles were found on the initial filter after resuspension in either of the samples that underwent the recovery test. This suggests that the resuspension step was 100% effective. Respectively 54% and 66% of all resuspended microplastics were found after the second treatment. The remaining particles were lost between the resuspension and the treatment. While it is not yet possible to determine an uncertainty or an estimate of all particles lost in each sample in the light of these recovery test results, they do suggest the possibility to measure a repeatable and realistic recovery rate with this method.

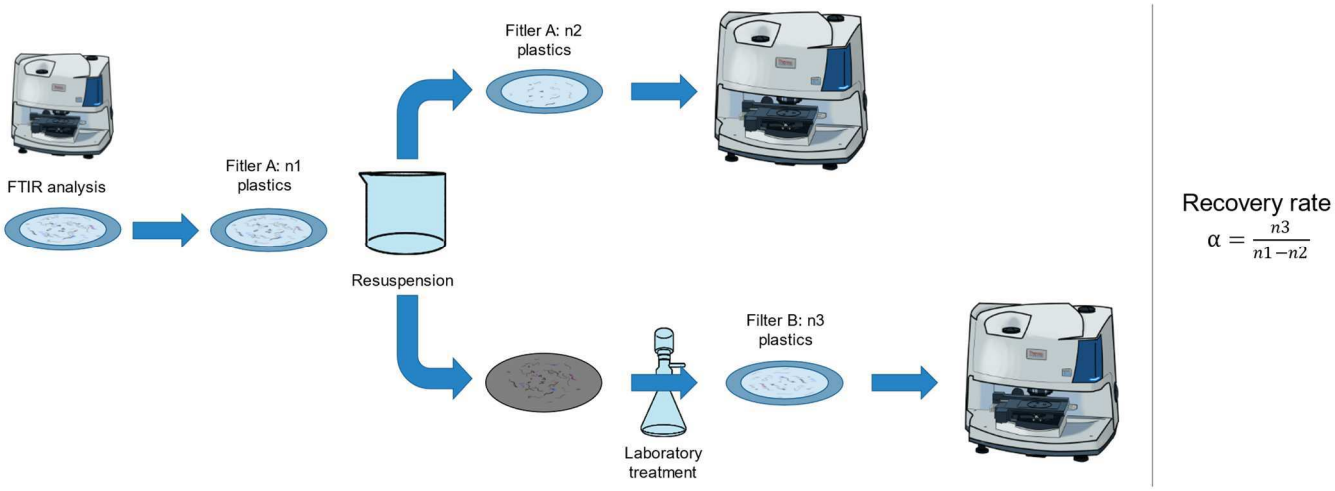

FIGURE 20: SCHEMATIC REPRESENTATION OF THE RECOVERY TESTS CONDUCTED IN THIS WORK

7.5 Specific QA/QC procedures for Py-GC-MS analyses

The standard and sample preparation process were adapted from a 2023 study by Albignac et al. (Albignac et al., 2023). Multiple procedures were conducted to minimize the risk of contamination. All materials including the pyrolysis cup, the SiO_2, and the glassware used to store the standard solutions were calcined at 500°C for 24 hours before any use. The soils samples, the SiO_2, and the polymer standards were manipulated with stainless-steel tools.

Additionally, multiple procedural blank analyses (without pyrolysis cup) were performed at the beginning, during, and at the end of each sequence run in order to assess potential contamination. Laboratory blanks were analysed using 15 µL $CHCl_3$ and 2.50 mg of SiO_2 in triplicates. All blank analyses reported contamination levels below the limit of detection.

Recovery tests were conducted to assess the potential loss of material prior to analysis. Three control samples consisting of 1.10 µg of standard SBR and 2.50 mg of SiO_2 were analysed during the soil samples sequence. The recovery rates ranged from 104 to 110 %.

Finally, a limit of quantification (LOQ) for the method was determined by assessing the standard deviation (S) of the three replicates of the smallest mass used to form the calibration curve (i.e., 19 ng). The signal-to-noise ratio for these replicates exceeded 10 and the LOQ of 3.83 µg SBR+BR g^{-1} was calculated.

8 Discussion, conclusion – evolving methodologies

As presented throughout the chapter, the methodologies used for microplastic sampling, treatment, and analysis are far from homogeneous. Few published studies present a complete set of comparable methodologies. For example, an investigation of studies on microplastic contamination in river environments showed that almost no study was fully comparable with another (Dris et al., 2024). This lack of homogeneity can be explained in two ways.

First, the study of microplastic contamination in the environment is an attractive topic that continues to gather experts from multiple scientific fields. These experts bring their own knowledge and practices, and study different aspects of this emerging pollution. As a consequence, the array of methods used to collect and analyse samples are adapted to address diverse problematics.

Secondly, the methods currently used are far from optimal. The majority of published studies analyse a fraction of all microplastics using spectroscopic methods, and several concerns remain with the potential contamination of loss or particles during the preliminary treatment. Consequently, methods are still evolving and should keep being developed before they become truly standardized.

Figure 21 is a summary of the scientific strategy selected in the remaining of this PhD. In the second chapter, the atmospheric compartment is considered as a potential secondary source for microplastics. In order to assess the deposition rates of microplastics ranging from 25 to 500 µm, continuous bulk atmospheric deposition monitoring campaign are conducted with passive

samplers. The collected samples are successively treated with NaI and the Fenton reagent, or NaI and 30% vol/vol H_2O_2, before their microplastic contents are quantified by micro-FTIR imaging analysis and the SiMPle software.

In the third chapter, the spatial distributions and infiltration of microplastics ranging from 25 to 500 µm, as well as TRWP in the soils of a roadside sustainable urban drainage system are assessed. Samples are collected by manual coring and split to undergo specific treatments, before their microplastic abundance is quantified by micro-FTIR imaging, and the TRWP concentration is indirectly measured by Py-GC-MS analysis.

In the fourth chapter, macrolitter accumulation is monitored by monthly collections and are characterized chemically and functionally.

The scientific strategy and set of practices selected in this PhD are the result of multiple decisions. Some were made to conform to the dominant practices or recommendations in the literature, while others were made in order to avoid clear limits that these practices prevented. Some choices were made to efficiently address the scientific questions raised by this project. Finally, some decisions were taken arbitrarily, or were constrained by technical limitations such as the need to optimise the cost or time of the sampling campaigns.

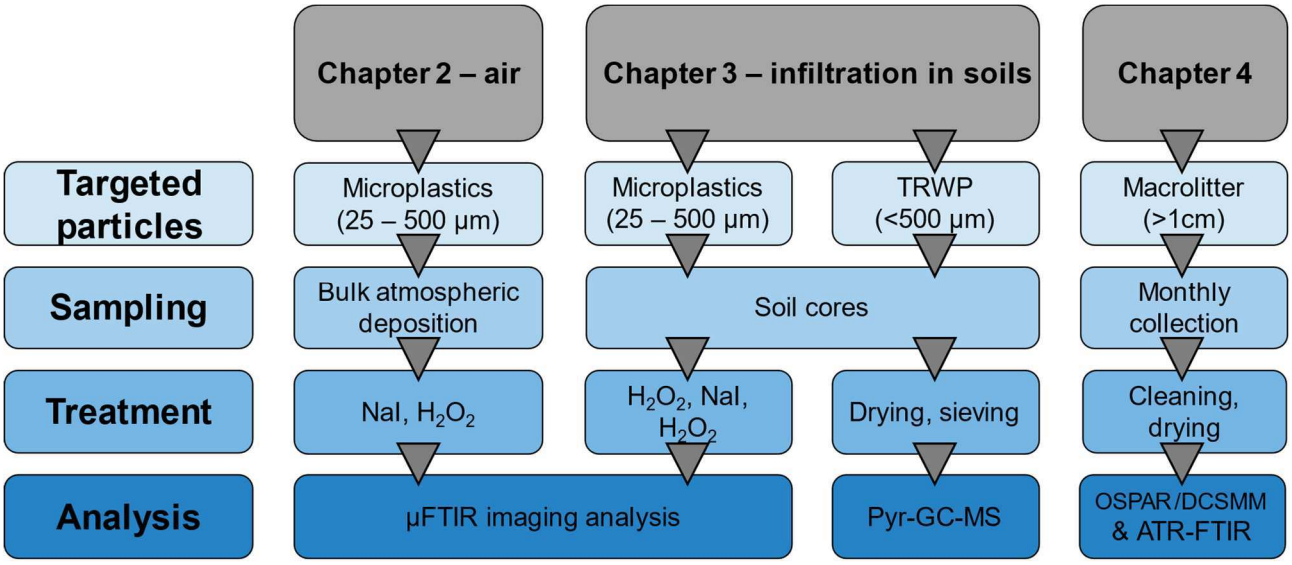

FIGURE 21: SUMMARY OF THE MAIN PRACTICES SELECTED FOR THE FOLLOWING CHAPTERS OF THIS PHD

Chapter 2 – Microplastic transfer through atmospheric deposition

1 Contents

2 Introduction

The atmosphere is the first compartment microplastics are susceptible to interact with as they are continuously produced from the abrasion of urban environments. It is thus likely to play a major role in microplastic transfer dynamics from sources into receiving environments.

The methodological strategy of this PhD now established, this chapter focuses on the impact of urban activities on microplastic transfer by the atmospheric compartment. First, a literature review of the current major results on microplastics in the atmospheric compartment highlights the major knowledge gaps of the field, and the way this work can contribute to address them. The results of five atmospheric deposition monitoring campaigns are described and compared with each other and with the literature. In order to assess the effect of human activity, atmospheric deposition is compared in multiple urban and rural sites. Moreover, the impact of the reduction of traffic caused by the 2020 national lockdown on microplastic atmospheric deposition in an urban site is highlighted.

At the moment, the effect of human population density and related activities on atmospheric microplastic concentrations or deposition rates is unclear. While MP studies in the ocean air found lower concentrations than in other environments (Allen et al., 2020; K. Liu et al., 2019d; Wang et al., 2020), studies of atmospheric deposition in terrestrial rural areas found similar concentrations as in urban environments (Allen et al., 2019; Klein and Fischer, 2019). In a study by Klein & Fischer, the authors compared both atmospheric deposition in urban and rural environments, and surprisingly obtained higher particle concentrations in the rural sampling sites (Klein and Fischer, 2019). However, no other study confirmed this observation, and no study has directly compared suspended atmospheric deposition concentration in remote and less remote environments. Klein & Fischer suspected that the higher particle concentrations are caused by local effects: the proximity of a highway in one of the rural sites, and a wash-out effect of particles stuck in leaves during rain events in the second rural site. Despite the lack of clear evidence, authors suspect that atmospheric microplastics are more concentrated in high human activity areas.

3 Bibliographical contextualization – knowledge and knowledge gaps of atmospheric microplastic studies

The content of this section is inspired from the following review: Microplastics in the atmospheric compartment: a comprehensive review on methods, results on their occurrence and determining factors – Max Beaurepaire, Rachid Dris, Johnny Gasperi, Bruno Tassin – 2021 – https://doi.org/10.1016/j.cofs.2021.04.010

Investigations on the atmospheric component of this PhD began in late 2020 with the redaction and subsequent publication of a literature review. Indeed, an article was published in April 2021 in the journal *Current Opinion in Food Science*. The article is entitled *Microplastics in the atmospheric compartment: a comprehensive review on methods, results on their occurrence and determining factors* (Beaurepaire et al., 2021). The graphical abstract of the document is shown on Figure 22.

In that study, the literature on microplastics in the atmospheric compartment was reviewed and commented. The dominant methodologies used by the literature were exposed, and are presented earlier in this PhD on chapter 1. In addition, the general orders of magnitude of microplastic abundances in the atmosphere, as well as atmospheric microplastic deposition rates, were exposed and commented on. The possible factors affecting the sources and transfer of microplastics into other environments were discussed. A short insight into the modelling – or lack thereof – of

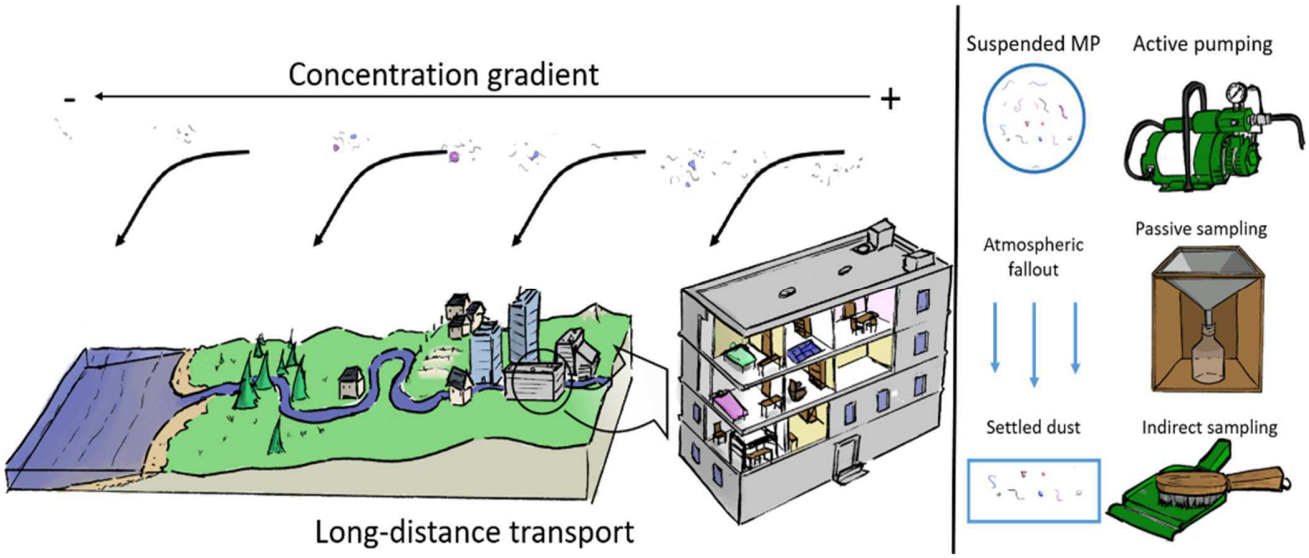

FIGURE 22: GRAPHICAL ABSTRACT OF THE REVIEW ARTICLE (BEAUREPAIRE *ET AL.*, 2021)

microplastic transport in the atmospheric compartment was provided. Finally, the study highlighted the current knowledge gaps and research insights on the topic.

The aim of this initial review was not to delve into the details of each study, but rather to provide a comprehensive overview of the state of knowledge at the start of this PhD. In this section, the findings of the review are complemented by insights into the more recent literature on microplastics in the atmospheric compartment. In particular, it highlights the current state of knowledge and identifies knowledge gaps that this PhD aims to fill.

3.1 Bibliographical methodology and commentary

The literature was gathered for the preliminary review using the Web of Science® search engine. In order to obtain all relevant studies, papers were sorted both by relevance and by date, and an array of keywords were used. The main query used was as follow:

TI = (microplastics AND (~air OR ~airborne OR ~atmosphere OR ~atmospheric)) OR KA = (microplastics AND (~air OR ~airborne OR ~atmosphere OR ~atmospheric)).

The objective of the query was to gather all papers relating to microplastic pollution in the atmospheric compartment, either indoor or outdoor, targeting either suspended particles or atmospheric deposition. While precipitations and snow samples are indirect representations of microplastics in the atmospheric compartment, studies on microplastics in snow or rainwater samples were not gathered.

By December 2020, a total of 45 published articles were found on the subject of microplastics in the atmosphere. This number includes a high fraction of bibliographical reviews: a fifth (10 out of

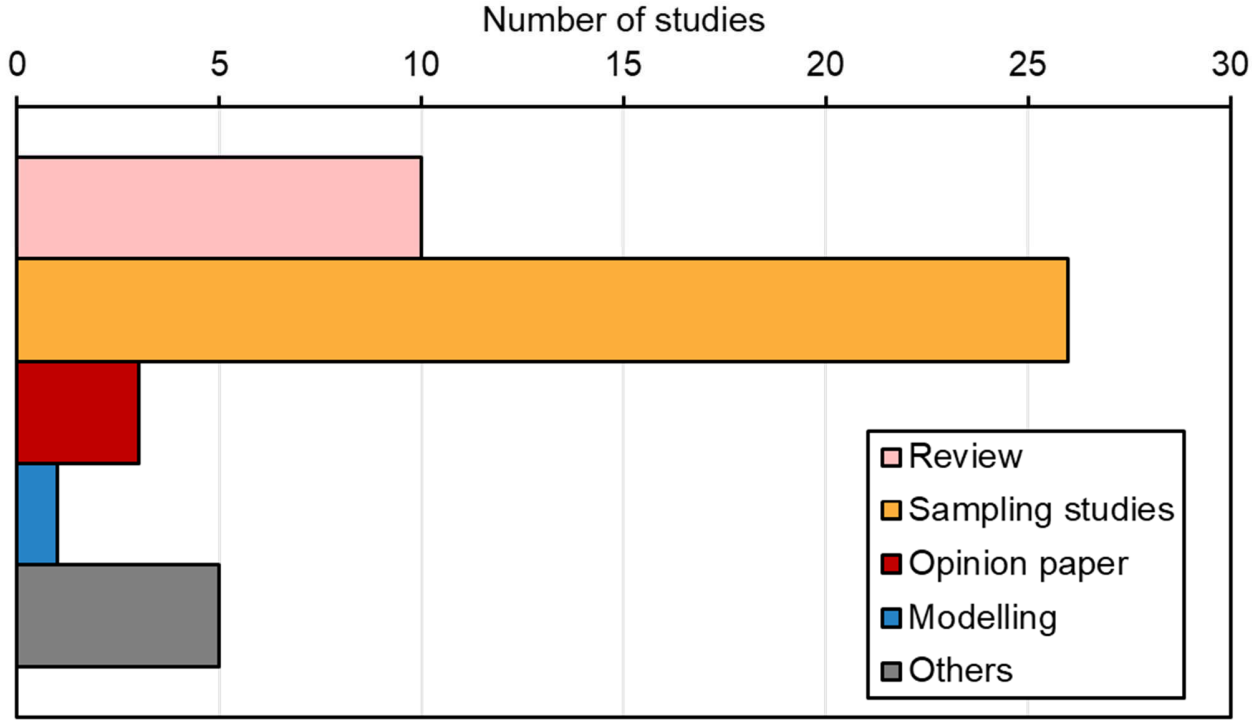

FIGURE 23: DISTRIBUTION OF STUDIES IDENTIFIED IN THE 2021 LITERATURE REVIEW

45) of the papers found were reviews. The review specifically aimed at providing a comprehensive and comparative overview of methods and results used. Twenty-six articles include samples of microplastics from the atmospheric compartment. Other articles include physical models of microplastic transport by the atmosphere, ecotoxicity assessments, methodology presentations and opinion papers. Figure 23 represents the respective number of studies of each major types. Excluding reviews and opinion papers, 77% (24 out of 32) of all studies found date from 2019 or later, while only 9% (3 out of 32) date from 2015, indicating a major acceleration of research on the topic. No study was found earlier than 2015, with the founding paper by Dris et al. (Dris et al., 2015). The total number of published studies dramatically increased since the publication of this

first study. As mentioned on chapter 1, when the same query was conducted in late December 2023, **239** studies were identified. 49 of these published studies are identified as review articles. As this number of studies is too high to be manually analysed in an extensive manner, the majority of the bibliographical discussion of this section is conducted on the results of the 2021 review, and is only completed with observations from the more recent literature.

3.2 Targeted particles and particle sizes

As was discussed in chapter 1 of this manuscript, the definition of microplastics and the category of particles targeted in microplastic studies remains a complex issue. The chemical definition of plastics is often implicit and left unmentioned. This observation remains true in studies dedicated to the atmospheric compartment. In many studies, a distinction between fibres and particles is made by the studies, with the focus being made on atmospheric fibres (Dris et al., 2017; Stanton et al., 2019).

As for the study of microplastics in other environments, the targeted size of particles is highly variable from study to study. The smaller identified size is largely dependent on the analytical method selected. Studies using visual identification in part to identify microplastics are unable to target particles as small as studies using a micro-FTIR or a micro-Raman. This variability in target sizes of microplastics is likely to reflect on the quantification of microplastics. Figure 24 shows the lower limit of detection of studies focusing on suspended atmospheric microplastics, along with the microplastic abundance in MP m^{-3} obtained by these studies. Figure 25 shows the lower limit of detection of studies focusing on atmospheric deposition of microplastics, along with the deposition rates obtained in MP m^{-2} d^{-1}. The highest limits of detection are typically noted in older studies, and are observed in studies focusing on atmospheric deposition of microplastics. No clear correlation is noted between the cutoff size of studies and the number of particles.

FIGURE 24: LOWER CUTOFF SIZE IN µM (A) AND CONCENTRATION IN N/M^3 (B) OF SUSPENDED AIR SAMPLES. THE COLOURS INDICATE THE LOCATION TYPES OF SAMPLES: YELLOW SAMPLES WERE TAKEN IN URBAN AREAS, ORANGE REPRESENT INDOOR SAMPLES, AND BLUE WERE SAMPLED IN REMOTE OR OCEANIC ENVIRONMENTS. THE ORDERS OF MAGNITUDE ARE SHOWN IN A LOGARITHMIC SCALE.

3.3 Quantification of airborne microplastics

The quantification of microplastics in the atmospheric compartment is represented using different units based on the sampling strategy used for a given study. In the case of samples collected from **atmospheric deposition**, the objective is to assess the transfer of microplastics from the atmospheric compartment into other environments. Thus, results are presented as deposition rates,

calculated in count of microplastics per unit of surface area per unit of time. The most common representation is MP m^{-2} d^{-1}.

When **suspended particles** were directly collected, usually via active air pumping, the objective of the study is to directly assess the level of contamination of the air. Results are indicated as a microplastic abundance, in counts of microplastics per unit of volume. The most common representation is MP m^{-3}.

In several studies, microplastic atmospheric deposition is indirectly assessed by quantifying the microplastic content of settled dust. In these studies, results are presented as a microplastic abundance per unit of mass : abundances were indicated in MP mg^{-1} number of MP per sample, each sample weighing 15g of dust (Abbasi et al., 2019; Dris et al., 2017). In order to directly compare these results to other studies on microplastics in atmospheric deposition, an extrapolation of the microplastic deposition rate must be conducted using studies that evaluated dust deposition rates over a surface (Norouzi et al., 2017; Seifert et al., 2000).

As quantitative results vary over 3-4 orders of magnitudes, log scales are used to compare the

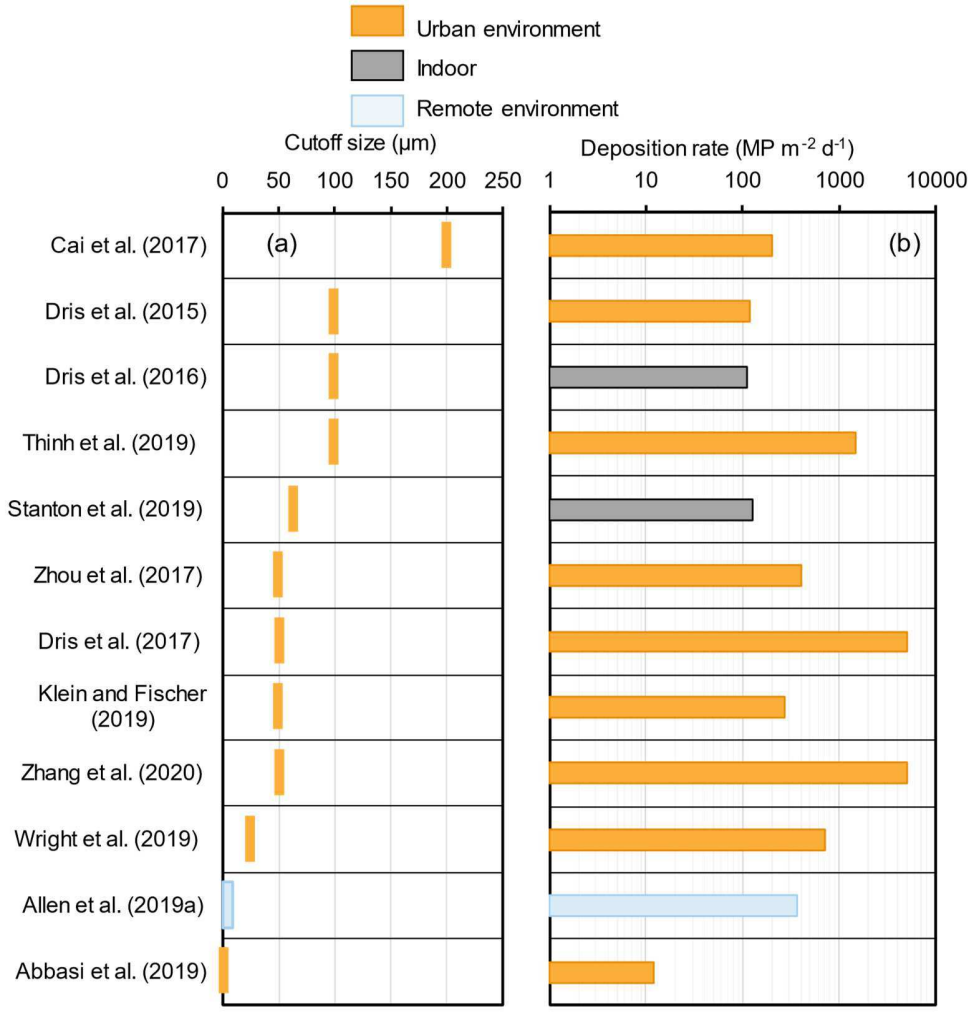

FIGURE 25: LOWER CUTOFF SIZE IN µM (A) AND DEPOSITION RATE ORDERS OF MAGNITUDE IN ATMOSPHERIC DEPOSITION SAMPLES IN N/M²/D (B) FOUND BY THE LITERATURE. YELLOW SAMPLES WERE TAKEN IN URBAN AREAS, ORANGE SAMPLES REPRESENT INDOOR DEPOSITION, AND GREEN SAMPLES WERE TAKEN IN A RELATIVELY REMOTE AREA. THE ORDERS OF MAGNITUDE ARE SHOWN IN A LOGARITHMIC SCALE

results of the different studies. Figure 24 and Figure 25 represent the air concentrations and deposition rate orders of magnitudes of studies along with the cutoff sizes of studies. According to Figure 24, orders of magnitude ranged between 0.01 and 10 MP/m^3.Samples taken in oceanic environments seem to have lower concentrations than in urban or indoor areas. Figure 25 shows that for a cutoff size of 50 or 100 µm, deposition rates were found in the order of 100 MP/m^2/d. Beside the average order of magnitude, numerous studies presented a high variability among samples, often reaching one order of magnitude of internal variations.

While this is not a systematic observation, studies wherein cutoff size is lower often obtain higher orders of magnitude than studies with a higher cutoff size. In particular, Allen *et al.* (Allen et al., 2019) obtained a higher order of magnitude than Dris *et al.* (Dris et al., 2016b, 2015) or Cai *et al.* (Cai et al., 2017a) when considering all size classes, despite sampling in a rural area. However, when considering only size classes shared with the other studies, the particle count becomes lower for Allen *et al*. This suggests that lower size classes represent a large number of particles that are yet to be investigated. Indeed, most studies mentioned that the most numerous size class of samples was either the smallest size class, or the size class just above. The smallest class of particles is often underrepresented because of identification artefacts. Smaller atmospheric microplastics are likely to represent a greater health concern than larger particles. (Davidson et al., 2005; Gasperi et al., 2018).

In most studies, higher concentrations were observed in indoor air than in outdoor air (Dris et al., 2017; Gaston et al., 2020; Prata et al., 2020). A similar difference has regularly been reported when comparing indoor and outdoor contamination for other pollutants (Monn, 2001). In the case of other pollutants, the presence of air conditioning and dust filtration was shown to reduce indoor pollution relative to outdoor. In a 2022 study, air conditioning filters were found to represent both sinks and potential sources of indoor microplastics (Chen et al., 2022). In one study by Prata *et al.,* suspended fibres were observed in higher concentrations outdoor than indoor. However, the authors reported a high number of fibres in field blanks, which reduced the reliability of results (Prata et al., 2019a). Outdoor, size and concentration of particles may be affected by sampling height. In one of their studies, Liu *et al.* (K. Liu et al., 2019b) compared the suspended atmospheric microplastics obtained for three different heights (with 78.3 meters between the lowest and highest site). Lower concentrations were in the highest location. The largest particles recorded were also lower at a higher altitude.

Indoor deposition rates seem to be related to human activity. In a study by Song *et al.*, one office and 2 houses were studied over the course of several months (Song et al., 2020). Week days and weekends were separated. Higher counts of particles were noted during week days in the office sampling site, and on the weekend in the house. Human activity has been suggested to cause deposited particles to get back into suspension. According to the National Human Activity Pattern Survey, 89% of human activities are conducted indoor (Klepeis et al., 2001). As a result, indoor air represents most of human exposure to airborne MP. While no direct effect on health of current MP

concentration have been observed, that risk of exposure is heightened by the higher concentrations found indoor.

A correlation between MP and rainfall has been observed by Dris *et al* (Dris et al., 2017, 2016b). During high precipitation periods, the particle counts were higher and more variable than during dry periods. This observation has been confirmed by Liu *et al.* (K. Liu et al., 2019b) and Allen *et al.* (Allen et al., 2019). Although there is no direct correlation between daily rainfall and MP deposition, the authors suggest a washout of MP during rain events.

In a recent study by Parashar and Hait, wet atmospheric deposition was collected (Parashar and Hait, 2023). The wet deposition rates obtained were several orders of magnitude superior to deposition rates from studies based on bulk atmospheric deposition, suggesting a major role of precipitation on atmospheric microplastic deposition.

3.4 Characterization of the pollution

As discussed on chapter 1 of this manuscript, microplastics are not a monolithic category of micropollutants, but they rather represent a diverse family of objects, including shapes ranging from spheres to fibres of particles, sizes ranging over 5 orders of magnitude, and hundreds of thousands of chemical compositions. In order to understand the sources and fate of microplastics in an environment, it is necessary not only to quantify the microplastics but also to describe and characterize the particles observed.

In studies dedicated to the atmospheric compartment, microplastics are characterized by size, shape and colour. The distribution of identified polymers is also described. In a majority of studies, fibres seem to represent the most common microplastic shape, followed by films and fragments. Microbeads are not always found, and represent the least frequent MP shape when found. A wide array of polymers is identified by studies, including PE (LDPE and HDPE), PP, PS, PVC, PET and others. No clear pattern of composition repartition is noted from the literature. In some studies, PE is noted as the main polymer type (Gaston et al., 2020; Klein and Fischer, 2019). PET is the main polymer among fibres in several studies (Dris et al., 2017, 2016b; Stanton et al., 2019).

The higher proportion of fibres is still to be put in perspective. According to Cai *et al.* (Cai et al., 2017a), the proportion of identified fibres that were confirmed of synthetic origin was significantly

lower than other particles. Only two studies found fragments to be the dominant shape identified in samples, respectively 88% and 95% of found MPs (Allen et al., 2019; Klein and Fischer, 2019). Another issue caused by shapes is on the definition of researched particles. In two studies, fibres were the only researched particle types (Stanton et al., 2019; Zhang et al., 2020). As a result, concentrations were only indicated in number of fibres per volume unit.

Figure 26 represents the cumulative size distribution of microplastics according to the size classes indicated in all studies. Higher size classes always appear to represent a smaller proportion than size classes closer to the cutoff point. Moreover, while size repartitions were variable between studies, size repartitions of fibres and fragments separately remained relatively comparable. Fibres were generally longer than the major dimension of fragments, and can reach sizes up to several millimetres while fragments seldom reached 1 mm. Because fragments are typically smaller than fibres, the observed predominance of fibres may be caused by the methodologies used by the authors. Smaller particles may still be dominated by fragments.

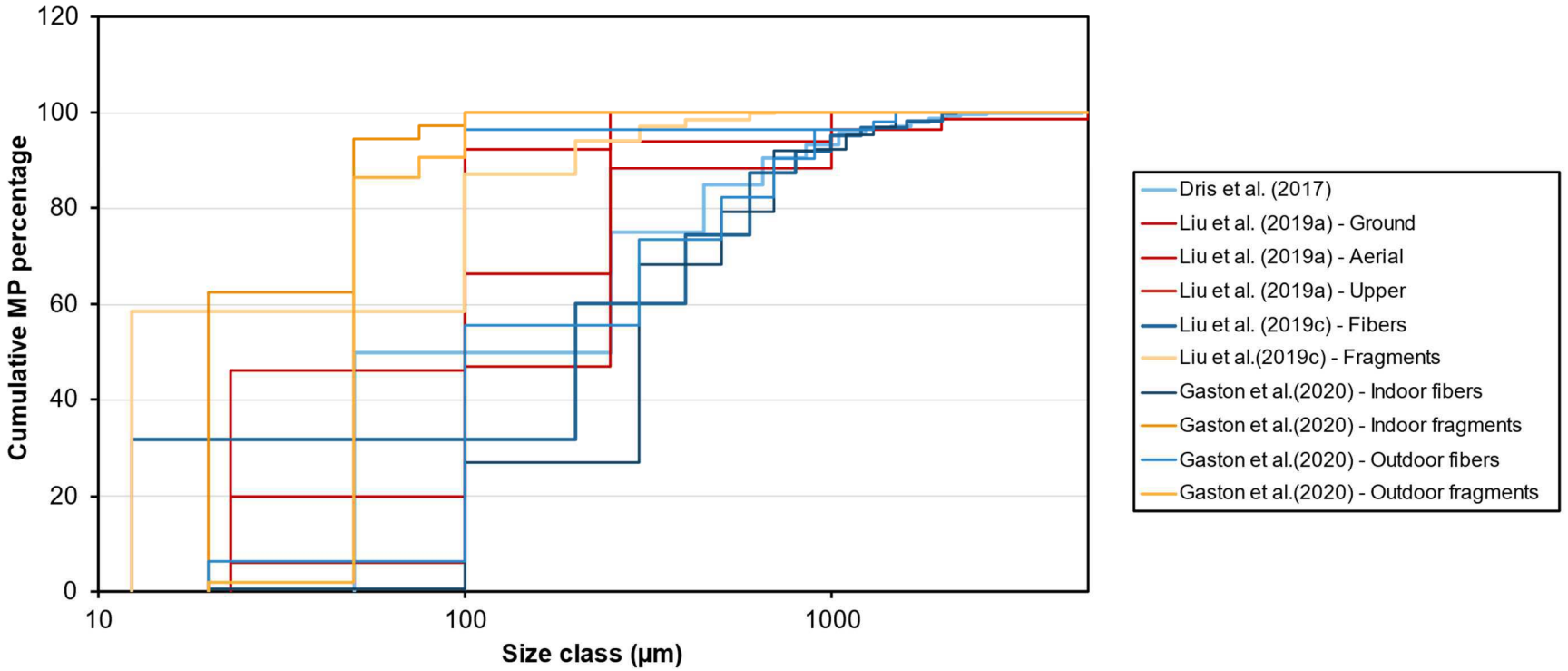

FIGURE 26: CUMULATIVE SIZE DISTRIBUTION OF SUSPENDED MICROPLASTICS FOUND BY DIFFERENT STUDIES. ORANGE LINES REPRESENT THE SIZE DISTRIBUTION OF FRAGMENTS. BLUE LINES REPRESENT THE SIZE DISTRIBUTION OF FIBRES. RED LINES REPRESENT THE SIZE DISTRIBUTION OF MICROPLASTICS REGARDLESS OF GEOMETRY

3.5 Sources and transport of airborne microplastics

Most studies suggest that textile wear off is a significant source for airborne fibres. However, actual results on sources of microplastics in the air are limited. In one study by Zhang *et al.*, the authors sampled textiles from the room where they recorded particle depositions (Zhang et al., 2020). They found great similarities between the sampled textiles and the infrared spectra of sampled particles. In a study published by O'Brien *et al.* in 2020, the fibre release caused by laundry driers was evaluated (O'Brien et al., 2020). While only fibres were estimated, their concentration was on average 10 times higher in air out of the laundry drier than in a room blank. In a study published by De Falco *et al.* in 2020 (De Falco et al., 2020), the textile wear off caused by laundry washing was compared to the wear off caused by everyday use. The annual release of microfibers by one person was calculated to be on a similar order of magnitude as the release caused by one laundering.

Several sources of other atmospheric microplastics shapes are suspected. Road paint, tyre and brake wear off, and general urban wear off are likely major sources of MP into the atmosphere. Landfill emission is also currently suspected, and the deposition of MP in a landfill area has been recently assessed (Thinh et al., 2020) However, no actual result has been obtained on the subject. The high variability of polymer types and additives among MP, along with the difficulty to sample all potential MP sources makes such results challenging to obtain.

The finding of microplastics in high-altitude and largely remote areas by several studies not directly linked to the atmosphere suggest a long distance transport of airborne microplastics (Bergmann et al., 2019; Napper et al., 2020b; Zhang et al., 2021). However, few studies actually produced a transport assessment of microplastics in the air. In particular, no comprehensive model of MP transportation by the atmospheric compartment has yet been computed. Allen *et al.* identified the possible transport trajectories of deposited MPs in a remote area (Allen et al., 2019). Major wind events and precipitation event trajectories over the sampling period were determined and compared to the major MP trajectories. Wind was determined to be a key factor in atmospheric microplastics transport. Similarly, Liu *et al.* suggested a long distance transport from the land to the ocean in two separate studies. (K. Liu et al., 2019d; Liu et al., 2020).

Evangeliou *et al.* modelled the transport of car tyre and brake particles from urban areas to remote environments (Evangeliou et al., 2020). In their study, the particle emission of car tyres and brakes

was calculated based on tyre weight loss measurement over their lifetime. Data was extrapolated worldwide by using national CO_2 emissions as a proxy for car use. While all particles were transported, smaller particles were dispersed more widely than larger ones

3.6 Conclusion – major knowledge gaps and objectives of this work

Some similarities can be observed among the sampling analysing methods of suspended and deposited MPs. These methods still need to be even more standardized to facilitate data comparison. In particular, the types of particles identified and quantified need to be better defined: it is difficult if even possible to compare the data obtained in one study that exclusively counted fibres to the results of another study that counted all particles. Similarly, the cutoff size of quantified data needs to be more clearly indicated and compared to that of other studies.

Despite these dissimilarities, a convergence of results was noted. Atmospheric microplastic concentrations seem to be affected by elevation and human presence. Larger atmospheric microplastics mainly consist of fibres, while smaller particles are more varied.

The atmosphere is currently recognized as a major vector of long-distance MP transport. However, there is still a lack of comprehensive models confirming or infirming this suspicion. Understanding the behaviour of MP in the atmospheric compartment is necessary to better understand the transport mechanics of MPs from their sources to their sinks. While MPs in dry atmospheric deposition and wet atmospheric deposition may behave differently, the integration of the role of precipitation will require to sample lower time periods.

In light of these knowledge gaps, this work aims to address the following objectives:

- Provide reliable data on microplastics transfer fluxes from the atmospheric compartment in different contexts
- Contribute to evaluate the effect of urban activity on atmospheric deposition of microplastics
- Evaluate the influence of meteorological parameters on atmospheric deposition of microplastics

4 Sites of interest

In this PhD, atmospheric deposition was monitored in 4 sampling sites, over the course of 5 sampling campaigns from 2020 to 2022. Two sites of interest were centred around the Paris megacity, an agglomeration of 10.9 million inhabitants. The other two were centred around the Nantes agglomeration, a regional metropolis in the west of France with an urban population of 672,000 inhabitants. The location of these two regions is represented on Figure 27.

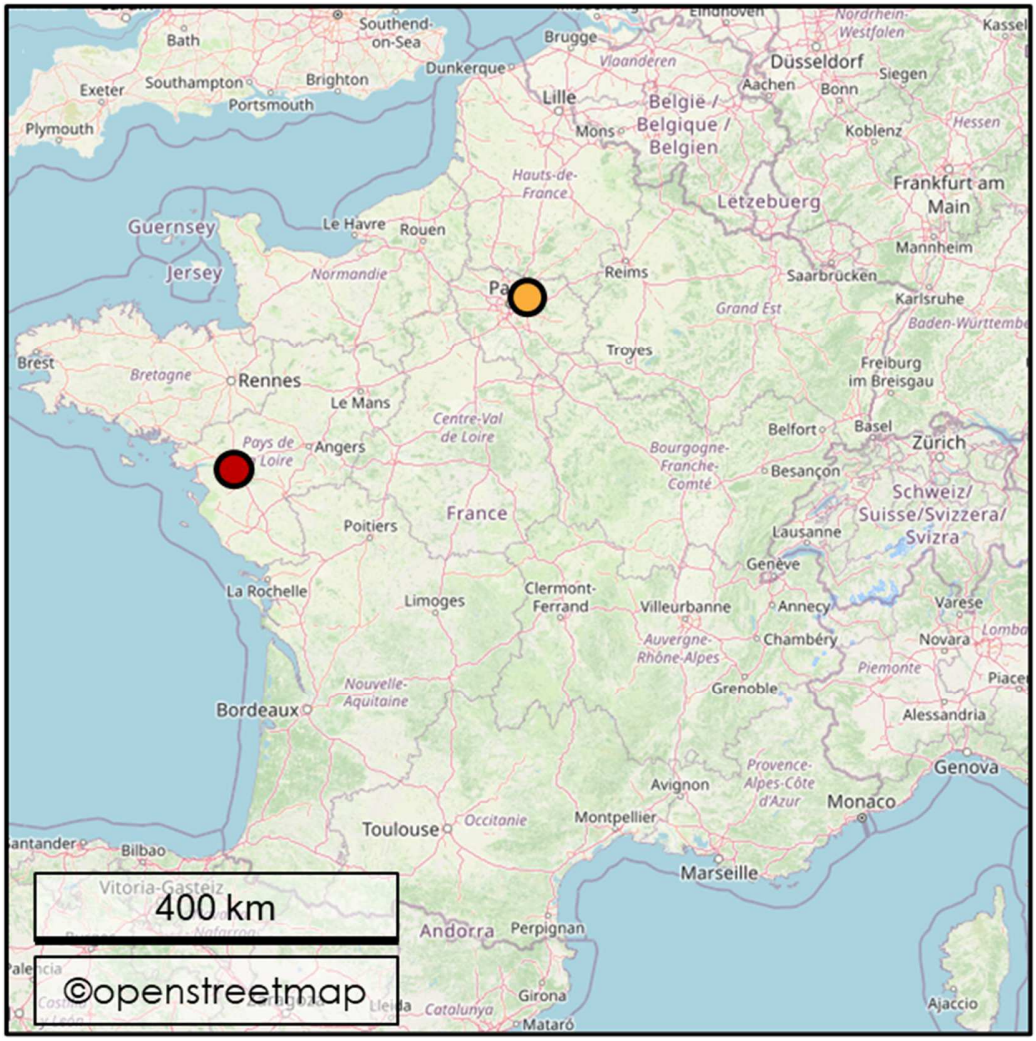

Figure 27: Location of the two main regions of interest for atmospheric deposition samples. The yellow circle indicates the Paris region sampling area, the red circle indicate the Nantes region sampling area.

4.1 Paris region sampling sites

4.1.1 Geographical context

The first two sites of interest in this chapter are located in the Greater Paris area. Paris is located in the Ile de France administrative region, which is subdivided into 8 departments. The two sites of interest presented here are located in the Seine et Marne department.

With a surface area of 2,850 km² and a population of 10.8 million inhabitants, the Paris agglomeration is the largest urban area in France and in the European union. It is a centre of economic activities including industries, logistics, and office work. The surrounding rural area is used for intensive agriculture, particularly cereal farming (Insee, 2021).

The region experiences an oceanic climate. Spring is not characterized by a significant wet season, but rather by frequent downpours lasting a few hours with limited intensity. Extended periods of dry weather lasting longer than one week are infrequent.

4.1.2 Description of the sampling sites

The sites of interests' location in regards to the Paris urban area are represented on Figure 28a. Site A, (48.84227N, 2.58833E) is located in a suburban campus located in Champs-sur-Marne, a city with a population of 25,230 inhabitants that is part of the Paris conurbation, 15 km east of Paris. This site was also considered by Dris et al. in their first study on microplastic atmospheric deposition in the greater Paris(Dris et al., 2016b). It is surrounded by an approximate population density of 3,500 inhab km^{-2} within a radius of 5 km. The sampler itself was located at a height of ~10m above ground, on the flat section of a vegetated roof on a campus building. Figure 28b shows a satellite view of the site, with the vegetated roof highlighted in black and the sampler's location marked in colour. Although the site was unobstructed within a radius of 30 m, a taller building was located 30 m north of the sampler.

Several potential microplastic sources were identified surrounding the sampling site. Firstly, several transport infrastructures are located around the site. Public transit train tracks pass near the sampling site and are located 100m north at their closest point. A high traffic highway is located 1km south, which represents a major source of traffic in addition to the surrounding traffic in the campus. Secondly, several construction works were noted during the period of normal activity.

Major construction works has taken place in a train station located 500m north-west since 2018, and were paused in 2020. Repairs to the roofs of a nearby construction building were debuted in March 2021. Finally, the site is a campus and thus is marked by the daily presence of students and workers.

Site B (48.82406N, 3.13965E) is located in Boissy-le-Châtel, a town with a municipal population of 3,200 inhabitants. Figure 28c shows a satellite view of the sampling site. The site is located 70 km East of Paris, and is a relatively rural area surrounded by intensive agricultural activities. The municipal area has a population density of approximately 323 inhab km^{-2}, with a population density of approximately 500 inhab km^{-2} in a radius of 5 km around the sampler. The site is well-equipped and monitored for precipitation and weather events.

FIGURE 28A – LOCATION OF THE TWO SAMPLING SITES FROM THE PARIS REGION; B – SATELLITE VIEW OF THE SUBURBAN SITE; C – SATELLITE VIEW OF THE RURAL SITE

4.2 Nantes sampling sites

4.2.1 Geographical context

The two other sites of interest for this chapter are located in the Nantes urban area. Nantes is located in the Pays de la Loire region, in the Loire-Atlantique department. It has a municipal area of 65.2 km² for a municipal population of 320,000 inhabitants. Its conurbation is the 8th largest agglomeration in France, with a surface area of 499 km² and a population of 672,000 inhabitants. This represents a population density of 5,500 inhab km^{-2}.

Nantes is located at the estuary of the Loire River, the longest and second-highest flowing French river. It experiences an oceanic climate, similar to that of the Paris region. The surrounding rural area is used both for forage farming, and for intensive cereal farming (Insee, 2021).

4.2.2 Description of the sampling sites

Figure 29a represents the location of the two sites of interest in the Nantes region. The first site, noted site C, is located at the La Bouteillerie cemetery in the centre of Nantes (47.222209N, 1.537428W). A satellite view of the site is represented on Figure 29b. While the sampling site is in the eastern corner of a cemetery, it is surrounded by residences, traffic, and industrial activities. The nearest street is 40 m to the east. The nearest streets in the prevailing wind directions (south west to north west) are located 150 m away. A major passenger train station is located 600 m south-west from the site, with the track passing 400 m south of the sampler at their closest. The site is close to a sport complex 300 m to the north-west and a fire station 200 m to the east. Additionally, a church was located 20 m to the south-east of the site.

The second Nantes site, noted site D, was located in Bouguenais, a peri-urban municipality approximately 10 kilometres southwest of Nantes centre (47.155701N, 1.637061W). Similarly to the selection of site B to contrast agricultural activities with the urban activities surrounding site A in Paris, the sampler in site D was placed on an open field in a campus surrounded by agricultural activity. The municipality has a population of 20,450 for a population density of 650 inhab km^{-2}. The population density in a 5 km radius is around 500 inhab km^{-2}. The sampler was placed at a height of 2.15m above ground. While the site was unobstructed within a radius of 50m, a building

was located 50 m north. The site was located 2 km west of the Nantes airport. Figure 29c represents a satellite view of the position of the sampler on site D.

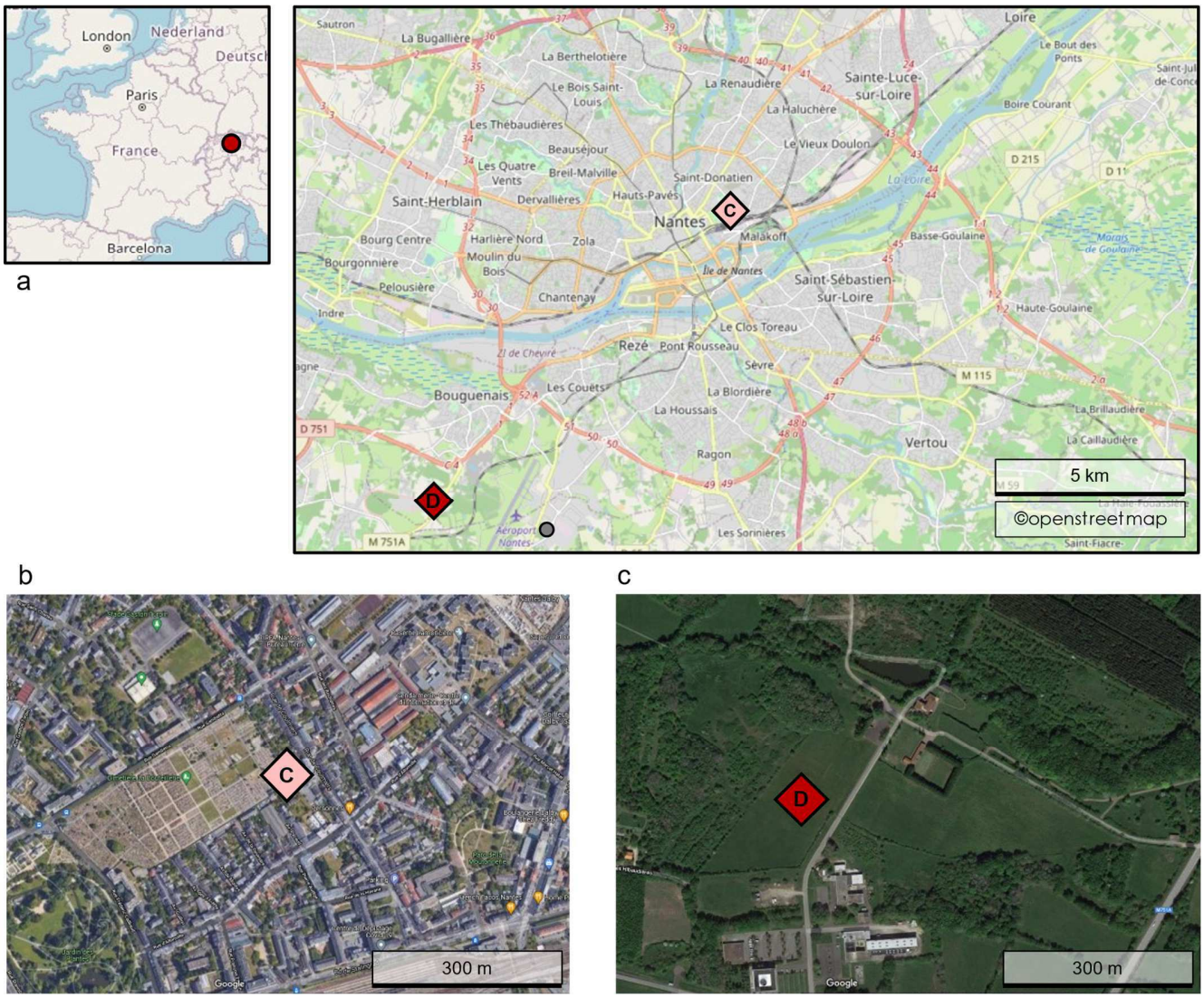

FIGURE 29A- LOCATION OF THE NANTES SAMPLING SITES; B- SATELLITE VIEW OF SITE C; C- SATELLITE VIEW OF SITE D

5 Paris region monitoring campaigns

A total of three monitoring campaigns were conducted in the greater Paris area between April 2020 and August 2021.

As detailed in the sampling section of the first chapter of this manuscript, as well as in the introduction of this chapter, the objectives of this work on the atmospheric compartment are not to assess the abundance of microplastics in the atmospheric compartment, but rather to assess the role of the atmosphere as a vector of microplastic transport into other environments, as well as the effects of urban activity on this transport. In light of this objective, the sampling campaigns for this work consist in atmospheric deposition monitoring campaigns conducted by passive bulk atmospheric deposition samplers.

5.1 Sampling setup

The passive samplers used in sites A and B had the same general structure, shown on Figure 30a. These samplers were first used in earlier studies by Dris *et al.* (Dris et al., 2015). The samplers consist in a wooden structure encasing a stainless-steel square funnel with a surface area of 0.325 m^2.Figure 30a represents the structure of the samplers used. The funnel is connected to a glass bottle at all times, and collects both settling dust and precipitation. Whenever a sample is collected, the funnel is thoroughly rinsed with tap water previously been vacuum-filtered on a glass fibre filter (porosity 0.45µm). It is then rinsed a second time with filtered analytical grade ethanol, and one last time with filtered deionised water.

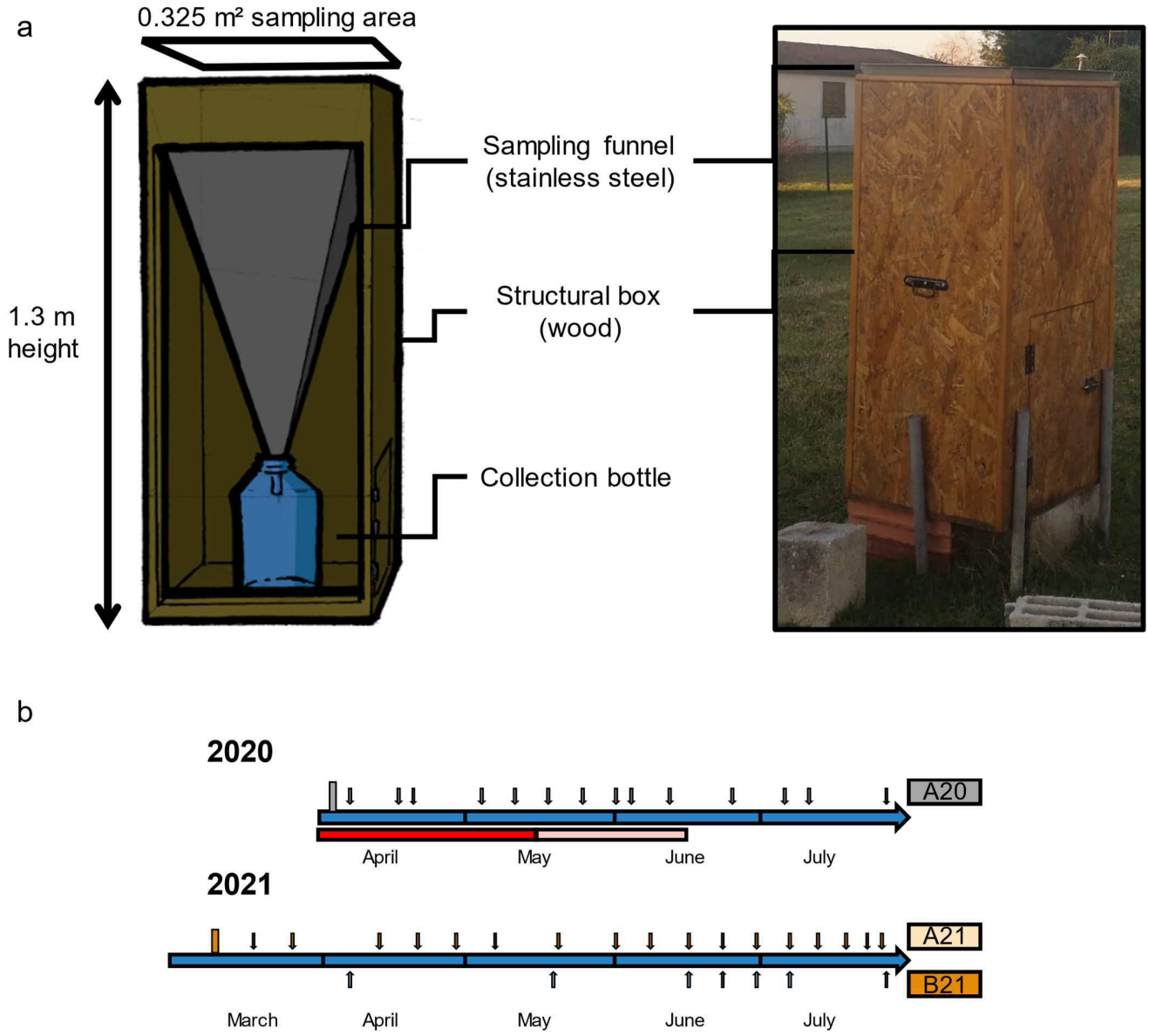

FIGURE 30A – SCHEMATIC REPRESENTATION AND PHOTOGRAPH OF THE SAMPLING SETUP USED IN SITES A AND B; B – TIMELINE OF THE CAMPAIGNS CONDUCTED IN SITES A AND B. FOR ALL CAMPAIGNS, THE FIRST MARK INDICATES THE BEGINNING OF THE MONITORING. EACH SUBSEQUENT MARK INDICATES THE COLLECTION OF A NEW SAMPLE. IN 2020, THE RED MARK INDICATES THE DURATION OF THE NATIONAL LOCKDOWN. THE PINK MARK REPRESENTS THE DURATION OF THE REGIONAL CONTINUATION OF THAT LOCKDOWN.

5.2 Monitoring campaign duration

Figure 30b represents the timeline of sampling campaigns conducted in sites A and B. Two campaigns were conducted on site A. The first campaign (A20) started on April 3rd 2020, 16 days after the beginning of the first national lockdown caused by the SARS-CoV2 pandemic. It lasted until the end of July 2020, while the lockdown lasted until June 15th. During the lockdown period, the campus was completely closed and most surrounding activities such as building sites were stopped. Traffic was reduced by more than 90% at the peak of the lockdown ("TomTom Traffic Index," 2020) During the following 45 days of monitoring, while activity slowly recovered around the sampling site, the campus remained closed. In total, 14 samples were collected in that period, 10 of which were collected during the lockdown.

Campaign A21 was used as a comparison point with campaign A20. Samples were collected in the same site, and the surrounding traffic, construction works and campus activities were operating normally. While a lockdown was installed from April 3rd to May 3rd 2021 during that period, its effect on urban activity was reduced. University courses were still conducted, surrounding construction work was maintained and the level of activity was higher than in 2020. The campaign was conducted between March and August 2021, and collected 17 samples in total.

Finally, campaign B21 was used as a point of comparison with both campaigns. While the surrounding activity was operating normally throughout the monitoring campaign, the dominant activities surrounding site B differ from the activities surrounding site A. The campaign lasted between April 7th and August 4th 2021, and collected 7 samples over that period. The two samplers were deployed at the same time for 111 days during campaigns A21 and B21. Collecting days were however not synchronized.

In site A, the exposure period between the collection of new samples ranged from 4 to 11 days. Weather forecasts from official weather websites such as https://meteofrance.com, https://meteo-paris.com and https://windy.com were followed to determine when to retrieve samples and to specifically target periods with different rain characteristics (single rain events, dry period, etc.).

Because it was 60 km away from the laboratory, site B was significantly less accessible than site A. Because of this difficulty of access, new samples were collected less regularly in site B, the time

separating samples ranging from 7 to 42 days. In order to specifically target periods with different rain characteristics (single rain events, dry period, etc.), rain events were followed daily.

5.3 Precipitation monitoring

In order to compare microplastic atmospheric deposition rates, cumulative rainfall and instances of rain events were continuously monitored from 2019 to 2021 by the Taranis Observatory (https://hmco.enpc.fr/portfolio-archive/taranis-observatory/), in a station located less than 100 m away from the sampling site. The observatory provides daily cumulative rainfall graphs which were used to read the daily rainfall with a 0.2 mm uncertainty.

Rain data for site B was collected from the INRAe's open data repository BDOH Oracle (https://bdoh.irstea.fr/ORACLE/). The data consist in hourly cumulative rainfall, and is clustered together to produce daily cumulative rainfall.

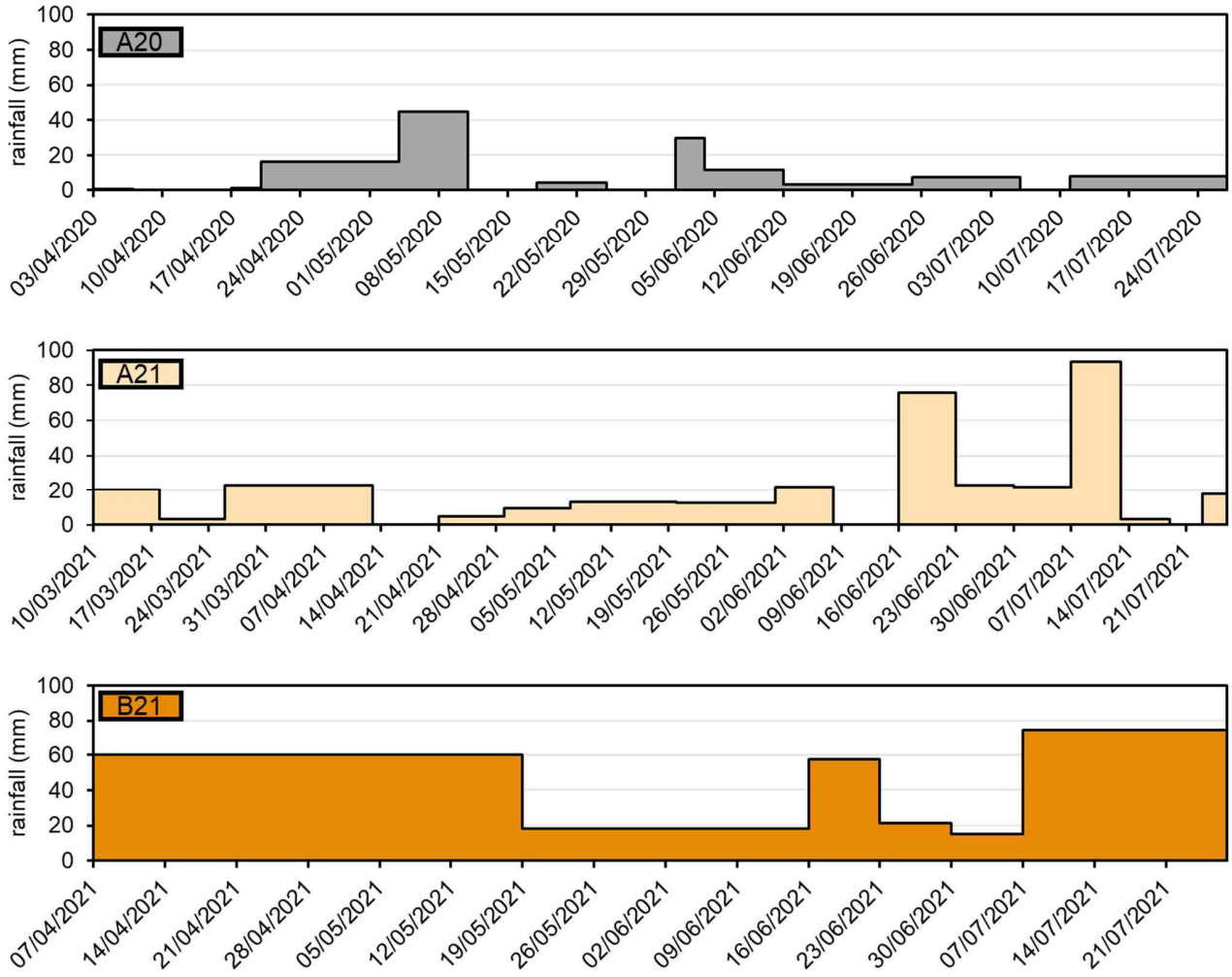

FIGURE 31: CUMULATED RAINFALL OVER THE SAMPLES OF THE THREE PARIS REGION CAMPAIGNS

6 Nantes region monitoring campaigns

6.1 Sampling setup

Two monitoring campaigns were conducted in the Nantes region between December 2021 and December 2022. These campaigns are named C22 and D22. In order to ensure the comparability between deposition rates in sites C and D, new samples were collected simultaneously at both sites

and used the same model of passive of sampler. The samplers, shown on Figure 32a, were adapted from the Norwegian Institute for Air Research particulate deposition collector (NILU, n.d.). They consist in stainless steel, conical funnels with a diameter of 200 mm. The samplers were mounted on a stainless-steel stand and were adjusted to remain at a constant height. To avoid obstruction by a wall to the east, the sampler in site C was placed at a height of 2.85 m, in order to remain 50 cm above a wall east of its location. In site D, it was placed at a height of 2.15 m. Throughout the campaigns, the samplers were maintained in a level position to ensure consistent sample collection. The metal funnel was connected to a glass bottle, which served to collect rainwater during sampling or rinsing activities. To replace samples, the metallic funnel underwent a thorough rinsing process with tap water that had previously been vacuum-filtered on glass-fibre filters, ethanol, and a third rinse with water.

6.2 Monitoring campaign duration

As the samplers used in site C and D are smaller than the ones used in site A and B in the Paris region, atmospheric deposition had to be integrated over longer time periods to ensure the retrieval of a number of microplastics superior to the number of microplastics in the blanks. In campaigns C22 and D22, samples were collected on a monthly basis, with a time interval between successive sample collections ranging from 28 to 34 days. The campaigns were conducted over the course of 12 months, and a total of 12 samples was collected at each site. Figure 32b summarizes the campaigns collected.

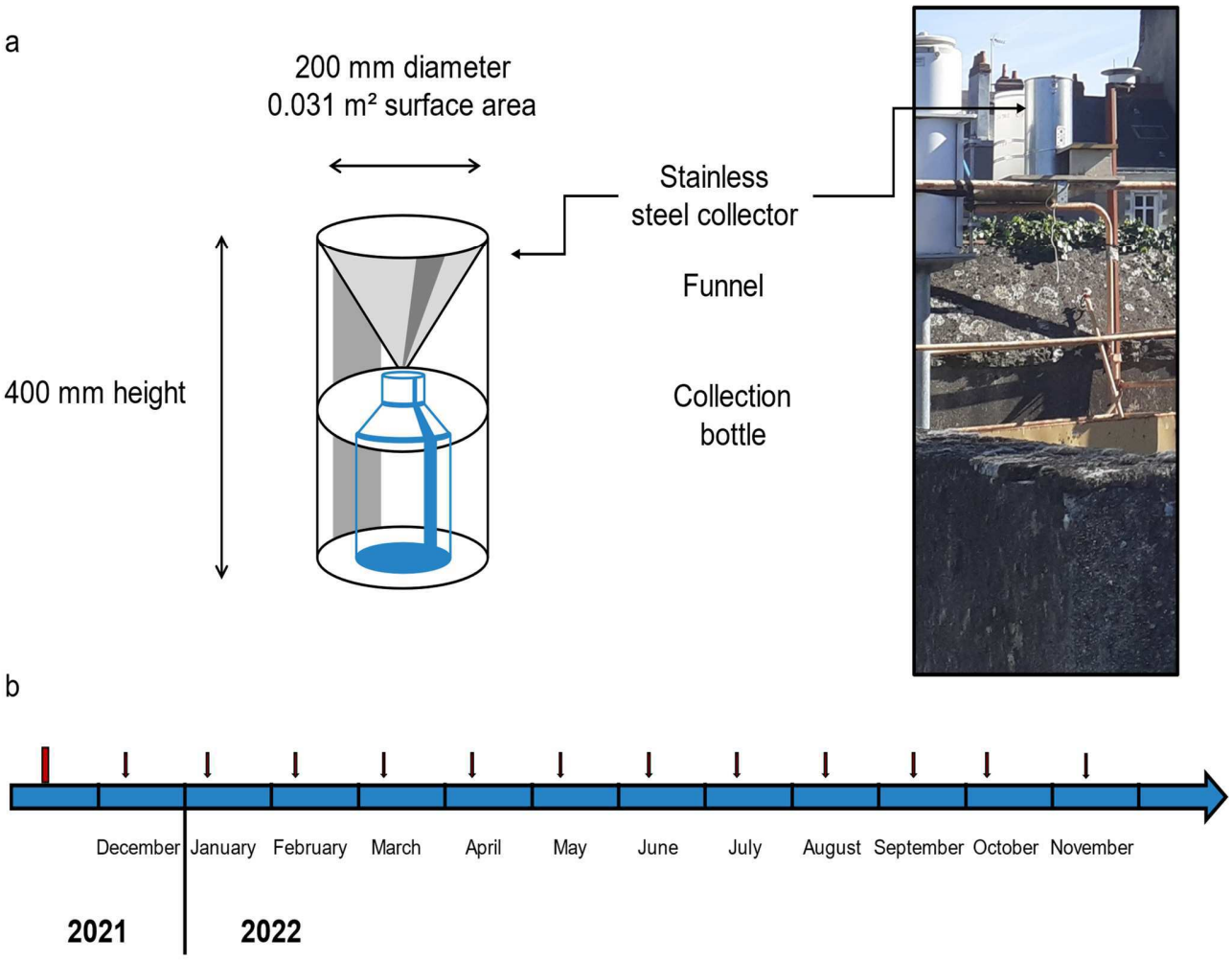

FIGURE 32A – DIAGRAM AND PHOTOGRAPH OF THE BULK ATMOSPHERIC DEPOSITION SAMPLERS USED IN SITES C AND D; B – TIMELINE OF SAMPLE COLLECTION FOR THE CAMPAIGNS C22 AND D22. THE FIRST MARK INDICATES THE BEGINNING OF THE MONITORING CAMPAIGN. ALL FOLLOWING MARKS INDICATE THE COLLECTION OF A NEW SAMPLE.

6.3 Precipitation monitoring

In order to assess the relation between microplastic atmospheric deposition and weather events such as precipitation, meteorological data such as wind speed and direction, temperature, or daily rain were collected from public meteorological stations close to the sampling sites. A meteorological station located in the centre of Nantes was used for campaign C22, and a station located in the Nantes airport, 2 km east of site D, was used for campaign D22. Data were extracted from the site https://publitheque.meteo.fr. Figure 33 represents the cumulated rainfall over each sampling period in both sites. As shown on the figure, precipitations are often similar in both sites throughout the campaign. Exceptions were however noted in January, and March 2022 where cumulated rainfall differences of more than 10% were measured. Differences of more than 20% were noted in May and September 2022.

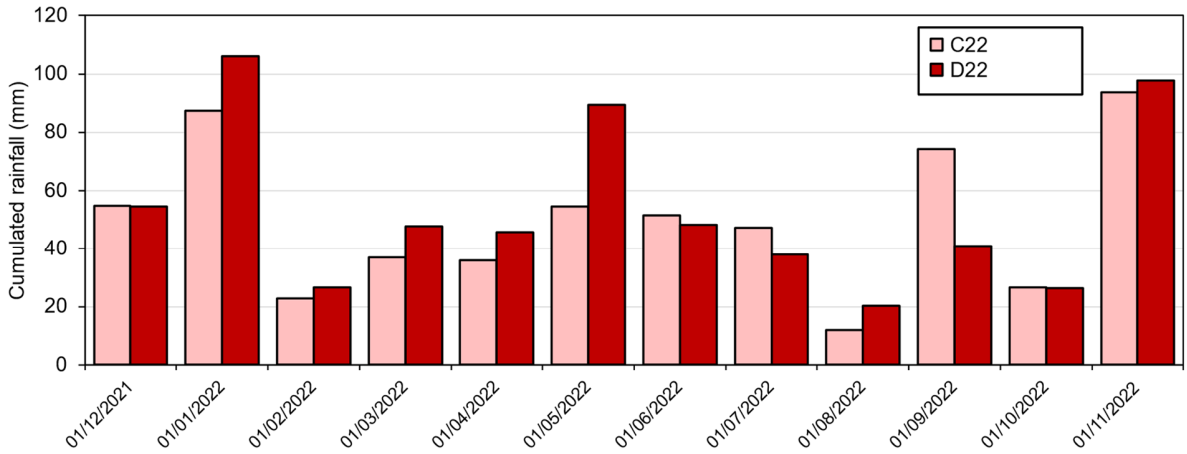

FIGURE 33: CUMULATED RAINFALL IN EACH SAMPLING SITE FOR EACH SAMPLING PERIOD FROM METEOFRANCE STATIONS ON THE AIRPORT AND IN THE CITY

7 Treatment and analysis

After their collection, samples were sieved on 500 µm stainless steel meshes to remove insects and larger plant debris from the matrix. The present work only focuses on the fraction smaller than 500 µm. Samples were then vacuum-filtered onto 47 mm diameter stainless steel filters with a pore size of 10 µm. Three to twelve filters were required to completely deposit each sample without clogging.

Figure 34 is a summarized representation of the concentration treatment and analysis for the different monitoring campaigns. As the first chapter of this manuscript was dedicated to the methodology used throughout this PhD, the details regarding the different treatment steps, µFTIR imaging analysis, and post-treatment with SiMPle are provided on that chapter.

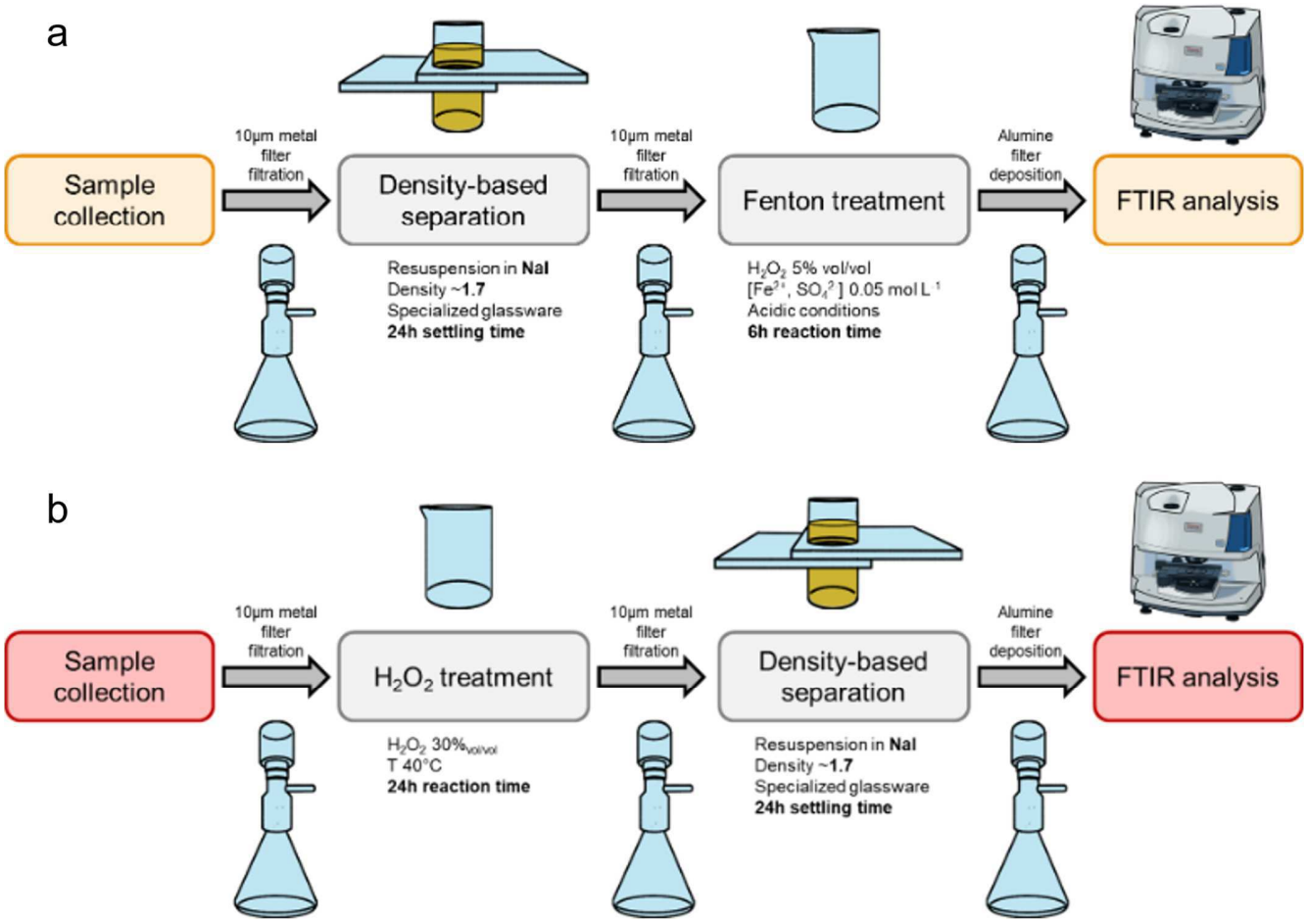

FIGURE 34: SCHEMATIC REPRESENTATION OF THE SUCCESSIVE TREATMENT STEPS CONDUCTED FOR THE PARIS REGION SAMPLES (A) AND THE NANTES REGION SAMPLES (B)

Samples from the Paris region campaign first underwent a density-based separation using a NaI solution set at a density of 1.7 g cm^{-3} and dedicated glassware for 24h. After this first treatment, samples were filtered and submitted to an oxidative treatment using the Fenton reagent for 6h.

Samples from the Nantes monitoring campaigns underwent a concentration treatment similar to that of the Paris region monitoring campaigns. However, the order of steps was slightly different. Samples first underwent an oxidative treatment with H_2O_2 at a concentration of 30% vol/vol before they underwent the density-based separation. As discussed in chapter 1, the Fenton reagent was

exclusively used at the beginning of this PhD and was abandoned for a more usual treatment process.

After treatment, all samples were deposited onto 25 mm diameter, 0.2 µm pore size Whatman Anodisc® alumina filters for FTIR analysis. The entire content of each sample was deposited onto one filter, that was then analysed via micro-FTIR spectroscopy.

8 General results of the monitoring campaigns

8.1 Deposition rates

A total of **61** bulk atmospheric deposition samples were obtained in the 5 monitoring campaigns conducted. **6,889** microplastics were identified in these samples. This includes 1,864 microplastics identified in the Paris monitoring campaigns (282 in campaign A20, 1,216 in campaign A21, 366 in campaign B21) and 5,039 microplastics identified in the Nantes monitoring campaigns (2,944 in campaign C22, 2095 in campaign D22).

In order to assess the temporal variability of the atmospheric microplastic deposition, a deposition rate in microplastics deposited per square metre per day (MP m^{-2} d^{-1}) was determined for each sampling period at both sites. Table 5 summarizes the figures obtained for each campaign. Figure 35 represents the deposition rates obtained for all sites.

Clear differences are noted between the campaigns. First, campaign A20 conducted during the lockdown seems to have lower deposition rates than all other campaigns. Median deposition rates of 5.36 MP m^{-2} d^{-1} and a mean of 14.3 ± 23.7 (standard deviation) MP m^{-2} d^{-1} were obtained. A single particularly high deposition rate of 95.6 MP m^{-2} d^{-1} was noted in one sample, increasing the overall standard deviation of the dataset. Deposition rates lower than 6.5 MP m^{-2} d^{-1} were reported for 9 of the 14 samples collected. Higher values were measured in campaign A21, with a median of 29.2 MP m^{-2} d^{-1} and a mean of 34.4 ± 18.8 (standard deviation) MP m^{-1} d^{-1}. No deposition rate lower than 12.5 MP m^{-2} d^{-1} was observed in 2021. The median deposition rate of the 2021 campaign was higher than the median deposition rate of the 2020 campaign by a factor of around 5.5.

Secondly, the urban campaigns seem to present higher deposition rates than the rural campaigns from the same region. Campaign B21 retrieved a median of 11.3 MP m^{-2} d^{-1} for a mean deposition

rate of 17.3 ± 13.2 (standard deviation) MP m^{-2} d^{-1}, lower than the results in campaign A21. Similarly in Nantes region, campaign D22 retrieved a median of 40.3 MP m^{-2} d^{-1} for a mean of 46.4 ± 38.8 (standard deviation) MP m^{-2} d^{-1}, lower than the deposition rates obtained in campaign C22 in the centre of Nantes (median 60.4 MP m^{-2} d^{-1}, mean 64.5 ± 22.3 MP m^{-2} d^{-1}). Additionally, campaign D22 seems more widely distributed than campaign C22.

TABLE 5: SUMMARY OF THE MAJOR FIGURES OBTAINED FOR EACH ATMOSPHERIC DEPOSITION MONITORING CAMPAIGN

Campaign	Number of samples	Number of microplastics	Median deposition rate (MP m^{-2} d^{-1})	Mean deposition rate (MP m^{-2} d^{-1})	Standard deviation (MP m^{-2} d^{-1})
A20	14	282	5.36	14.3	23.7
A21	17	1,216	29.2	34.4	18.8
B21	6	366	14.3	17.3	13.2
C22	12	2,944	60.4	64.5	22.3
D22	12	2,095	40.3	46.4	38.8

In order to assess the significance of these differences, non-parametric Mann-Whitney U tests are conducted between the different campaigns (Mann and Whitney, 1947). The deposition rates in campaign A20 were statistically different from the deposition rates in the same site in campaign A21 (p values < 0.05). Similarly, campaigns A21 and B21 are statistically different. However, the null hypothesis is not rejected when comparing campaigns A20 and B21. The difference in deposition rates is not sufficient to consider the two populations statistically different.

The null hypothesis of a Mann-Whitney test is not rejected when comparing campaigns C22 and D22. Unlike the Paris region campaigns, sampling occurred at the same time in both Nantes campaigns. The two statistical populations are paired, and a Wilcoxon signed-rank test can be conducted to assess the difference between the two campaigns. Conducting a paired Wilcoxon test showed that the difference between the deposition rates of these two sites is not sufficient to be considered statistically significant, with a rejection probability of p=0.1. Several differences can be noted between the two datasets.

As shown in Figure 35, deposition rates appear more variable in site D than in site C. This higher variability may explain the absence of a significant difference between deposition rates in campaigns C22 and D22. In particular, the deposition rates were lower than the limit of quantification for five samples out of twelve for site D, including 4 consecutive months of low

microplastic deposition. In contrast, all deposition rates were above a minimal value of 34.5 MP m^{-2} d^{-1} in site C. Overall, 6 samples from D22 retrieved deposition rates lower than 11 out of the 12 samples collected in C22. Deposition rates in C22 were higher than in site B for 8 out of the 12 sampling periods.

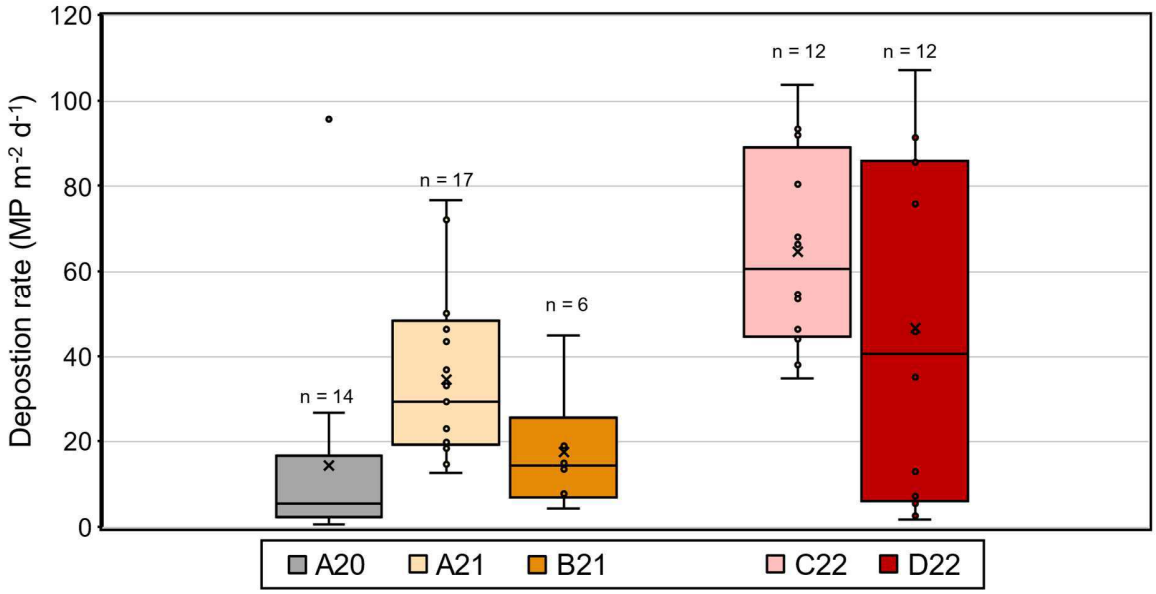

FIGURE 35: MICROPLASTIC DEPOSITION RATES FOR ALL ATMOSPHERIC MONITORING CAMPAIGNS

8.2 Characteristics of the pollution

For each microplastic identified, several parameters are measured. These parameters include the polymer of the identified microplastics, and geometric information such as the major and minor dimension of the particle, as well their surface area on the identified filters.

8.2.1 Dominant polymers identified

13 different polymer groups from the siMPle library were identified in the five campaigns. These include PP, PE (LDPE and HDPE), PS, Polyesters including PET, acrylics such as PMMA, PA, PVC, PVA, PU, ABS, PAN, and cellulose acetate. Of these polymers, 7 groups were identified in all campaigns: PP, PE, PS, polyesters, acrylics, PA and PVC.

Figure 36 represents the percentage distribution of these 7 major polymers identified in each monitoring campaign. Overall, PP and PE represent the majority of microplastics identified, representing 62 to 88% of all microplastics in each campaign.

In the Paris region monitoring campaigns, PP remained the dominant polymer in all samples and every campaign and represented more than 50% of all microplastics. It was followed in frequency by PE and PS in campaigns A20 and A21. PS were more common in campaign B21, making it the second most common polymer, followed by PE.

In the Nantes region, differences were observed between the polymer distribution in campaigns C22 and D22. While the dominant polymers in both sites were the same, their order of frequency differed. PP dominated the samples in site C where it represented 56% of all identified microplastics. It was followed in frequency by PE, PS and PA. In site D however, PE was the most common polymer, representing 54% of all identified MPs. They were followed by PP, PA, polyesters and PS.

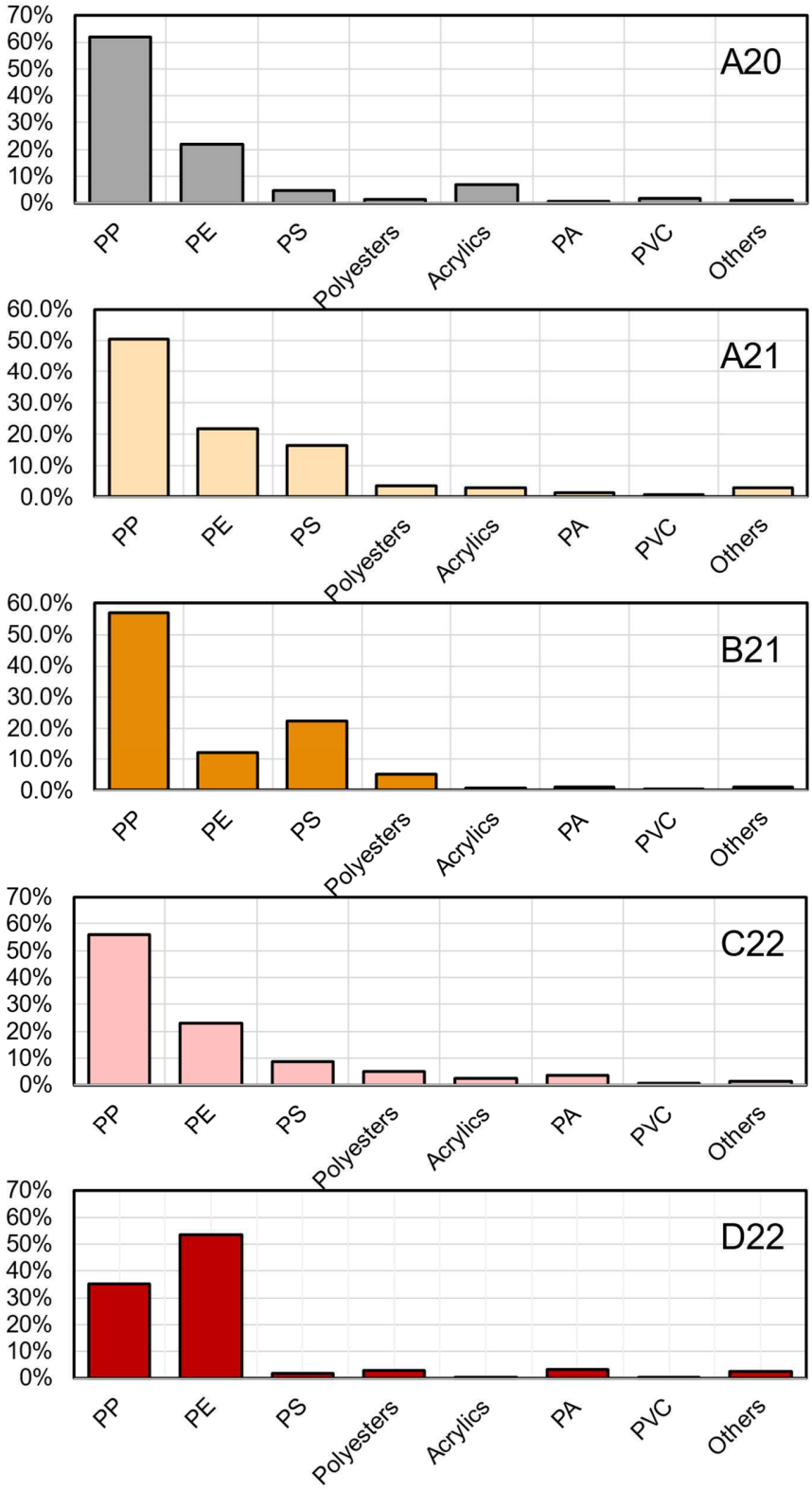

FIGURE 36: DISTRIBUTION OF THE DOMINANT POLYMERS OBSERVED FOR EACH ATMOSPHERIC DEPOSITION CAMPAIGN

8.2.2 Size distribution of the identified microplastics

Figure 37 summarizes the distribution of the minor dimension of all identified microplastics in each monitoring campaign. The targeted sizes of this work ranged from 25 to >500 µm, the lower size limit was caused by analytical limitations. In all campaigns, microplastics appear more frequent in the lower size ranges than they are in the higher size ranges. This observation is common in the literature: independently from the targeted size range of a study, authors often seem to find that the majority of identified microplastics are close to the lowest studied size class (Allen et al., 2019; Cai et al., 2017a; Dris et al., 2016b; Jenner et al., 2022). In all campaigns, the majority of the microplastics identified had a major dimension smaller than 125 µm. While smaller particles were more observed than larger particles, the modal class for the 2021 campaigns is not the smallest possible class, but rather slightly above the cutoff size. The modal class for campaign A21 is]75, 100] µm.

The modal class for campaign B21 is]100, 125] µm. This was also observed in similar studies from the literature (Cai et al., 2017a; Dris et al., 2016b; Jenner et al., 2022). It is likely that the smallest microplastics are underestimated due to methodological limitations. The smaller a particle is, the less pixels it represents on a 25 x 25 µm grid, and the more likely its signal may be hidden by the surrounding matrix. Smaller particles are also more likely to be lost during treatment.

Interestingly, the modal class for campaign A20 is the smallest size class identified,]25, 50] µm. While it is likely that the smallest microplastics are still underestimated in this campaign, it is possible that they represent a much higher fraction of all particles, leading to this difference in observed size distribution. Table 6 provides a comparison between campaigns A20 and A21 in number of particles. Campaign A20 presents lower numbers of larger particles (>50µm) but similar numbers of smaller particles (<50 µm).

TABLE 6: SIZE DISTRIBUTION COMPARISON FOR THE SMALLER SIZE CLASSES IN ALL CAMPAIGNS

Size class (µm)	A20 (n)	A20 (f)	A21 (n)	A21 (f)	B21 (n)	B21 (f)	C22 (n)	C22 (f)	D22 (n)	D22 (f)
]25, 50]	53	18.8%	49	4.0%	15	4.1%	7	0.2%	10	0.5%
]50, 75]	46	16.3%	161	13.2%	50	13.7%	368	12.5%	193	9.3%
]75, 100]	45	16.0%	255	21.0%	59	16.1%	684	23.2%	382	18.4%
]100, 125]	23	8.2%	163	13.4%	62	16.9%	425	14.4%	251	12.1%
]125, 150]	23	8.2%	134	11.0%	43	11.7%	272	19.2%	213	10.2%
>150	92	32.6%	454	37.3%	137	36.5%	1188	40.4%	1032	49.6%

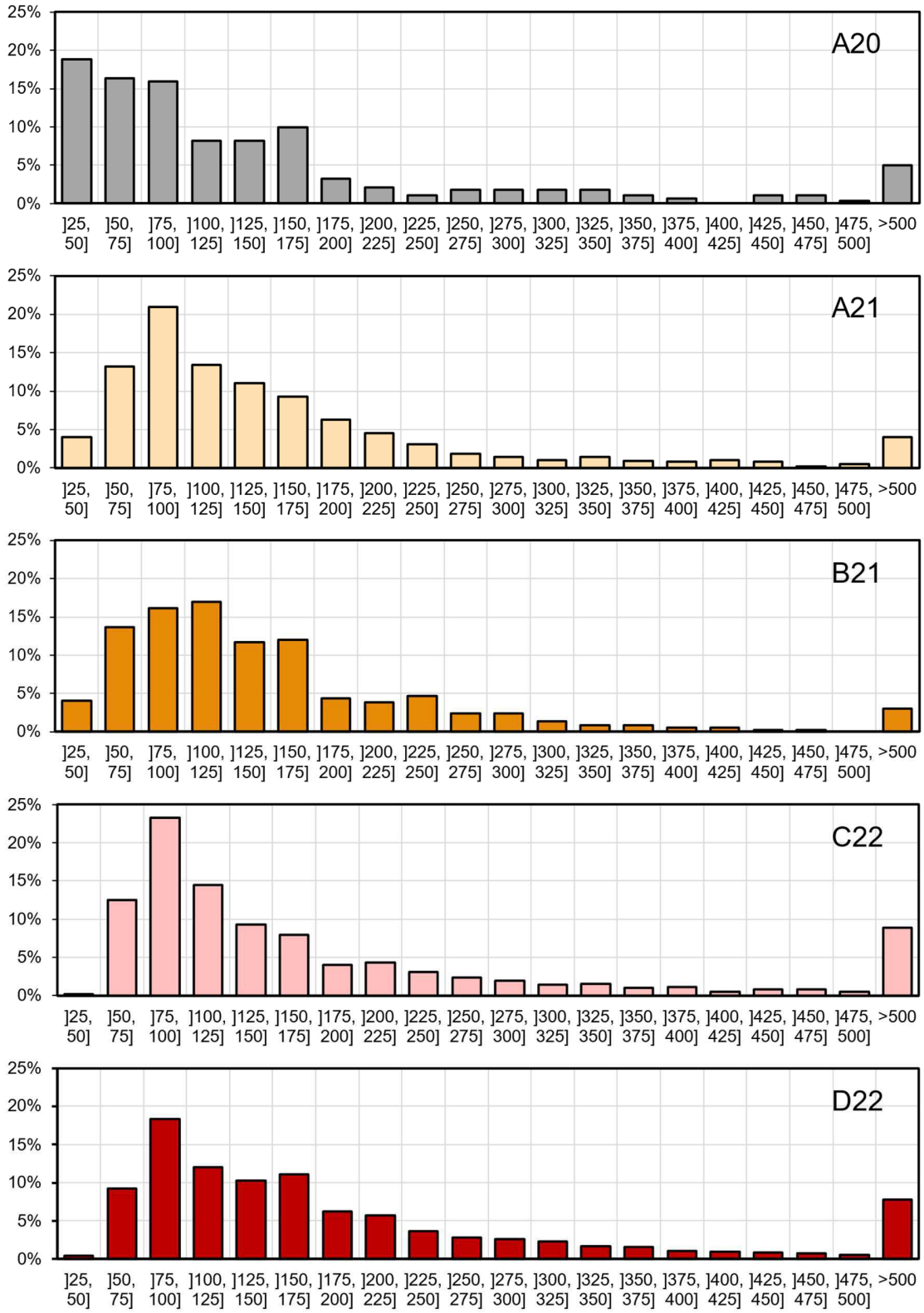

FIGURE 37: SIZE DISTRIBUTIONS FOR EACH ATMOSPHERIC DEPOSITION MONITORING CAMPAIGN

9 Effect of temporal variations of human activities on microplastic atmospheric deposition

The content of this section is inspired from the following article: COVID lockdown significantly impacted microplastic bulk atmospheric deposition rates – Max Beaurepaire, Rachid Dris, Johnny Gasperi, Bruno Tassin – 2024 – https://doi.org/10.1016/j.envpol.2024.123354

In order to slow down the spread of the COVID 19 pandemic in France and in Europe, lockdowns installed by many countries in 2020 caused a dramatic reduction in the economic activity and the mobility of urban populations (Insee, 2020). For instance, traffic activity in the Greater Paris area was reduced down to 11% of its 2019 value at the peak of the first lockdown ("TomTom Traffic Index," 2020). This reduction in urban activity and traffic led to a reduction in CO_2 emission in cities across Europe, although emissions recovered once the lockdowns were lifted (Nicolini et al., 2022; Schulte-Fischedick et al., 2021; Shan et al., 2021). The lockdown was also correlated to a significant reduction in concentration of air quality markers such as NO_2 concentrations in urban environments such as Milan, Paris, London, Berlin and Lyon (Collivignarelli et al., 2021; Sbai et al., 2021; Schatke et al., 2022), which are indirect indicators of traffic and outdoors human activity. In particular, a 2021 study recorded that the lockdown-induced traffic reduction caused a decrease of 65.7 to 79.8% in NO_2 concentrations in Paris (Collivignarelli et al., 2021). In campaign A20, this drastic reduction in urban activities is treated as a unique sampling opportunity. Usually, in order to assess the impact of human activity on a phenomenon, one has to compare the same factor in two sites marked by different levels of activity. During the national lockdown of 2020, however, sites that are normally marked by intense human activities were temporarily deserted. This provided an opportunity to collect samples with as close to a single parameter differing from the same site during periods of normal activity as possible.

Interestingly, the microplastic deposition rates in 2020 showed a similar order of magnitude of reduction to NOx, with a median reduction of 82% (mean reduction of 58%) when compared with the 2021 campaign. No direct correlation between NO_2 emissions and atmospheric deposition of microplastics is expected. Both are complex forms of pollution affected by multiple factors and possible sources. However, just as it is a source of atmospheric NOx, traffic can be an indirect source of microplastics through the fragmentation of macrolitter and the resuspension of deposited

particles. Traffic is also an indirect indicator of the overall level of human activity, which more directly affects microplastic emission and deposition.

In addition to a difference in deposition rates, the nature and size ranges of plastics deposited was also likely affected by changes in human activity. The relative dominance of the smallest size range of microplastics in the A20 campaign might suggest that smaller microplastics are more susceptible to long distance transport by wind. While the studied sizes are not directly comparable, a 2020 modelling study by Evangeliou *et al*. on emission and atmospheric transport of tyre wear and brake particles suggests that smaller particles are transported over longer distances, and can reach particularly remote environments (Evangeliou et al., 2020). In order to experimentally assess the atmospheric dynamics of smaller microplastics, further studies and methodological development need to be conducted (Luo et al., 2022)

10 Effects of spatial differences in urban activity on microplastic atmospheric deposition

In the previous section, the differences between the results for campaigns A20 and A21 suggested that variations in urban activity in a single site may be correlated with a reduction in atmospheric deposition. It is likely that similarly, spatial differences in level or type of human activity may affect the microplastic atmospheric deposition profiles.

In the Paris region, campaigns A21 and B21 were conducted in the same period in sites dominated by different activities, site A being a suburban campus while site B is peri-urban environment surrounded by agricultural activities. Similarly, in the Nantes region, campaigns C22 and D22 were conducted simultaneously in an urban and an agricultural site.

In this section, the differences between the results of these campaigns are highlighted and discussed.

10.1 Paris region

Although the two campaigns were not entirely simultaneous, campaign B21 was entirely conducted within the duration of campaign A21. In the section presenting the general results of the campaigns

(section 8), differences were noted between campaign A21 and B21. In particular, the deposition rate is significantly lower in campaign B21 than in campaign A21. Additionally, PS was observed to be a more common polymer in campaign B21 than in campaign A21.

As discussed on section 4.1.2 of this chapter, site A is an urban campus surrounded by an array of activities including public transportation, traffic, construction works and more. Site B is located in a peri-urban area with a lower population density. It is marked by less traffic. Overall, the dominant activity in the vicinity of the site is intensive agriculture.

It is likely the differences in human activity contributed to these differences. However, the low number of samples in campaign B21 limits the level at which the results of the two campaigns can be compared. In order to conduct a more in-depth comparison, longer monitoring campaigns should be conducted on site B, with the possibility to pair the results obtained there to the results of other simultaneous monitoring campaigns.

10.2 Nantes region

Unlike the monitoring campaigns in the Paris region, the Nantes monitoring campaigns were entirely simultaneous, making their direct comparison easier. As mentioned on section 8 of this chapter, differences were noted between the two campaigns. Deposition rates in campaign D22 were more variable and tended to be lower than campaign C22. Additionally, clear differences were noted between the polymer distributions in the two campaigns.

Figure 38 represents the size distributions for the three dominant polymer groups identified in campaign C22 and D22: PP, PE, PS. All samples are pooled together for each polymer group, as the size distributions were the same for polymers in both campaigns. While the majority of PP and PS particles were on the smaller size ranges, PE particles were more evenly distributed across all sizes. In particular, the modal class for PP and PS is 50 to 100 µm, while it is 150 to 200 µm for PE particles. In addition, PE particles were the most common large particles (>500 µm) across all samples. Because they were the largest particles, PE particles dominated the extrapolation of the mass distribution of the identified polymers.

As discussed above, a size distribution with a modal class around 50 to 100 µm may be explained as an experimental artefact. However, the effect of the limit of detection of the micro-FTIR should affect all polymers similarly.

A size distribution with a higher modal class may be another form of experimental artefact. Because of the loss of particles, it is possible that small PE particles are harder to detect due to their simpler FTIR spectrum, and thus are more easily hidden by the surrounding matrix. It is also possible that a majority of PE particles are observed around this modal class due to specific fragmentation processes leading to the formation of larger PE particles than other microplastics. In a 2019 study, Julienne *et al.* studied the fragmentation processes of PE films, and observed the dominant formation of large microplastics (>1 mm) (Fanon Julienne et al., 2019).

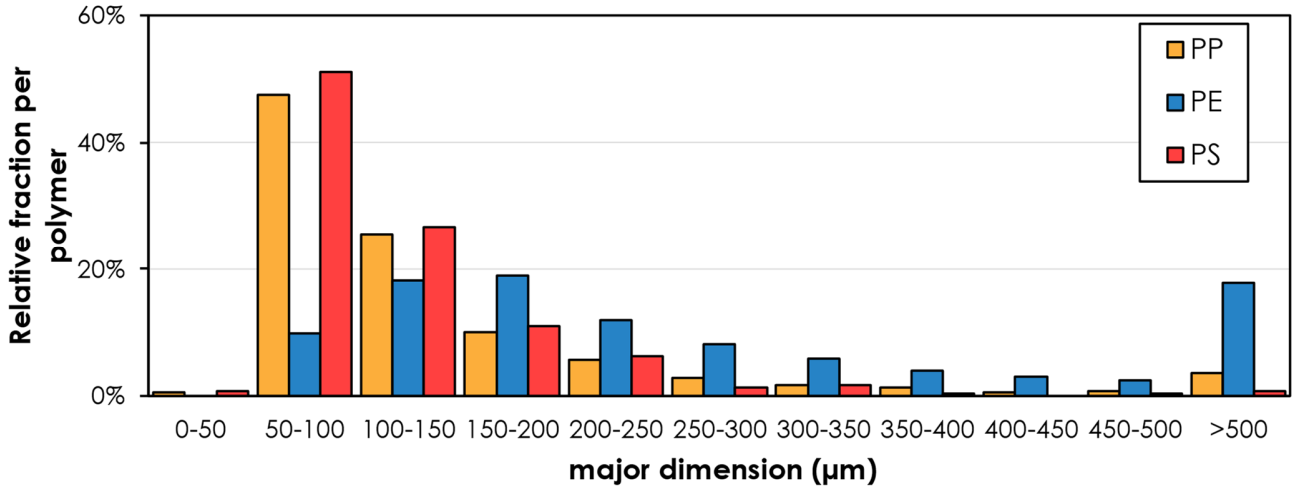

FIGURE 38: DISTRIBUTION OF THE MAJOR DIMENSION FOR THE MAJOR POLYMER GROUPS IDENTIFIED IN CAMPAIGNS C22 AND D22.

10.3 Comparison between the two regions

While a comparison can be made between the urban and rural sites in the Paris region and Nantes region campaigns, a direct comparison between the campaigns from the two regions does not show a clear effect of urban environments. As shown in Figure 35, overall deposition rates were lower in the Paris Region campaigns than in the Nantes Region campaigns. Mann-Whitney U tests show that the deposition rates in campaign A21 are not statistically different from campaign D22, but are lower than in campaign C22 ($p<0.05$).

The level and type of human activity in site A is expected to be similar to that of site C. The two sites are in areas of similar population densities, and are surrounded by similar types of activities. Likewise, the type of activity surrounding site B is similar to that of site D, suggesting the influence of activity should be similar in campaign B21 and D22

It is likely that the difference between the Paris region and the Nantes region campaigns is partly caused by a difference in methodology. In particular, the Nantes monitoring campaigns used a smaller passive sampler, with a circular shape.

11 Comparison with literature results

As mentioned at the beginning of this chapter, multiple studies published the result of atmospheric microplastic deposition monitoring campaigns. Table 7 provides a comparison between the results of some of these studies and the campaigns of this work.

11.1 Deposition rates

Deposition rates identified in the literature range from 5.4 to 365 MP m^{-2} d^{-1}, with a median of 73 MP m^{-2} d^{-1}. Overall, the deposition rates measured in the Paris region campaigns are on the lower range of values reported in the literature (Beaurepaire et al., 2021). In particular, the median deposition rates for all campaigns were lower than the median deposition rates from the first study on microplastics in atmospheric deposition, conducted in the same region (Dris et al., 2016b). The results from campaigns C22 and D22 in the Nantes region are on a similar order of magnitude as the range of values reported in the literature.

However, as discussed in the first chapter of this manuscript, a direct comparison with the rest of the literature remains compromised by the differences in methodologies between studies. While the 2016 study by Dris *et al.* was conducted in the same region, analytical tools evolved a lot since. The earlier study focused on artificial fibres and was largely based on visual identification of microplastics using a binocular. Not all particles were chemically characterized, and only relatively large fibres could be identified. This study on the other hand uses a more robust method based on the chemical identification of all particles, and can identify smaller microplastics. It is likely the difference in microplastic deposition rates is caused by these analytical differences, and a different category of targeted particles between studies. The present study uses a method that allows to greatly reduce the risk of having false positives during the identification of microplastics.

Another study by Allen *et al.* (Allen et al., 2019) was conducted on microplastic atmospheric deposition in France. In that study, the authors collected samples in the Pyrenean mountains, and

proceeded to some treatment before analysis. Microplastic identification was however different from this work. Larger plastics were visually inspected. In the case of smaller particles, suspected plastics were first noted, before they were identified using micro-Raman spectroscopy. Because they were using micro-Raman spectroscopy, the authors had a lower size limit of detection than what could be achieved using FTIR micro-spectroscopy. Their average deposition rate (365 ± 69 MP m^{-2} d^{-1}) was also higher than deposition rates observed in this work.

Human activity had been suspected to affect microplastic deposition rates in several earlier studies. While microplastics have been found in particularly remote environments where they could only have been transported by wind (Napper et al., 2020a), they have typically been found at lower concentrations in such sites than in more densely populated area (Allen et al., 2019; Beaurepaire et al., 2021; Cai et al., 2017b).

The main parameter studied in this work is the difference in human activity between otherwise comparable monitoring campaigns. In a 2023 study, Klein *et al.* conducted bulk atmospheric deposition monitoring campaigns in 11 sites of Northern Germany, including urban, sub-urban and rural sites (Klein et al., 2023). Significant differences were observed between deposition rates in the urban centre and the sub-urban and rural sites. Population density was determined to be a significant factor for microplastic atmospheric deposition. While the sampling and analysis methodologies differ, these findings are in line with the findings of this work.

TABLE 7: COMPARISON BETWEEN THE RESULTS OBTAINED IN THE CAMPAIGNS OF THIS WORK AND OTHER STUDIES

Location	site type	Campaign ID/ Number of sites	Monitoring period	Sampler surface area (m^2)	Sample collection interval (days)	Treatment strategy		Quantification strategy	Targeted size range	Deposition rates	Dominant polymers	Source
						Organic removal	Density					
Paris region, France	Urban	A20	4 months	0.325	4 – 11	✓	✓	Automated µFTIR imaging	25 – 5,000 µm	14.3 ± 23.7 MP m^{-2} d^{-1}	PP, PE, PS	This work
		A21	5 months	0.325	4 – 11	✓	✓	Automated µFTIR imaging	25 – 5,000 µm	34.4 ± 18.8 MP m^{-2} d^{-1}	PP, PE, PS	This work
	Rural	B21	4 months	0.325	7 – 45	✓	✓	Automated µFTIR imaging	25 – 5,000 µm	17.3 ± 13.2 MP m^{-2} d^{-1}	PP, PS, PE	This work
Nantes region, France	Urban	C22	12 months	0.0314	28 – 34	✓	✓	Automated µFTIR imaging	25 – 5,000 µm	64.5 ± 23.3 MP m^{-2} d^{-1}	PE, PP, PA	This work
	Peri-urban	D22	12 months	0.0314	28 – 34	✓	✓	Automated µFTIR imaging	25 – 5,000 µm	46.4 ± 40.5 MP m^{-2} d^{-1}	PP, PE, PS	This work
Jakarta, Indonesia	Urban	1	12 months	0.0314	30	✓	×	Visual selection and confirmation with ATR-FTIR	300 – 5,000 µm	23.4 MP m^{-2} d^{-1} dry season 5.4 MP m^{-2} d^{-1} wet season	PET, PE, PB, PS	(Purwiyanto et al., 2022)
Ontario, Canada	Remote	6	13 months	0.25 0.0925	3 – 48	×	×	Visual observation, hot needle test and confirmation with Raman	50 – 5,000 µm	57 MP m^{-2} d^{-1} 4 – 9 MP m^{-2} d^{-1}	PA, PET	(Welsh et al., 2022)
Whitehorse, Canada	Remote	3	5 months	0.0314	30	×	×	Visual observation, hot needle test	100 – 5,000 µm	10 ± 9 fibres. m^{-2} d^{-1}	No information	(Postma, 2022)
Northern Germany	Urban and remote	11	12 months	Unspecified (0.0314?)	30	✓	×	Nile Red staining and confirmation	10 – 5,000 µm	89 ± 61 MP m^{-2} d^{-1}	PE, PET, PA	Klein et al. 2023 (Klein et al., 2023)

								of a subsample with µRaman				
São Paulo, Brazil	Urban	1	6 months – 6 months	0.48	15	×	×	Nile red staining, confirmation of subsample with ATR-FTIR	50 µm	123.20 ± 47.09 MP m^{-2} d^{-1}	PE, PET	(Amato-Lourenço et al., 2022)
Pyrenees mountains, France	Remote	1	5 months	0.0314	12 – 41	✓	✓	µRaman identification	10 µm	365 ± 69 MP m^{-2} d^{-1}	PS, PE	(Allen et al., 2019)
Greater Paris, France	Urban	2	12 months 6 months	0.325	10 – 40	×	×	Visual identification, confirmation of subsample with ATR-FTIR	50 µm	110 ± 96 MP m^{-2} d^{-1}	PET, PA	(Dris et al., 2016b)
Beijing, China	Urban and remote	3	6 months	0,0079	30	✓	×	µFTIR manual identification	25 µm	236.12 ± 122 .13 MP $m^{-2}d^{-1}$	PET, rayon	(R. Zhang et al., 2023)
Jiaozhou Bay, China	Urban	5	12 months	0.00	30	✓	×	Visual identification, confirmation of subsample with µFTIR	6.25 µm	46.7 ± 21.3 MP m^{-2} d^{-1}	PET, PE	(Zhao et al., 2023)

11.2 Characteristics of the microplastics

In several studies of microplastics in the atmospheric compartment, polyesters, specifically PET, represented a major fraction of identified microplastics (Dris et al., 2016b; Gaston et al., 2020; Huang et al., 2020; Roblin et al., 2020). This was not the case in this here: polyesters, including polyethylene terephthalate (PET), represented less than 10% of all identified microplastics in all campaigns.

It is likely that this observed difference is the product of a difference in methodology. The majority of PET observed in other studies are typically textile fibres. While these fibres can be several hundred micrometres long, they typically have a small diameter, close to or lower than this study's analytical cutoff size. As a result, it is possible that they were underestimated in this work. It is also possible that on the contrary, other studies underestimate or cannot identify microplastic fragments of the size range presented here. As shown on Table 7, few other studies are able to target a size range comparable to the sizes detected here. Smaller fragments may thus represent a much larger fraction of microplastics than other particles and fibres that was absent from previous works.

12 Effects of meteorological factors on microplastic atmospheric deposition

12.1 Absence of a clear influence of precipitation or wind

In several earlier studies, rain events and precipitation rates were suspected to affect atmospheric deposition microplastic content (Allen et al., 2019; Dris et al., 2015). However, earlier studies of microplastics in total atmospheric deposition were sampling on long timescales during which several rain events and dry spells followed one another, which limited the extent at which the effect of precipitation on microplastic atmospheric deposition could be assessed.

In this work, campaigns A20 and A21 were conducted by collecting new samples every 4 to 11 days according to the occurrence and intensity of rain events. In particular, dry spells of up to 7 days were collected separately from any rain event. Figure 39 compares the microplastic deposition rates found in each campaign with the cumulated rainfall over each sample. No clear correlation was found between atmospheric deposition and cumulative rainfall in either individual campaign nor in all combined samples. No correlation was found either by pooling all five campaigns together, nor by pooling the Paris or Nantes campaigns together. In all cases, the correlation coefficient remained $r^2 < 0.2$.

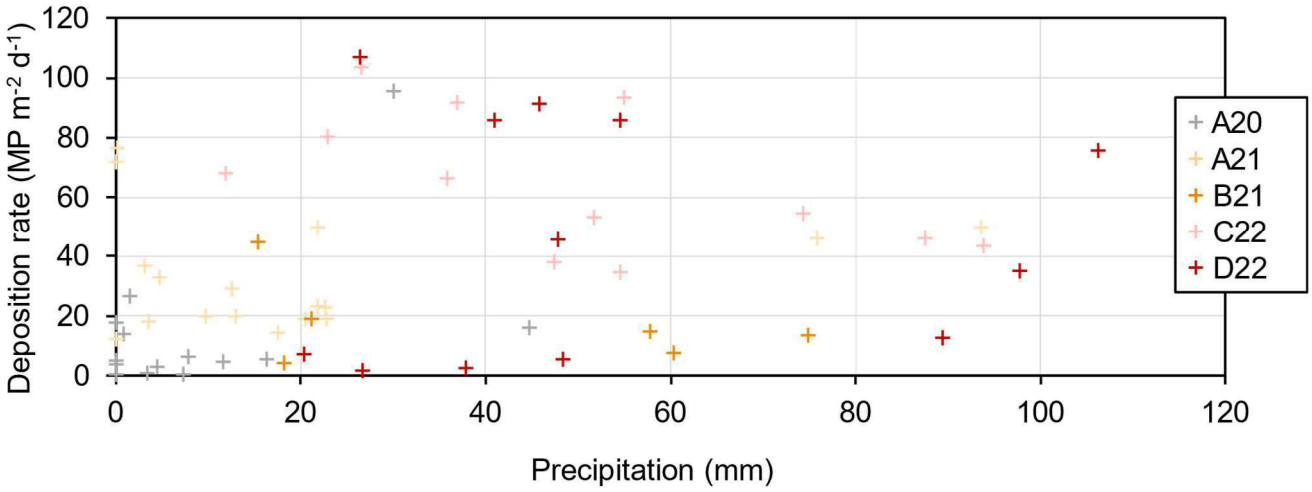

FIGURE 39: ATMOSPHERIC DEPOSITION RATES FOR EACH CAMPAIGN COMPARED TO THE CUMULATED RAINFALL OVER EACH SAMPLING PERIOD

12.2 Discussion and insights

The absence of a visible correlation between cumulated rainfall and microplastic deposition rates suggests that the dominant factor causing the observed differences between the monitoring campaigns is either a difference in methodology or the difference in human activity. It also suggests that the temporal variability of the deposition rates obtained is higher than the effects large-scale meteorological events may have on these deposition rates.

As shown in Table 7, in many studies focused on microplastic quantification from atmospheric deposition, the samplers used have an overall small surface area, with several studies using a bulk sampler smaller than 0.1 m² in total surface area (Allen et al., 2019; Klein et al., 2023; Postma, 2022; Welsh et al., 2022). While a smaller sampler is more practical for the sampling of air, in order to obtain results that are significantly above the blank levels, it becomes necessary for studies to sample over a prolonged period of several weeks. Because of this prolonged sampling period (1 month), only averaged, large scale meteorological factors can be

assessed. As shown on in Table 7, several studies including the current work collect samples on a monthly basis. It appears that at this collection rate, these large-scale meteorological factors affect microplastic transport and deposition less than the observed smaller-scale variability.

In order to better understand the factors affecting microplastic atmospheric transport and deposition, sampling over smaller time periods becomes necessary. In particular, it is possible that precipitations affect microplastic deposition by causing a washout effect, causing an increased microplastic deposition at the beginning of a rain event and a lowered deposition at the end of the event. Such washout effect of precipitation is well identified for other atmospheric pollutants such as PM2.5, PM10, O_3, CO, NO_2, SO_2 (Guo et al., 2016; Yoo et al., 2014). A direct observation of the evolution of microplastic content in rain would require a sequential sampling throughout a rain event, while sampling enough microplastics to remain above the analytical limit of quantification. Sequential sampling of microplastics throughout a rain event has been conducted in a study from urban runoff (Treilles et al., 2021), but remains to be conducted in atmospheric microplastics.

13 Conclusion – further steps

In this work, microplastic atmospheric bulk deposition was analysed for microplastics using an established, state-of-the-art analysis methodology that allows for replication and comparison with further studies. Significantly lower microplastic deposition rates were measured during a period of reduced human activity in an urban suburb from the greater Paris area. In particular, deposition rates of larger particles were proportionally lower when local human activity was reduced, whereas smaller microplastics appeared unaffected. This suggests that human activity was an important driving factor for microplastic deposition rates in the campaigns conducted.

Additionally, this work analysed the microplastic content of bulk atmospheric deposition samples from urban and rural sites. The nature of identified polymers and plastic sizes differed between both sites, suggesting an effect of local human activity on sources of atmospheric microplastics. Deposition rates were found to be more variable in the rural site than in the urban site. While neither rain events nor cumulative rainfall was found to have a significant impact on deposition rates, they may be affected by other, small-scale, meteorological events.

While precipitation is expected to affect deposition rates, no clear effect of either rain events or cumulative rainfall was evidenced, leading to the conclusion that the reduction in human activity was the main factor driving the reduction of the microplastic atmospheric deposition.

Further research should be conducted to better assess the relationship between human activities and atmospheric deposition of microplastics. In order to better assess the temporal variability of atmospheric microplastic deposition, future research should be conducted on smaller time scales, including the monitoring of single precipitation events. Separate sampling of dry and wet atmospheric deposition and may also help to better understand the effects of hydrometeorological events.

Chapter 3 – Spatial and vertical distribution of microplastics and TRWP in a roadside soil

1 Contents

2 Introduction

After being transferred through the atmospheric compartment and subsequently deposited, microplastics are prone to being transported by urban runoff and entering soil. As the previous chapter assessed the impact of human activities on microplastic transfer in the atmospheric compartment, this chapter focuses on plastics at a more local scale. In particular, the work presented here focuses on a single site of interest, a sustainable urban drainage system (SUDS) receiving and filtering runoff from a high traffic highway around 20 km north of Paris.

First, an analysis of the state of studies on microplastic contamination into non-agricultural soil environments and transfer by urban runoff highlights some of the major knowledge gaps in literature. In light of these knowledge gaps, the vertical distribution of microplastics in the SUDS of interest is characterized and quantified. Soil and accumulated roadside sediment samples are collected and analysed for microplastics and for TRWP. Finally, using these concentration profiles, the overall stocks of microplastics and TRWP are estimated.

3 Literature insights

The study of microplastic contamination in soil environments only gained traction recently. While the earliest identified study that collected and identified microplastics (namely, fibres) from soil samples was published in 2005, it was not followed by a scientific interest (Zubris and Richards, 2005).

Multiple factors can explain this relative lack of interest. Firstly, this work was published by authors separated from the scientific community dedicated to microplastic studies at the time. The word ‘microplastic’ had just been coined and was not used in Zubris and Richards’ work. The authors worked in environmental studies in terrestrial ecosystem, while the study of plastic and microplastic pollution in the environment was mainly conducted in oceanic environments.

Environmental studies in marine and terrestrial ecosystems are separated to some extent (Rillig, 2012), and the study of microplastic contamination in terrestrial ecosystems began later than their study in oceans: the first study on microplastics in river waters that caused the field to gain traction dates from 2011 (Moore et al., 2011). Even so, the jump from oceans to river environments is easier than from oceans to soils. Samples are of the same matrix, and studies can remain oriented towards marine environments by studying rivers are potential sources for marine microplastic contamination (Moore et al., 2011; Yonkos et al., 2014).

Finally, soil samples are a significantly more complex matrix to prepare and analyse than other samples (Rillig, 2012). Soil samples are as dense a matrix as sediment, but have a more complex and diverse composition, require multiple treatment steps (Hanvey et al., 2017; Prata et al., 2019b; Ling Yang et al., 2021).

The earliest study identified in the literature that targeted the phenomenon of microplastic contamination in soil environments dated from 2016, and did not actually measure or identify microplastics in soils. It was an ecotoxicity study on the potential impact of microplastics on *Lumbricus terrestris*, the common earthworm (Huerta Lwanga et al., 2016). First studies measuring microplastic contamination in actual soils were published later, in 2018 (Liu et al., 2018; Zhang and Liu, 2018; Zhou et al., 2018)

This section aims to provide some insight on the current state of knowledge on microplastic contamination in soil environments, and to highlight major knowledge gaps that this work is susceptible to address.

3.1 State of literature

In order to assess the current state of the literature, an initial general bibliographic search was conducted using the Web of Science® search engine. The main query used was as follow:

TI = ((microplastic OR microplastics) AND ~soil) OR AK= ((microplastic OR microplastics) AND ~soil)

As described in previous chapters, the elements following TI relate to the title of the papers. The elements following AK relate to the author keywords of the papers. In this query, the objective was to identify all studies referring to microplastic contamination in soil environments.

By the end of December 2023, a total of **1,010** studies were published on this topic, including **166** review articles. Figure 40 shows the distribution of these publications over the years since the first major publications in 2018 (Liu et al., 2018; Zhang and Liu, 2018; Zhou et al., 2018). As shown on the figure, the majority of the published content is very recent, with 62% of all identified publications dated from 2022 or 2023. Only a fraction of these studies collected soil samples to quantify their microplastic content, however. Other studies mainly consist in ecotoxicity studies (369 or 44% of all studies).

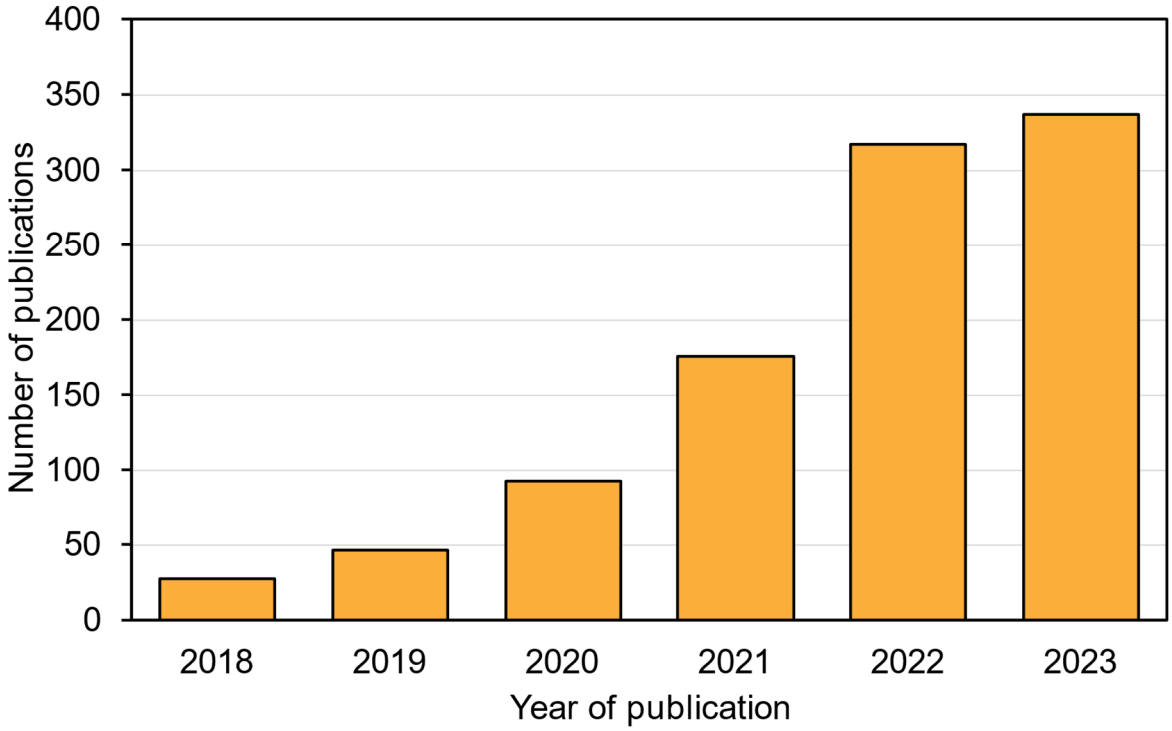

FIGURE 40: EVOLUTION OF THE NUMBER OF YEARLY PUBLICATIONS SINCE THE FIRST PUBLICATION MEASURING MICROPLASTIC IN SOIL ENVIRONMENTS

Several subsequent queries were conducted to better assess the state of literature related to the objectives of this work. In particular, only **9** studies were found to focus on the vertical distribution of microplastics in soil samples, including 2 studies that did not directly collect soil samples (Han et al., 2022; Li et al., 2021).

The vast majority of studies conducted appear to focus on microplastic contamination of agricultural soils. The following query was conducted:

TI = ((microplastic OR microplastics) AND (~soil OR ~agriculture OR ~crop OR ~farmland)) OR AK = ((microplastic OR microplastics) AND ~soil (~agriculture OR agricultural OR ~crop OR ~farmland))

The query retrieved a total of **858** publications, including 134 review papers. This represents 85% of all publications on microplastics in soil environments.

The aim of this section is not to provide an exhaustive review, but a general overview of the available knowledge that is directly relevant to the present study. The first historic papers on the subject are presented, and a secondary focus is placed on studies that assess the vertical distribution of microplastics in soils.

3.2 Major findings – microplastic accumulation in soils

Table 8 gathers the results of key studies on microplastics in soils. Authors typically present the level of contamination from samples in microplastic abundances, number of microplastics per gram or per kilogram. The units presented on Table 8 were homogenised for the sake of clarity.

Microplastic abundances range over 3 orders of magnitude in the literature, from 200 MP kg^{-1} in the lower ranges to 42,900 MP kg^{-1} in the more concentrated studies. In a 2020 review by Büks and Kaupenjohann, a more comprehensive inventory of the abundances recorded in the literature was conducted (Büks and Kaupenjohann, 2020). Abundances ranged over 4 orders of magnitude. The lowest abundances recorded were in the order of <0.1 MP g^{-1} (<100 MP kg^{-1}) (Liu et al., 2018; Zhang and Liu, 2018). A particularly low abundance of 0.3 was similarly recorded in a 2018 study by Piehl *et al.* (Piehl et al., 2018). In the first study by Zubris and Richards, abundances of 1,250 fibre kg^{-1} were measured (Zubris and Richards, 2005). On the other end of the spectrum, particularly polluted sites reach median abundances of up to 145 MP g^{-1} (145,000 MP kg^{-1}) (*Microplastic in Danish wastewater*, 2017).

As discussed in the first chapter of this manuscript, the methodologies used to collect, prepare and analyse microplastic samples are highly variable from author to author. Studies on microplastics in soil environments are no exception. Analytical methods vary from purely visual identifications to complete µ-FTIR characterization of samples, which is likely to highly affect the result of studies. A high degree of variability is also observed between sample in studies, with results varying over more than an order of magnitude in single studies. Soils are typically a very heterogeneous matrix, and such variability is partly expected.

In addition to a likely effect of the analytical methodology, several factors were observed to affect microplastic accumulation in soils. In all studies that compare contamination of soils amended with sludge produced in WWTP and soils not amended, higher MP concentrations were observed in amended soils. In studies that directly collected sludge samples, microplastic abundance was one to two orders of magnitude superior in the sludge samples than in soil

samples. These results suggest amended sludge represents a major microplastic source in agricultural soils.

A second potentially major microplastic is the fragmentation of plastic films and mulching used to cover agricultural soils. In a 2023 modelling study, Li *et al.* estimated that 6% of the 2,600 kton yr^{-1} of plastic used as agricultural mulching in China remained in the environment as a form of pollution (Y. Li et al., 2023). In a 2023 study, Kedzierski *et al.* collected microplastic data from 43 articles to estimate the global microplastic stock in agricultural soils (Kedzierski et al., 2023). A comparison of the microplastic inputs represented by amended sludge and by the degradation of plastic mulching was obtained, suggesting that both represent major sources, though sewage amendment represents the dominant source.

While not all studies focus on the vertical distribution of microplastics, studies that do mention this objective typically note lower abundances in the deeper soils than near the surface (J. Li et al., 2023; Liu et al., 2018; Schell et al., 2022). In a 2021 study dedicated to the vertical migration of microplastics, the type of vegetation cover was found to affect the vertical migration of microplastic in crop soils (Li et al., 2021). It is likely that tilling the soil similarly affects the microplastic vertical migration.

In a 2019 column experiment study, the vertical migration of microplastics was noted to be affected by the nature of soil. The number of dry-wet cycles of the soil was correlated to the microplastic migration rate, suggesting a faster vertical migration in coarse soils (O'Connor et al., 2019).

PE and PP represent the dominant polymers in the majority of studies. These are often followed by polyesters, particularly PET. It is likely that a majority of the polyesters consist in synthetic microfibres.

TABLE 8: RESULTS OBTAINED IN SEVERAL MAJOR RECENT STUDIES ON MICROPLASTIC IN SOILS

Location	Type of soil	Quantification strategy	Size range	Sampling depth	Abundance	concentration	Dominant polymers	Source
Ithaca, NY		Visual			1,250 fibres kg^{-1}			(Zubris and Richards, 2005)
Boghai Sea, China	Coastal soil	ATR-FTIR + SEM	<50 µm – 5 mm	2 cm	740 MP kg^{-1}		PE, PP, PEU	(Zhou et al., 2018)
Southwest China	Farmland soil	Visual	50 µm – 10 mm	0 – 5 cm; 5 – 10 cm	7,100 – 42,900 MP kg^{-1}, median 16,380 MP kg^{-1}		Unknown	(Zhang and Liu, 2018)
Shanghai, China	Farmland soil	Visual + µFTIR on subsample	20 µm – 5 mm	0 – 3 cm; 3 – 6 cm	78 MP kg^{-1} in shallow and 62.5 MP kg^{-1} in deep for micro, 6.7 and 3.5 for meso		PP, PE, PES	(Liu et al., 2018)
Mellipilla county, Chile	Farmland soil	Visual	100 µm – 5 mm	0 – 25 cm	Soil 200 – 700 MP kg^{-1} Sludge median 3,400 MP kg^{-1}		Unknown	(Corradini et al., 2019)
Spain	Farmland soil, sludge, runoff	Visual then ATR (>300 µm) or µFTIR for all	50 µm – 5 mm	0 – 15 cm	Soil 138–288 MP kg^{-1} Sludge 5,972–7,771 MP kg^{-1}		PE, PES, PP, Acrylic, PA	(Schell et al., 2022)
China	Farmland soil, compost	Visual + µFTIR on subsample	130 µm – 5 mm	0 – 10 cm; 10 – 20 cm; 20 – 30 cm;	Mean 144 MP kg^{-1}		PE, PP, PET, PAN	(J. Zhang et al., 2023)
Ontario, Canada	Farmland soil, sludge	Visual + TGA coupled to FTIR	5 mm – 2 mm	-		0.68 - 47 mg/kg median 1	PID, PET, PP, PE	(Chen et al., 2024)
France	Farmland soil	Visual + ATR-FTIR for 2 - 5 mm; SEM	2 – 5 mm	0 – 60 cm	Mean 291 MP kg^{-1}	3g/kg to 0g/kg in deep soil	PVC, PE, PP	(Wahl et al., 2024)
Shouguang, China	Farmland soil	Visual + ATR-FTIR	200 µm – 5 mm	0 – 20 cm; 20 – 40 cm; 40 – 60 cm	1,948.1 ± 992.5 1,349.4 ± 654 670.1 ± 341.6 MP kg^{-1}		PE, PP, PET, PVC	(J. Li et al., 2023)

3.3 Identified knowledge gaps and objectives of this work

While the number of studies greatly on microplastics in soil environment increased in recent years, studies remain centred around a limited number of topics, and multiple gaps in the overall understanding of microplastic distribution and fate in soil environments remain.

Firstly, as mentioned above, the majority of soil studies focus on the quantification of microplastics in agricultural environments. The main suspected microplastic source in these works is sludge amendment. However, not all soil environments are fields subjected to sludge amendments. In urban or remote soils, other sources such as atmospheric deposition, urban runoff, or local fragmentation of large plastic products may represent the main plastic sources. As these sources are harder to constrained, they are rarely assessed by authors (Bläsing and Amelung, 2018; Campanale et al., 2022).

Secondly, the fate of microplastics once they are in the soils remains poorly understood. Some studies mention that microplastics are likely stored over long time periods in the soils (Schell et al., 2022; J. Zhang et al., 2023). Others suggest that microplastics may migrate and potentially contaminate groundwaters (Bläsing and Amelung, 2018; O'Connor et al., 2019). There remains a lack of environmental studies that comparatively assess the vertical distribution of microplastics in soils.

In light of these limits, the objectives of this work are to i) gain information on the vertical distribution of microplastics in a roadside soil, ii) compare microplastic quantification from an imaging micro-FTIR analysis to the TRWP content of a site determined with a Pyr-GC/MS method, iii) use the obtained results to estimate the overall stock of microplastics in the soils for a further mass balance.

4 Site of interest – the Compans biofiltration swale

4.1 Site location

This chapter focused on one single site of interest. The site is located 20 km North-East of Paris as shown on Figure 41a, on the GPS point N48.995869, E2.647515. This site is located in the municipality of Compans, in the zone of industrial activities of Mitry-Compans. According to the Mitry-Mory official website, this industrial zone is home to 200 businesses, 60 of which are

considered Installations Classified for Environmental Protection (ICPE in French). In particular, 5 of these sites are SEVESO classified ("Risques naturels et technologiques," n.d.). Some of the industrial activities include gazes including dichlorine (Cl_2), ammonia (NH_3), sulfur dioxide (SO_2) and anhydric chlorhydric acid (HCl) production and storage (Gazechim, 2014); and the storage and distribution of hydrocarbon (CCMP, 2015).

In addition to the surrounding industrial activity, the site is located 8 km east of the Roissy-Charles de Gaulle international airport, and is under one of its major air corridors. Finally, the site is on the side of a high-traffic 2x2 lanes departmental highway road. An average of 11,000 vehicles pass through the road per day in each direction, including 50% of heavy-duty vehicles.

4.2 Description of the biofiltration swale

Figure 41b presents a photograph of the site, which structure is detailed on Figure 41c. It consists in a biofiltration swale (BFS) (Ballard and B. (Bridget), n.d.; Flanagan et al., 2018). The site was constructed in 2016 (Flanagan, 2018) in collaboration between the LEESU and the Departmental Council (CD77). It was equipped with instruments measuring flow rate and conductivity for hydrological monitoring, and is since used as a study site for several research works dedicated to the study of the fate of metals and organic micropollutants in infiltration devices (Flanagan, 2018; Kanso, 2021; Tedoldi, 2017).

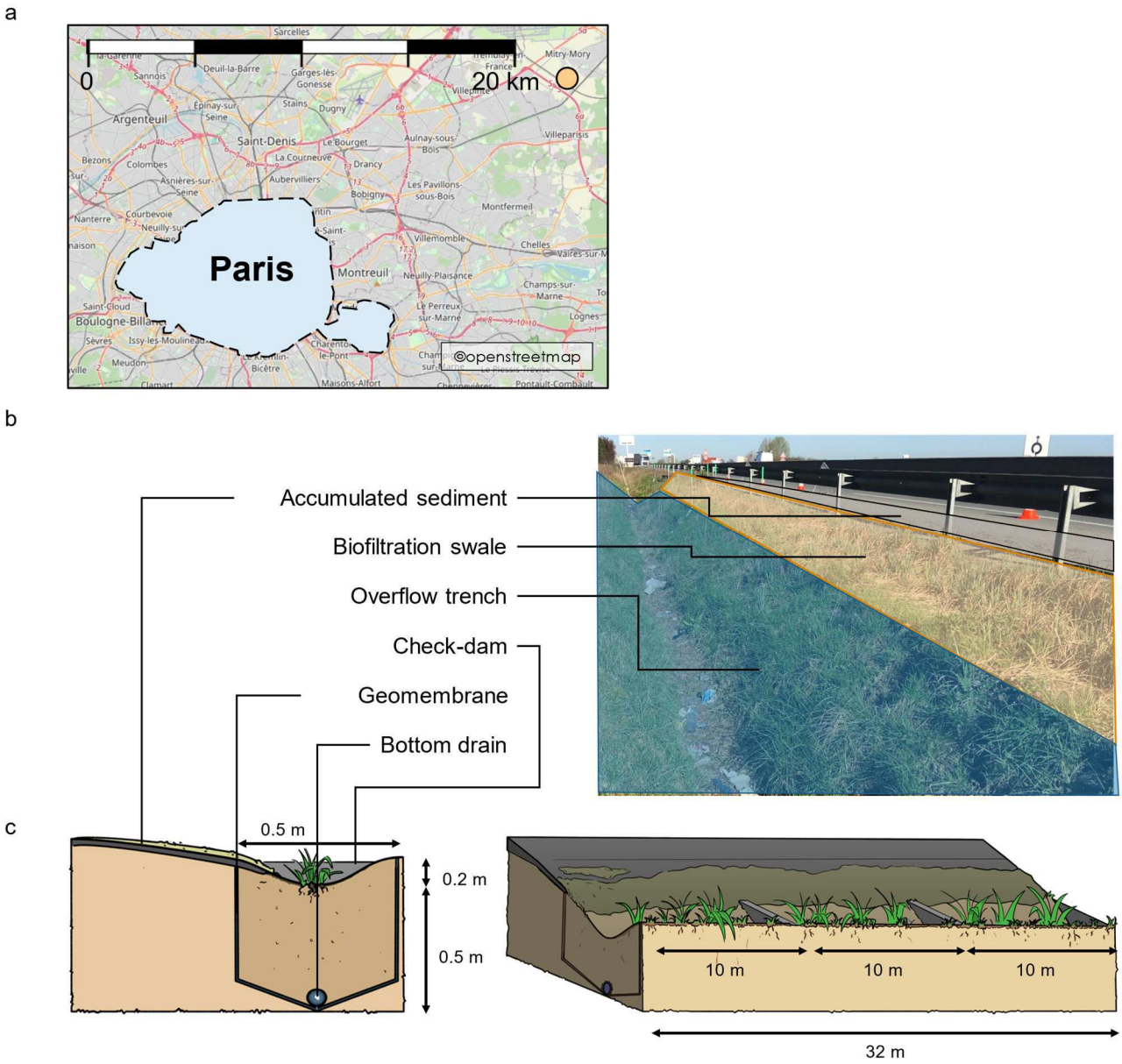

FIGURE 41A - LOCATION OF THE SITE OF INTEREST IN REGARDS TO PARIS; B- PHOTOGRAPH OF THE BIOFILTRATION SWALE AND THE OVERFLOW TRENCH LOCATED BEHIND, MACROLITTER IS VISIBLE ON SITE; C- STRUCTURE AND DIMENSIONS OF THE BIOFILTRATION SWALE

As shown on Figure 41c, the swale is 32 m long, 50 cm wide, and 20 cm deep, with a 50 cm thick filtration substrate. It is separated into three 10m-sections by two check-dams, and is connected to the road by a sloped bitumen shoulder. It diffusely collects runoff from a 352 m² section of the highway, which combined with the 16 m² surface area of the BFS itself produces a total drained surface area of 368 m². It is equipped with a drain at its bottom and is connected to an outlet leading to an infiltration trench. It is separated from the surrounding soil by an impermeable geomembrane out of high-density polyethylene (HDPE).

The initial soil used for the construction of the BFS was an artificial filtration substrate composed of a mixture of 40% topsoil and 60% limestone sand. Table 9 is a particle size

distribution of this substrate, showing that the initial soil used is relatively coarse, with a majority of the grain larger than 200 µm.

The BFS was planted with *Carex gracilis* when it was first constructed, and these remain the dominant vegetation. The CD77 mows the vegetation yearly, but doesn't export the cut vegetation away from the site.

A preliminary inspection of the site showed that its structure evolved after it was first built. In particular, the decomposition of the regularly mowed vegetation, as well as the particulate matter transported by runoff into the site accumulated on the sloped bitumen shoulder of the BFS producing a darker sediment placed on Figure 41c. Table 9 shows the particle size distribution of this accumulated sediment. Additionally, the site was noted to progressively accumulate macrolitter, which debris are visible on Figure 41b.

TABLE 9: PARTICLE SIZE DISTRIBUTION OF THE INITIAL SUBSTRATE AFTER SIEVING TO 2 MM. (MODIFIED FROM FLANAGAN, 2018)

Grain size	Fraction of the substract	
	soil	sediment
<2 µm	9.7 %	0.62 %
2 – 20 µm	9.0 %	2.9 %
20 – 50 µm	9.2 %	6.5 %
50 – 200 µm	15.4 %	27.6 %
200 – 2000 µm	56.7 %	62.4 %

5 Sampling campaigns and analyses

5.1 Soil and road accumulated sediment sampling campaigns

The main reservoir studied in site was the BFS itself. Specifically, solid matrix samples were collected in order to assess the spatial distribution of the microplastic stock in the BFS.

As mentioned above, studies on microplastics in soil typically focus on surface soil or combine samples from multiple areas of a site of interest in order to analyse a representative fraction of the site of interest (Liu et al., 2018; Wahl et al., 2024; J. Zhang et al., 2023)

On the contrary, in this work, the objective is to study the spatial variability of the microplastic and TRWP contamination of the soil of the BFS. The main objective was to determine the vertical profile of microplastic and TRWP concentrations, in order to better understand the role

of road runoff in the infiltration, or lack thereof, of microplastics and TRWP in soil environments.

Secondly, in order to assess the horizontal variability of this contamination, samples had to be collected from several points of the BFS. In particular, the BFS is separated by check-dams into three sections. While the working assumption is that runoff infiltration is diffuse across the BFS, samples were collected from all three sections in order to check for potential differences in levels of contamination or vertical profile.

Finally, the construction of the sampling strategy had to ensure the normal functioning of the BFS would not be compromised, so as not to interfere with other scientific works conducted on site. As mentioned earlier, the BFS is equipped with an array of materials since 2016, and is continuously monitored. The sampling procedure had to be as minimally invasive as possible. This specifically meant that the number of samples collected had to be limited, that the soil had to be replaced with a similar soil after collection, and that the sampling process had to ensure not to damage the drain

In this context, manual core sampling was considered the best-suited sampling method. Figure 42 summarizes the sampling process. A total of 9 cores were collected in the BFS, as well as 1 supplementary core collected out of the swale to be used as a reference point. Samples were collected at the section deepest point. In order to assess the horizontal variability of the BFS, three samples were collected in each section, 20 cm away from each other.

So as to avoid damaging the integrity of the BFS, the samples were collected at a maximal depth of 35 cm, above the drain and the geomembrane. A substrate identical to the one used during the construction of the BFS was used to close the sampling hole.

After collection, as shown on Figure 42, each core was divided according to depth into 4 samples: [0 – 5 cm [, [5 – 15 cm [, [15 – 25 cm [, [25 – 35 cm [. Each produced sample had a

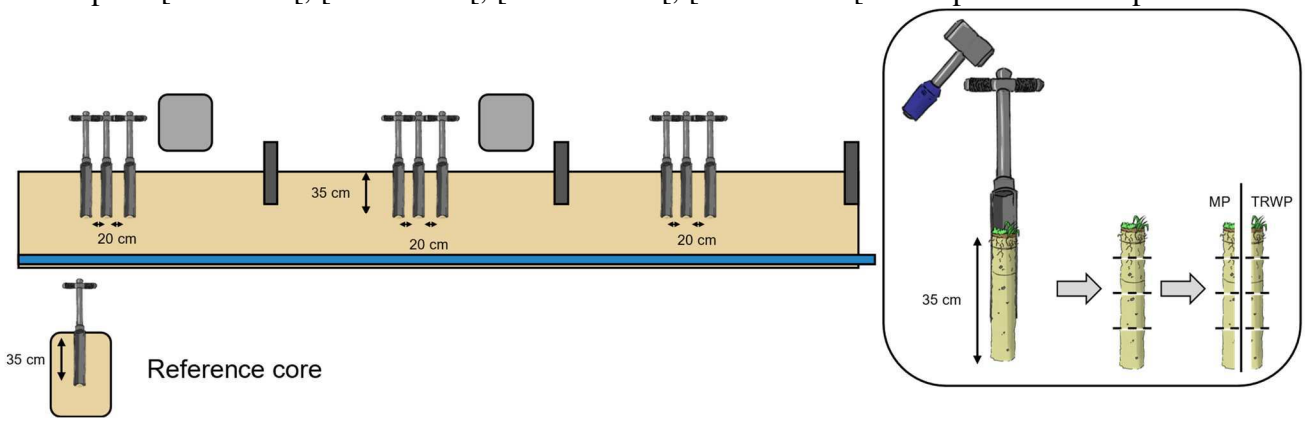

FIGURE 42: SAMPLING PROCEDURE AND SUBDIVISION IN THE BFS

dry mass of 10 to 12 g. Half of the mass of each sample was reserved for TRWP quantification, leaving a mass of 5 g for quantification of microplastics.

In addition to the cores collected on the BFS, a 10th core named Reference core was collected on the top of the overflow trench, 2m away from the road. While located on the same site, this core does not receive runoff from the passing road. However, it is likely subject to all other microplastic sources on site.

As mentioned earlier, over time after the construction of the site, sediment accumulated on the sloped bitumen shoulder upstream of the BFS. This sediment may represent a first barrier encountered by runoff before it infiltrates into the BFS, and is thus susceptible to be highly contaminated by microplastics and TRWP. A total of 6 sediment samples were collected, represented by squares on Figure 42. As the accumulated sediment represents a low height of only a few centimetres, samples could not be collected using a hand-held auger. Instead, sediment was scooped up using a metallic dustpan and a brush.

5.2 Treatment and analysis of microplastics

Figure 43 is a summarized representation of the concentration treatment and analysis procedures for all soil and sediment samples. The details on these procedures are provided on the first chapter of this manuscript.

During this treatment, the samples were first subjected to an oxidative treatment using a 30% H_2O_2 solution. Samples then underwent a density-based separation using NaI at a density of 1.7 g cm^{-3}. Finally, a second oxidative treatment was applied to the samples. After the treatment was finished, samples were deposited on Anodisc® alumina filters and their microplastic

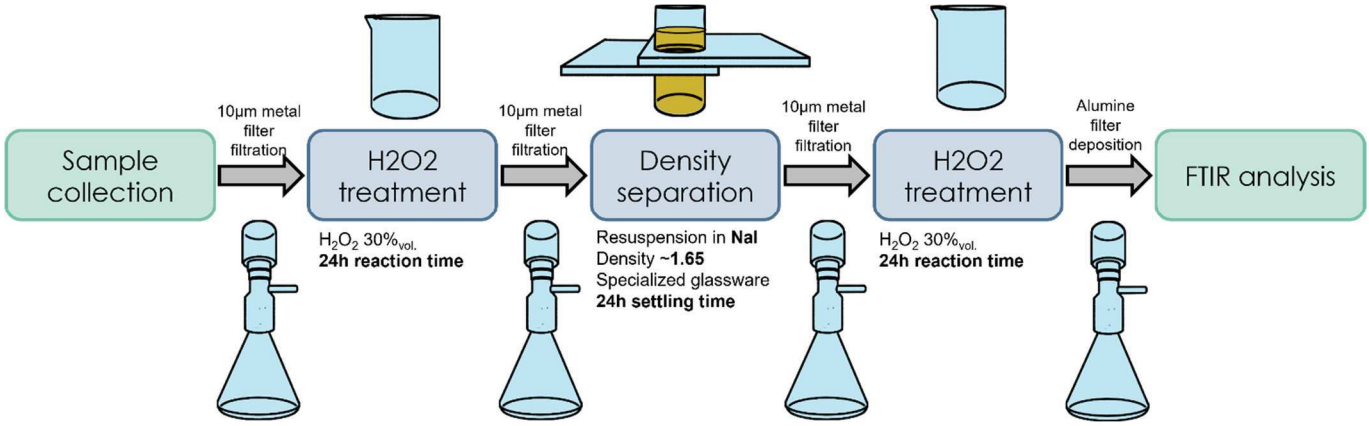

FIGURE 43: TREATMENT PROCESS FOR MICROPLASTIC ANALYSIS IN SOIL SAMPLES

content was quantified using a fully automated µFTIR imaging analysis using the procedure

described on chapter 1 of this manuscript. The obtained IR spectral maps were analysed for microplastics using SiMPle.

5.3 Treatment and analysis of SBR+BR from TRWP

As described on the first chapter of this manuscript, TRWP concentrations in the samples were indirectly obtained by quantifying the styrene-butadiene rubber and butadiene rubber (SBR+BR) content of the samples using a Py-GC-MS analysis. While Py-GC-MS allows for the analysis of solid samples, soil samples still required a preliminary treatment prior to analysis.

After collection, the fraction of samples reserved for TRWP quantification was dried at 105°C for 24 hours to eliminate the humidity and to limit the organic matter interferences with SBR and BR markers. Samples were then placed on a stainless-steel grid with a mesh size of 500 µm to remove organic debris and minerals larger than 500 µm, as the larger particles would reduce the relative signal strength of TRWP in Py-GC-MS. For each of the 44 samples analysed, around 3.90 mg was weighed in the pyrolysis cups.

Further details related to the standard and internal standard preparation, analysis, and post-treatment of samples are discussed in chapter 1.

The synthetic rubber fraction of a tyre is variable, representing 24% of a lightweight vehicle tyre, and 11% of a heavy duty vehicle (U.S. Tire Manufacturers Association, 2020). In a 2021 study gathering data from a wide range of tyres, this percentage varied from 0.05% to 28% of a tyre (Rauert et al., 2021). Additionally, TRWP are an an amalgamation of abraded tyre material and road mineral. The mass proportion of SBR+BR of an evironmental TRWP is thus even lower than these values. It is typically estimated by a conversion factor that is variable in the literature (De Oliveira et al., 2024; Kreider et al., 2010; Unice et al., 2012).

6 Results – vertical profiles of microplastic and TRWP contamination in the BFS

6.1 Microplastics accumulation in the soils and sediments

A total of 46 soil and sediment samples from Compans were analysed for microplastics using a µ-FTIR. These include 36 soil samples from the soil of the BFS, the 4 samples of the reference core, and 6 roadside accumulated sediment samples. After the µ-FTIR analyses, a total of 6,399 microplastics were identified in soil and accumulated roadside sediment samples. These included 3,311 in the roadside accumulated sediment, 2,027 in the surface soils, 708 in the deeper soil samples and 353 in the reference core. For each sample, a microplastic abundance in MP g^{-1} was measured. In order to assess the microplastic infiltration into the BFS, Figure 44 gathers the microplastic abundance obtained for each sample gathered by depth.

The roadside accumulated sediments resulted in median abundances of 108 MP g^{-1} with a mean ± standard deviation of 110 ± 58.0 MP g^{-1}. The surface soil samples from the BFS resulted in median abundances of 28.6 MP g^{-1} with a mean of 45.0 ± 42.8 MP g^{-1}. The deeper soil samples resulted in an overall median of 1.8 MP g^{-1} with a mean of 5.24 ± 8.40 MP g^{-1}. More specifically, samples collected from the 5 to 15 cm soil fraction resulted in a median of 3 MP g^{-1}; samples from the 15 to 25 cm soil fraction resulted in a median of 1.2 MP g^{-1}; samples from the 25 to 35 cm resulted in a median of 2.4 MP g^{-1}. As shown on Figure 44 the microplastic abundances were significantly higher in the accumulated roadside sediment than in all soil samples; in turn, the surface soil samples contained significantly more microplastics than the deeper soil samples (Mann-Whitney tests, p values < 0.05). Microplastic abundances in the reference core were in similar orders of magnitude as abundances in the BFS core samples, with a surface abundance of 32 MP g^{-1} in the surface and an abundance of 7.6 MP g^{-1}.

While the deeper soil samples presented significantly lower abundances than surface soil samples or sediments, microplastics were identified in all samples. However, one sample from the 15 to 25 cm soil fraction of a core in the third section of the swale retrieved a single particle, not enough to be considered statistically different from the blank samples.

No significant difference was observed when comparing samples by section of the BFS. The site's horizontal variability is lower than the vertical effects of microplastic accumulation on the surface. It also suggests the microplastic sources are homogeneous throughout the site.

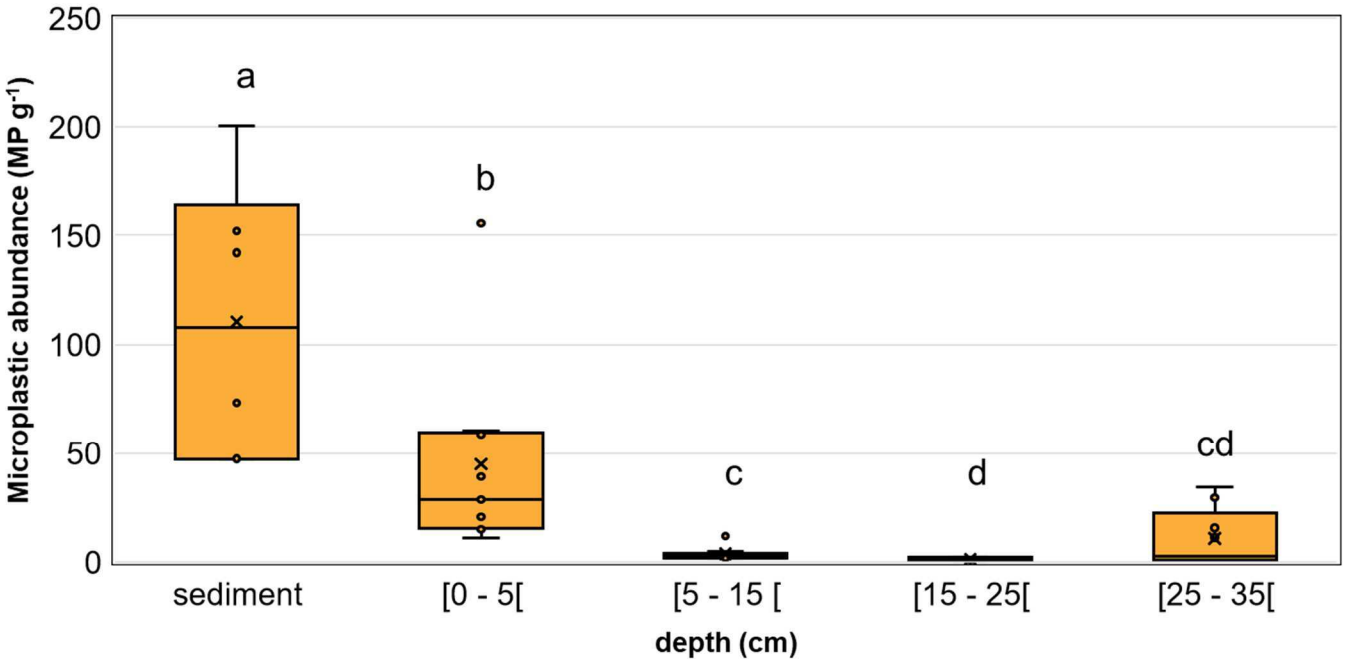

FIGURE 44: MICROPLASTIC ABUNDANCES IN THE BFS REPRESENTED BY DEPTH. DIFFERENT LETTERS INDICATE A SIGNIFICANT DIFFERENCE BETWEEN THE BOX CHARTS.

6.2 Microplastic characterization – shape, size, polymers

Figure 45a represents the distribution of polymers identified in the soil and sediment samples. A total of 12 distinct polymer groups were identified in the soil samples. These include in order of most to least abundant PP, PE, PS, PA, PVC, PU, polyesters, ABS, acrylates, Alkyds, PVA, vinyl copolymer, PAN, polycarbonate.

The 3 most frequent polymers from soil and roadside sediments represented 95% of all identified microplastics. PP in particular was the dominant polymer, representing 72% of all soil microplastics, and 84% of all sediment microplastics. The following dominant polymers in soil and sediment samples were PE and PS. Although the majority of polymers were similarly distributed across all depths, polyesters represented a significantly higher fraction of plastics in the [15 – 25 cm [soil fraction. This difference may be explained by a higher degree of variability due to the lower number of microplastics collected at that depth.

Figure 45b represents the size distribution of all samples collected from soils, and sediments samples. In all samples, this distribution is skewed towards the smaller microplastics, with a modal major dimension of 50 to 100 µm. It is likely that particles smaller than 50 µm are underestimated in this study, as they are close to the 25 µm pixel size of the detector.

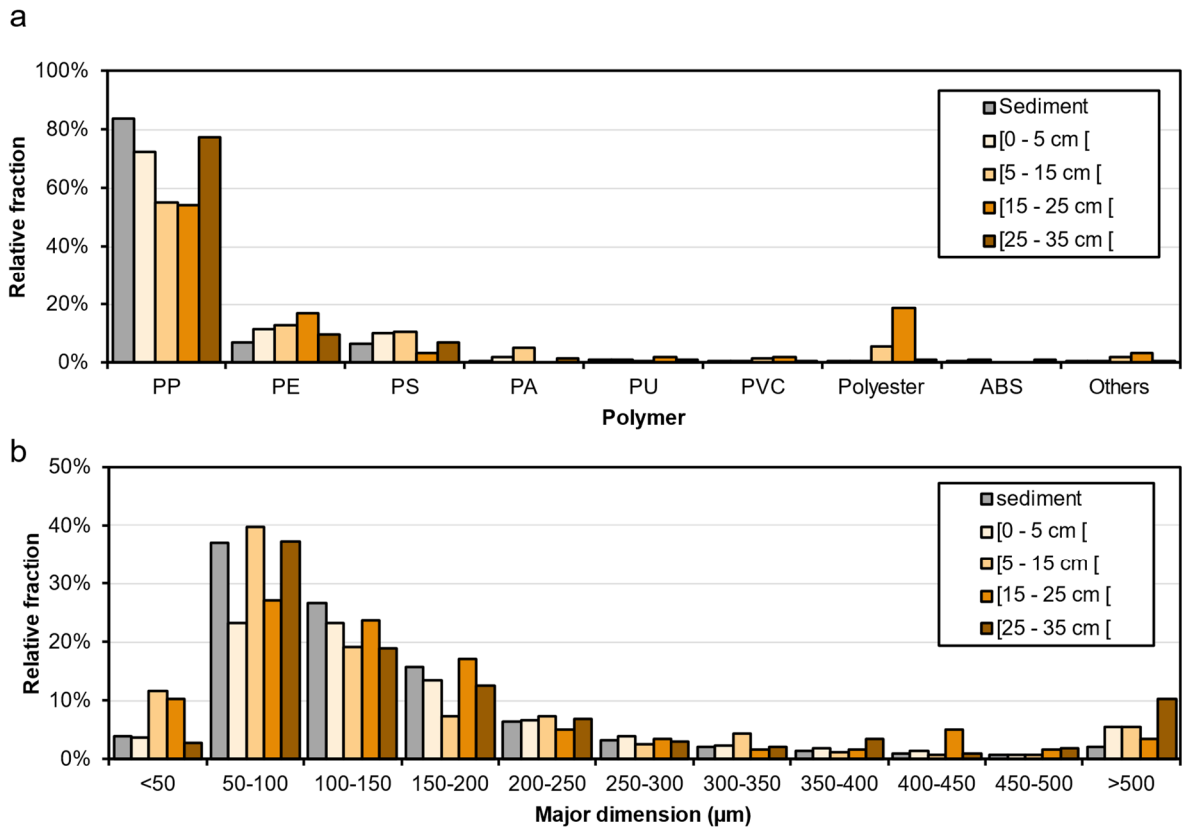

FIGURE 45A - DISTRIBUTION OF POLYMERS IN SOIL AND SEDIMENT SAMPLES; B – SIZE DISTRIBUTION OF SOIL AND SEDIMENT SAMPLES ACROSS DEPTH

Figure 46 represents the size distribution of the three dominant polymers identified in soil and sediment samples. All identified polymers presented a similar size distribution with a modal class at 50 to 100 µm. However, PE particles were observed to have a higher fraction of large microplastics, with 17% of all soil and sediment PE particles having a major dimension higher than 500 µm. A 2019 study on plastic weathering and secondary microplastics formation observed different fragmented microplastics size distributions for PE and PP after an exposition to similar weathering conditions (F. Julienne et al., 2019). It is possible that the higher abundance of large PE microplastics is related to a different weathering behaviour than other major microplastic polymers identified.

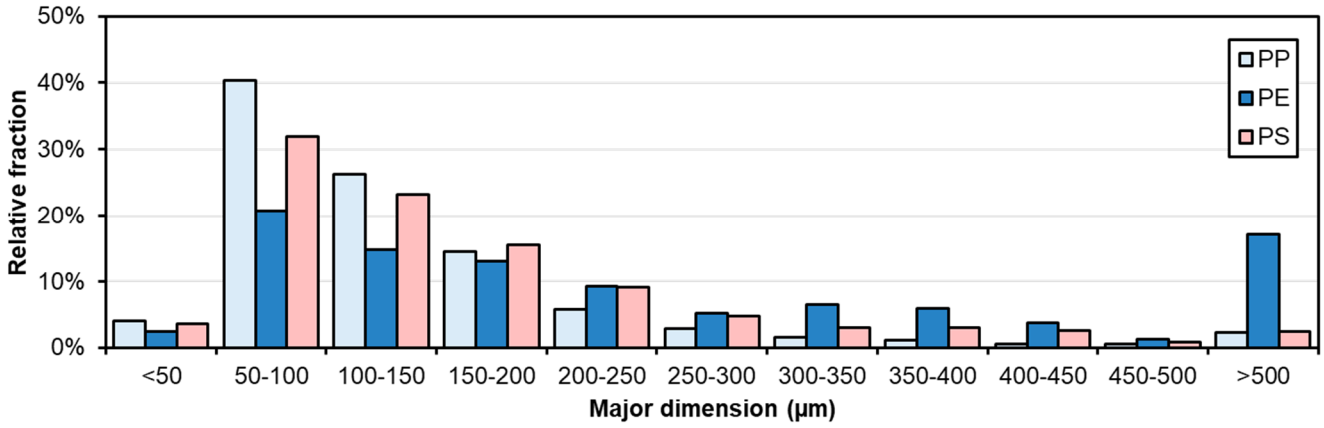

FIGURE 46: SIZE DISTRIBUTION OF THE THREE MOST COMMON POLYMERS ACROSS SOIL AND SEDIMENT SAMPLES

6.3 Vertical profile of TRWP contamination of the swale

A total of 48 soil and sediment samples were analysed by Py-GC-MS. These include 36 distinct soil core samples from the BFS, 3 of which were analysed in triplicate, 4 samples from the reference core, and 2 roadside sediment samples. Figure 47 represents the distribution of SBR and BR concentrations obtained, clustered by depths. An overall median SBR concentration of 0.21 mg g^{-1} was obtained on soil and sediment samples, with a mean ± standard deviation of 0.88 ± 1.19 mg g^{-1}. Similarly to microplastics, higher concentrations were measured in the surface soils and the sediment samples than in the deeper samples. Surface soil samples retrieved a median of 2.32 mg g^{-1}, with a mean of 2.19 ± (standard deviation) 0.93 mg g^{-1}. Only two roadside sediment samples were analysed for SBR, against 6 samples analysed with the FTIR. As a result, no significant difference could be noted between SBR concentrations in roadside accumulated sediment and in surface soils. The mean concentration in these samples was 1.32 mg g^{-1}

By contrast, a mean concentration of 0.11 ± 0.14 mg g^{-1} was measured in deeper soil samples. As shown on Figure 47, surface samples were significantly more concentrated than all deeper samples (Mann-Whitney tests, p values < 0.05).

Additionally, in 18 out of the 27 deeper soil samples analysed, the SBR concentration was lower than the analytical limit of detection. In particular, only 4 out of the 9 samples from a depth of 15 to 25 cm retrieved a SBR concentration above the limit of detection. As a result, while the surface SBR + BR concentration is significantly higher the deeper soil samples, no further correlation can be made between the deeper layers.

Interestingly, though Py-GC-MS analyses were conducted for the reference core, all samples were below the analytical limit of detection, and no SBR+BR could be measured. This suggests the TRWP contamination is very limited to absent in that soil.

Extrapolating the SBR + BR concentrations to assess the level of TRWP contamination in the soils is uncertain. While SBR and BR are a partial component of tyres, the fraction of a tyre they represent varies from less than 10% to 28% of a tyre (Rauert et al., 2021; U.S. Tire Manufacturers Association, 2020). Secondly, TRWP contain a significant and variable mineral fraction in addition to their rubber and additives content (Spanheimer and Katrakova-Krüger, 2022). It is likely that overall, the SBR+BR quantified through Pyr-GC/MS represents 5 to 20% of the total mass of TRWP from the samples. From this estimate, the TRWP could reach median concentrations of 11 to 21 mg g^{-1} in the surface samples, or up to 2.1 % in mass of the surface soil.

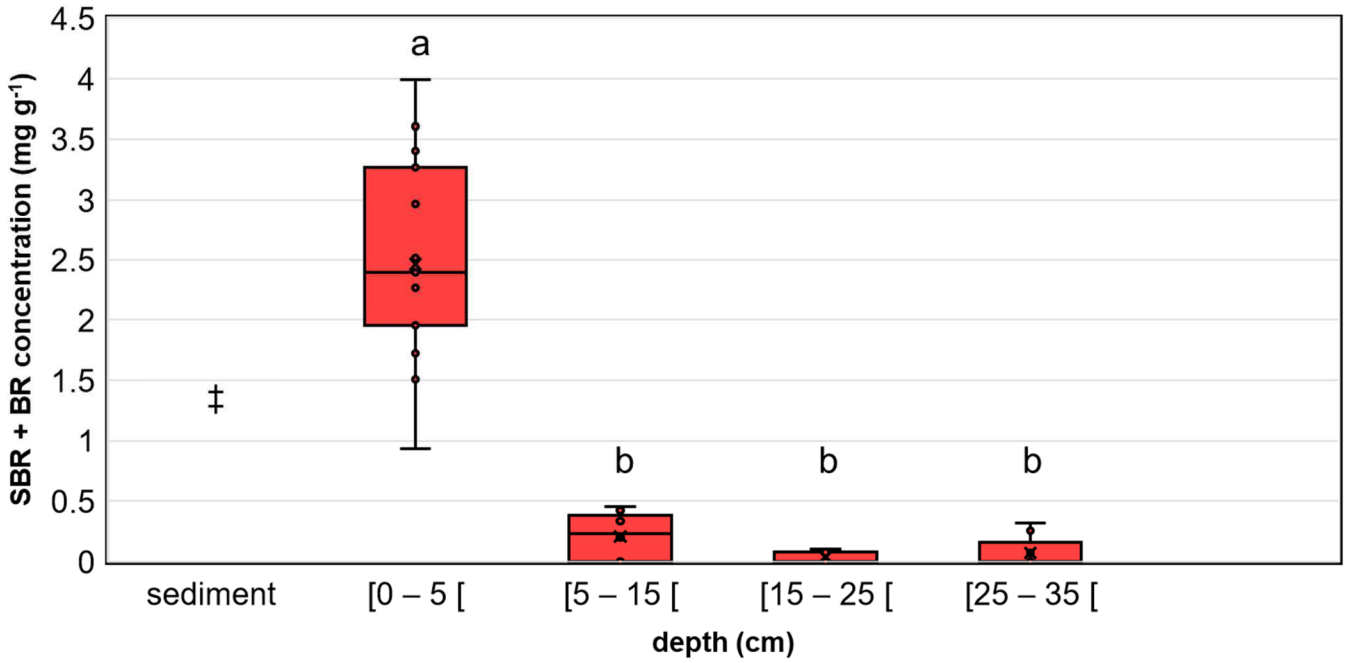

FIGURE 47: SBR+BR CONCENTRATIONS IN THE BFS REPRESENTED BY DEPTH.

6.4 Comparison of the two contaminations

In order to compare the concentrations profiles obtained by FTIR with the SBR quantification obtained by Pyr-GC/MS, an extrapolation produced by siMPle is used to estimate the mass concentration of microplastics in soil and sediment samples. In the software, a particle's volume is calculated by assuming the particle is an ellipsoid, with its vertical dimension equal to 0.6 times its minor horizontal dimension (F. Liu et al., 2019a; Simon et al., 2018). Its mass is then estimated according to the polymer's density in the library. A resulting overall microplastic concentration of 0.005 mg g^{-1} was obtained, with a mean of 0.14 ± 0.58 mg g^{-1}. Figure 48 represents the comparative concentration profiles of roadside sediment and soil samples using this extrapolation for µFTIR results, and SBR estimates.

Figure 48 compares the concentration profiles of microplastics and SBR+BR in the soil and sediment samples. Similar vertical profiles are observed, with higher concentrations at the

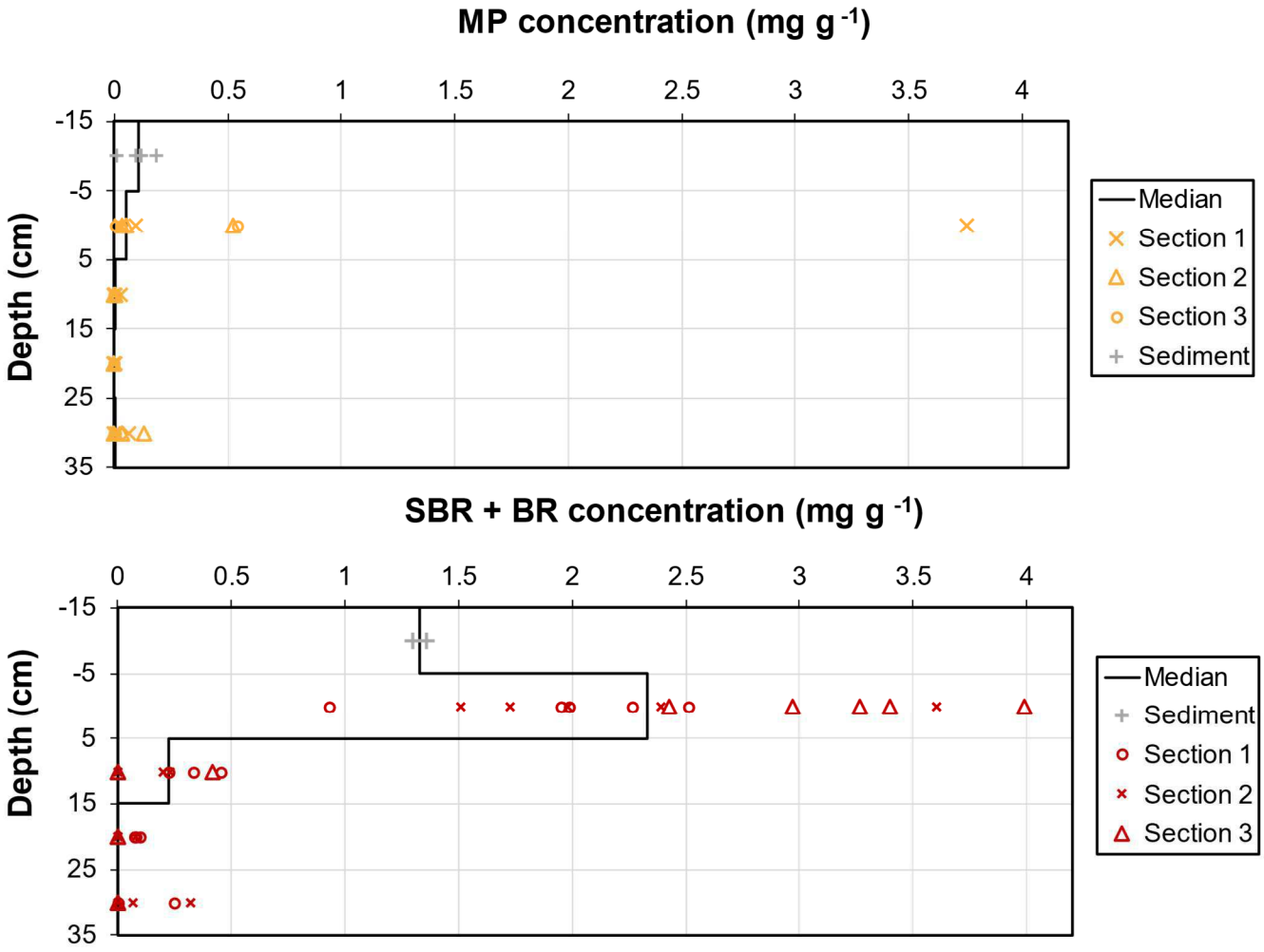

FIGURE 48: COMPARATIVE CONCENTRATION PROFILES OF SOIL AND SEDIMENT SAMPLES FOR MP IDENTIFIED BY FTIR AND SBR+BR IDENTIFIED BY PYR-GC/MS

surface and lower concentrations in the deeper layers. However, a paired Wilcoxon test shows that on average, the SBR+BR concentration in a soil sample is higher than the microplastic concentration ($p<0.05$). Given that SBR and BR only represent a small fraction of a TRWP,'s mass, the difference in concentration between microplastics and TRWP is even more significant.

While microplastics were quantified in the soils of the reference core with a concentration ranging from 0.025 to 0.065 mg MP g^{-1}, SBR+BR concentrations were below the limit of detection in the same reference core samples. This difference may be caused by a difference in the major sources for microplastics and TRWP in the system.

7 Estimates of microplastic and TRWP stocks

Using the results obtained in this chapter, an extrapolation to the total stocks of microplastics and TRWP in the BFS system is conducted.

7.1 Microplastic stock in the BFS

The vertical distributions obtained earlier in this chapter are extrapolated into the overall dimensions of the BFS. As described earlier, the BFS is 32 m long, 0.5 m large. It is 20 cm deep, with an additional depth of 0.5 m of soil below. This represents a total volume of 9.6 m^3. Field observations suggest that the layer of accumulated sediment on the road has a relatively constant thickness of 1 – 2 cm, and extends up to 50 cm away from the BFS. Figure 49 represents these dimensions on a schematic representation of the BFS.

Overall, the mean microplastic abundance in the BFS is 15.2 MP g^{-1}. However, the results discussed above show that microplastics are not homogeneously distributed in the structure. Abundances are significantly higher in the surface and sediment layers than in the deeper soil. For each collected depth, the mean microplastic abundance obtained is applied to entirety of the layer. The sloped areas of the surface of the BFS are considered to have an abundance equal to the mean abundance of the surface samples. The layers below the deepest soil layer collected are considered to have an abundance equal to the mean abundance of the deepest soil layers collected. The BFS is considered horizontally homogeneous, with no significant difference in microplastic abundance or concentration between its different sections. Finally, the soil's apparent density was estimated to be 1.48 g cm^{-3} (Kanso, 2021). Figure 49 summarizes the different layers and the concentrations considered for these layers.

Table 10 provides a summary of the estimated values of microplastic stock in the BFS and in the surrounding sediment. A total of **2.9 x10^{8}** microplastics are estimated to be stored in the BFS, for a mass of **2.2 kg**. Although the sediment and surface layers (< 5 cm) only represent 27% of the total volume of solid, they are estimated to store 74% of all microplastics and 92% of the mass of microplastics in the system.

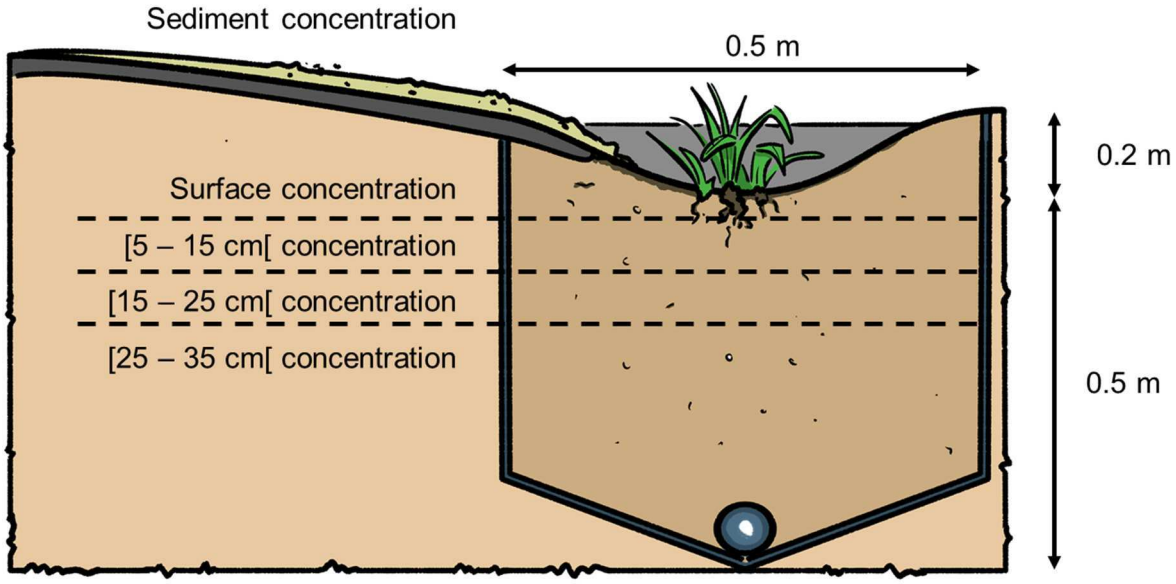

FIGURE 49: DIMENSIONS AND WORKING CONCENTRATION HYPOTHESES IN THE BFS

TABLE 10: SUMMARY OF THE MICROPLASTIC STOCK DISTRIBUTION IN THE BFS

	Overall mass estimate (kg)	MP abundance (MP/g)	MP number	MP concentration (mg/g)	MP mass (kg)
Mass sediment	473	110	5.2 x10^{7}	0.090	0.043
Mass 0 - 5	3,550	45.0	1.6 x10^{8}	0.56	2.00
Mass 5 - 15	2,370	3.62	8.6 x10^{6}	0.0049	0.012
Mass 15 - 25	2,370	1.31	3.1 x10^{6}	0.00049	0.0012
Mass 25 - 35	5,920	10.8	6.4 x10^{7}	0.027	0.16
Total BFS	14,200		2.4 x10^{8}		2.17
Total	**14,600**		**2.9 x10^{8}**		**2.21**

7.2 TRWP stock estimate in the BFS

The total stock of TRWP in the BFS system is estimated with the same working hypotheses as microplastics. However, while microplastic masses were obtained from the extrapolation of

their geometric characteristics on siMPle, the quantification of TRWP in the samples directly provides a mass of the synthetic rubber polymers found in the TRWP, SBR and BR. Overall, an SBR+BR mass of **10.5 kg** was estimated in the BFS system.

Synthetic polymers represent 24% of a lightweight vehicle tyre and 11% of a heavy duty vehicle tyre (U.S. Tire Manufacturers Association, 2020). Additionally, TRWP are composed of a significant fraction of road minerals, that can represent up to 50% of the mass of the particle (Rødland et al., 2022a; Spanheimer and Katrakova-Krüger, 2022). From these two assumptions, a range of TRWP stock in the BFS can be obtained. At the lower bound, all TRWP in the BFS are considered to originate from lightweight vehicles and are considered to have no mineral fraction. This represents a total mass of 43.8 kg in the BFS system. At the upper bound, all TRWP are considered to originate from heavy duty vehicles and have a mineral fraction of 50%. This represents a total mass of 191 kg. Table 11 summarizes these results.

Like microplastics, an estimate of 90% of all TRWP in the BFS system are stored in the sediment or surface layers of the BFS.

TABLE 11: SUMMARY OF THE TRWP STOCK DISTRIBUTION IN THE BFS

	Overall mass estimate (kg)	SBR + BR concentration (mg/g)	SBR + BR mass (kg)	TRWP mass (min)	TRWP mass (max)
Mass sediment	473	1.33	0.63	2.62	11.43
Mass 0 - 5	3,550	2.50	8.89	37.04	161.63
Mass 5 - 15	2,370	0.21	0.49	2.05	8.93
Mass 15 - 25	2,370	0.037	0.09	0.36	1.59
Mass 25 - 35	5,920	0.071	0.42	1.76	7.68
Total BFS	14,200		9.89	41.21	179.83
Total	**14,600**		**10.52**	**43.83**	**191.27**

7.3 Limits of the stock estimates

Though these estimates are sufficient for the objectives of this work, they are only first-order extrapolations and present several limitations.

First, some regions of the BFS were not sampled. While the assumption that the concentrations are horizontally homogeneous, the assumptions that the concentrations in the sloped areas of the surface of the BFS are the same as the sampled surface concentrations is unclear.

Similarly, the layers below 35 cm were not sampled so as not to damage the impermeable geomembrane. Multiple factors are susceptible to cause an increase in microplastic concentration in these deeper layers. For example, if microplastics and TRWP can be infiltrated in the deeper soil but cannot exit the BFS through the drain, these particles may accumulate near the deeper layers. If the geomembrane is susceptible to degradation, it may also be a source of microplastics in the deeper layers.

Finally, it is impossible to determine the fraction of the stock that was present in the substrate at the construction of the BFS and the fraction that accumulated since its construction. The vertical distribution of microplastics and TRWP, and particularly the low concentrations in the deeper layers, suggest that either the initial stock migrated deeper than what was sampled or out of the BFS, or that the initial stock was limited.

8 Insights and conclusion

This chapter focused on the soils and accumulated road sediment of a BFS receiving urban runoff from a high-traffic highway. To assess the vertical distribution of microplastic and TRWP contamination in these soils, core samples were collected and analysed using two state-of-the-art, complementary analytical methodologies.

While microplastics were present at all depths, concentrations were significantly lower in deeper samples than at the surface. This suggests most microplastics are trapped in the top layers of the soil, with little downward transport. Similarly, TRWP were significantly more concentrated in the supper soil layers and accumulated sediment.

Additionally, TRWP were found to reach significantly higher concentrations than other microplastics. Their concentration in the upper soil layers is likely reaching 1% in mass. Such a high concentration underlines the importance of studying the TRWP content in runoff, particularly urban runoff, as part of microplastic quantification studies.

Using these results, first-order estimates of the stocks of microplastics and TRWP in the soils of the site of interest were obtained. These estimates suggest that the vast majority of microplastics and contaminants are stored at the surface, and were likely not present in the BFS when it was first constructed.

Chapter 4 – First order mass balance of microplastics and TRWP accumulation in a sustainable urban drainage system

1 Contents

2 Introduction

2.1 Objectives

In the previous chapter, vertical profiles of microplastics and TRWP abundance and concentration were measured in the soils and sediments of a BFS on the side of a high traffic highway. Using these concentration profiles, an estimate of the microplastic and TRWP stock in the BFS was obtained.

In order to better understand the BFS system, the sources of microplastics and TRWP, and their relative importance, remain to be assessed. Building upon the results of chapter 3, this chapter produces a mass balance of microplastics and TRWP at the scale of a single SUDS, the Compans BFS. Its objectives are to i) identify the major sources and sinks of the BFS for microplastics and TRWP, ii) provide estimates of the yearly fluxes from these sources and sinks, and iii) compare these yearly fluxes to determine whether some dominant microplastic and TRWP sources emerge.

2.2 Identification of the major microplastics and TRWP pathways in the BFS

Multiple potential microplastic and TRWP sources and sinks were identified on and around the BFS. Figure 50 summarizes these potential sources and sinks.

Three main microplastic sources were identified. The first is atmospheric deposition, which represents a direct microplastic flux into the BFS. Microplastics also deposit on the road, and indirectly end up in the BFS via the second potential source, which is road runoff transported and infiltrated in the BFS. A third potential source is the fragmentation of macrolitter accumulated on site. As mentioned in chapter 3 of this manuscript, preliminary observations of the sampling site revealed it was cluttered with an abundance of debris and macrolitter, ranging from discarded tobacco products to car accident debris. This macrolitter is susceptible to produce microplastics through their fragmentation by moving vehicles on the road, or the regular mowing of vegetation in the BFS.

While the atmospheric deposition and runoff pathways are the same as for microplastics, the heavy traffic must be considered as a major supplementary TRWP source. Vehicles represent a

major source of TRWP deposited on the road and transported through the abrasion of tyres (Rødland et al., 2022a; Ziajahromi et al., 2023). These particles can either directly deposit and be further transported in runoff (Ziajahromi et al., 2023), or be suspended in the atmosphere and deposit further away (Evangeliou et al., 2020; Spanheimer and Katrakova-Krüger, 2022). In particular, this abrasion is thought to be higher in zones of dynamic driving such as acceleration or braking (De Oliveira et al., 2024).

Out of these multiple sources, the outlet of the BFS can be considered the main potential microplastic outlet of the system. As described at the beginning of chapter 3, the BFS is separated from the surrounding ground by an impermeable geomembrane, and is drained by a punctual outlet into an overflow trench.

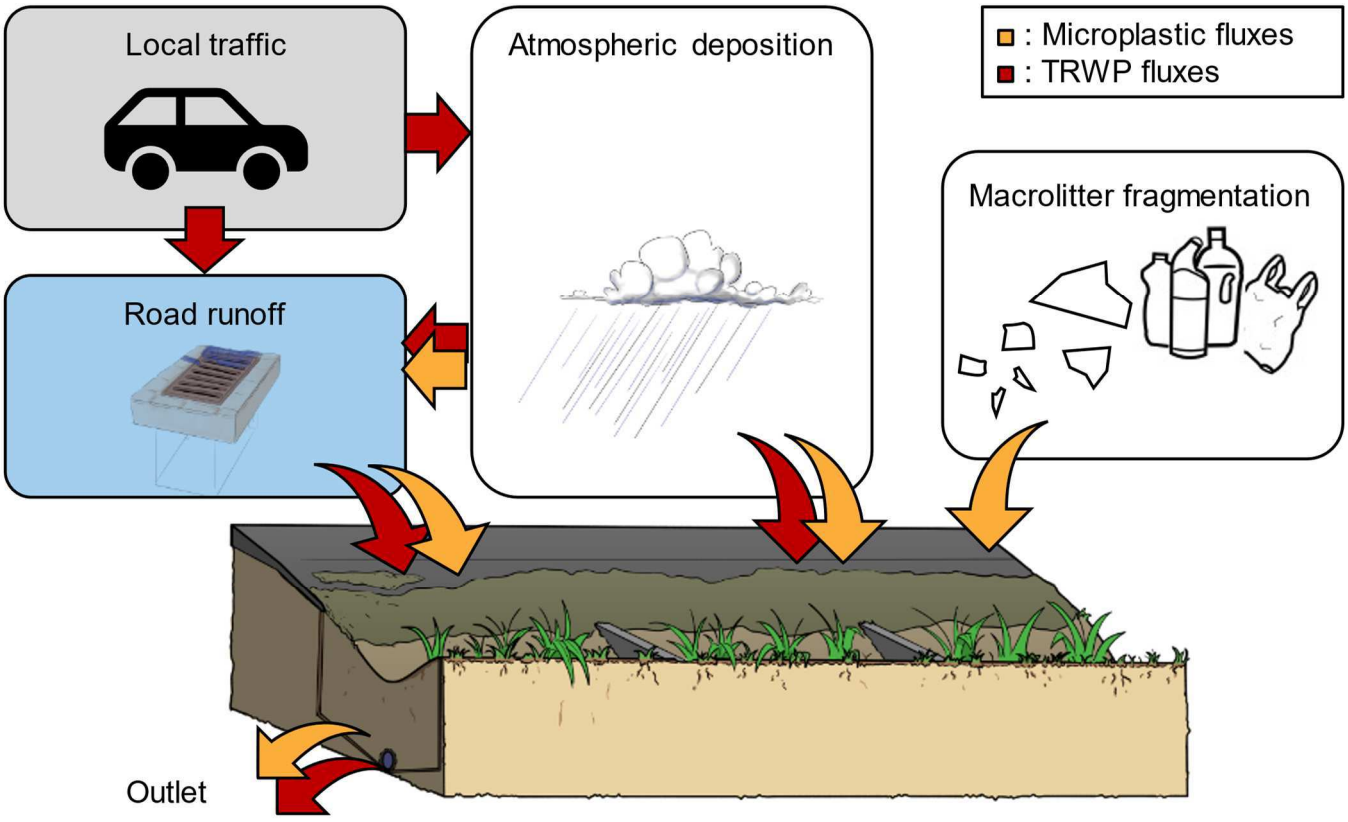

FIGURE 50: IDENTIFICATION OF THE MAJOR MICROPLASTIC AND TRWP PATHWAYS IN THE COMPANS BFS SYSTEM

2.3 Presentation of the mass balance

Overall, the mass balance for microplastics in the system of interest can be summarized in the following equation:

$$Q_{total} = Q_{atmosphere} + (Q_{runoff} - Q_{outlet}) + Q_{fragmentation}$$

- Q_{total} represents the overall microplastic accumulation rate in the BFS.
- $Q_{atmosphere}$ is the yearly contribution from the atmosphere
- Q_{runoff} is the yearly microplastic input from raw runoff in the system
- Q_{outlet} is the yearly microplastic flux leaving the BFS from the outlet
- $Q_{fragmentation}$ is the yearly microplastic flux produced from the fragmentation of macrolitter accumulated on site.

In the following sections, estimates for each of these values are obtained and compared.

3 Microplastic atmospheric deposition fluxes in the BFS

3.1 Description of the flux

The first potential source is atmospheric deposition. The site is part of the Paris urban area, which represents a large-scale diffuse source of microplastic that can be transported in the atmospheric compartment. Atmospheric deposition is both a direct and an indirect microplastic source, as particles can either directly deposit on the 16 m^2 surface area of the BFS, or deposit on the 352 m^2 of road that drains into the BFS.

3.2 Flux estimate

Several atmospheric deposition monitoring campaigns were conducted during this PhD. Their results are presented in chapter 2. While no monitoring campaign was conducted in immediate proximity to the Compans BFS, atmospheric deposition from campaign A21 is considered a suitable first order approximation for the deposition occurring in the BFS. A mean deposition rate of 34.5 MP m^{-2} d^{-1}, or 0.19 mg MP m^{-2} d^{-1} was measured during campaign A21. This value can be extrapolated to a yearly deposition rate over the surface area of the BFS:

$$Q_{atmosphere} = \overline{D_{A21}} \times l_{BFS} \times w_{BFS}$$

- $\overline{D_{A21}}$ is the mean deposition rate during campaign A21
- l_{BFS} is the length of the BFS
- w_{BFS} is the width of the BFS

This represents a yearly flux of 2.02 $\times 10^5$ MP yr^{-1}, or 1.1 g MP yr^{-1}.

$Q_{atmosphere}$ = 1.1 g MP yr^{-1}

4 Stormwater fluxes in and out of the BFS

4.1 Description of the fluxes

Microplastics that accumulate on the road represent a second direct source. They are introduced into the BFS through urban runoff, and are susceptible to accumulate into the soil. Urban runoff has been suspected to represent a major transfer pathway for microplastics by several authors. In a 2019 study, Liu *et al.* noted microplastic accumulation in stormwater retention ponds near highways (F. Liu et al., 2019b). Studying microplastics in the water of a harbour in the Cook's River estuary, Hitchcock noted significantly higher microplastic abundances during storm events, suggesting stormwater runoff was the dominant microplastic transfer pathway (Hitchcock, 2020) More recently, multiple studies quantified microplastics in stormwater runoff in urban environments (Cho et al., 2023; de Jesus Pinon-Colin et al., 2020; Lange et al., 2021; Treilles et al., 2021; Werbowski et al., 2021). Abundance estimates range from 1.1 – 26 MP L^{-1} (Werbowski et al., 2021) to 54 – 639 MP L^{-1} (Cho et al., 2023), with high degrees of variability between studies and between samples in studies. Authors note that systems like bioretention systems and rain garden effectively trap microplastics, with removal rates in the orders of 90% (Garcia-Haba et al., 2023; Lange et al., 2021; Werbowski et al., 2021). These findings all the more suggest that road runoff is likely to be an important microplastic source in the BFS.

4.2 Microplastic sampling, characterization and quantification in raw runoff and outlet samples

In order to assess the microplastic input from runoff into the BFS, as well as the microplastic output from filtered water out of the BFS, one runoff and two outlet samples were collected.

Directly sampling runoff entering the BFS is not possible. As mentioned in chapter 3, the BFS diffusely receives runoff over its length of 32 m, which means it does not have a point where direct runoff collection is possible. Instead, in order to represent the water inlet into the BFS, untreated road runoff was collected on one sampling manhole located 140 m away in the direction of traffic on the same road as the BFS. This location was installed and used on earlier studies on the site (Flanagan et al., 2019, 2018). The equipped sampling manhole is shown on Figure 51a. It drains runoff from an 86 m length of road, which represents a 945 m² drainage area. The flow rate is continuously monitored in the manhole with a 17.4 L tipping bucket flow meter. A refrigerated automatic sampler (Sigma SD 900 P) was used to collect runoff in proportion to the site's flowrate.

The outlet of the BFS is equipped to enable its sampling. Water samples were collected passively by collecting a fraction of every second bucket tip from a 1 L tipping-bucket flow meter located in a manhole at the outlet of the BFS, ensuring a representative sampling of the totality of a rain event. Figure 51b represents the sampling equipment that allowed for this collection.

Unfortunately, technical issues limited access to the site and only one raw runoff sample approximating the inlet of the BFS could be collected, along with two outlet samples. The results presented in this section should therefore be considered as preliminary and interpreted with caution. They will mainly serve as a first-order estimate for the runoff influx into the BFS. Additionally, four supplementary runoff samples were collected on another high-traffic site for comparison purposes.

After collection, all runoff samples were subjected to a preliminary treatment, which is detailed on Figure 51c. Each treatment step was conducted in accordance to the description provided on chapter 1. Samples first underwent a density-based separation with NaI, followed by an oxidative treatment using H_2O_2. After treatment, samples were deposited on alumine filters for µ-FTIR imaging analysis.

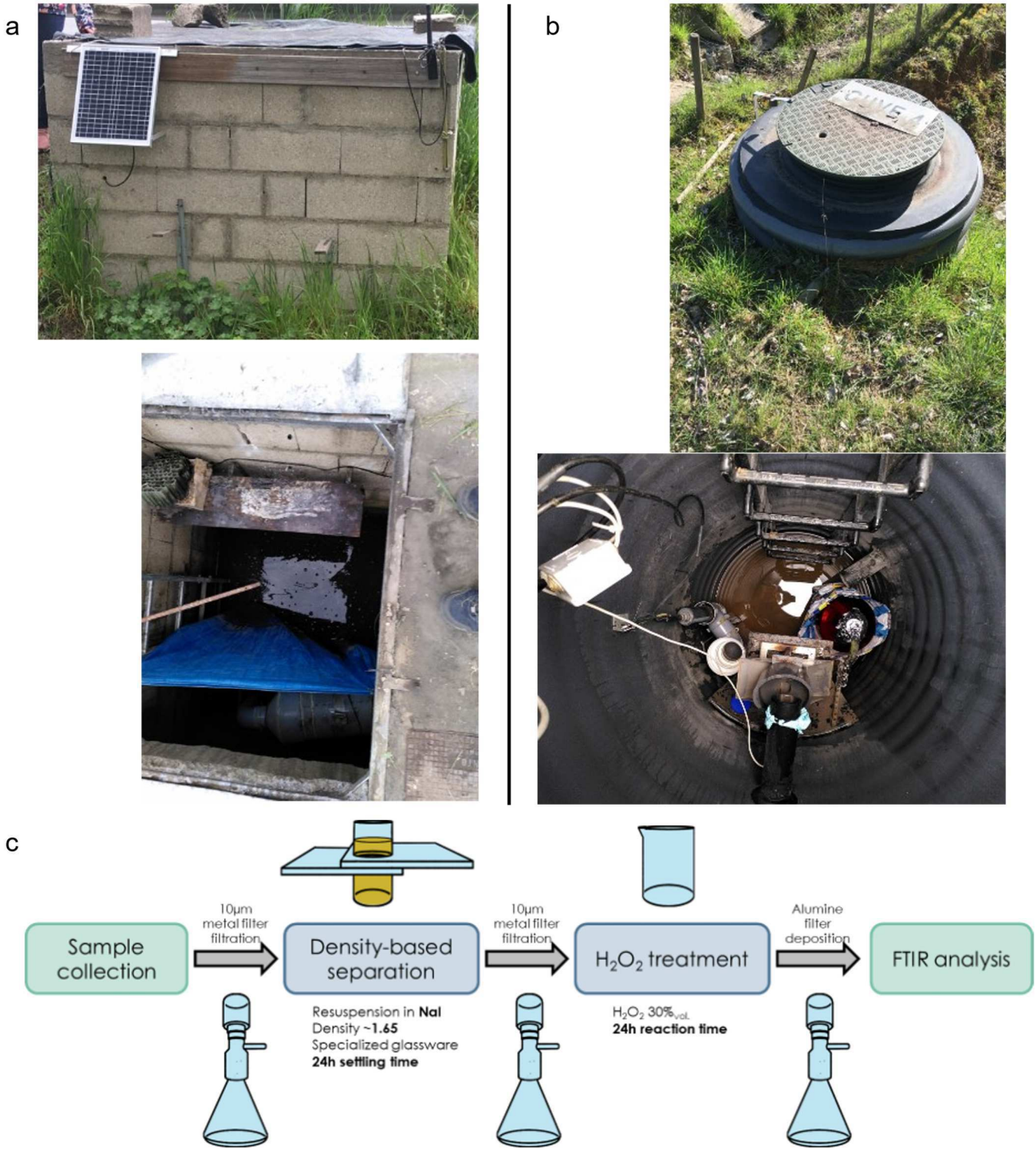

FIGURE 51A – PHOTO OF THE STRUCTURE AND INTERIOR OF THE RAW RUNOFF SAMPLING MANHOLE; B – PHOTOGRAPHS OF THE STRUCTURE AND INTERIOR OF THE OUTLET SAMPLING MANHOLE; C – DESCRIPTION OF THE RUNOFF TREATMENT PROTOCOL

4.3 Results – microplastic characteristics and abundances in the runoff and the outlet of the BFS

Though 12 different polymer groups were identified in the soil and sediment samples of the BFS, only 6 different polymers were identified in the water samples: PP, PE, PS, PA, polyesters and PVC. Overall, PP represents 56% of all polymers, followed by PE and PVC. Interestingly, Polyvinyl chloride (PVC) were the second dominant samples in the outlet water samples, representing 23% of all identified particles, while they only represented 0.7% of all soil and road accumulated sediments.

Similarly, to other matrices collected throughout this PhD, [50 – 100 µm [is the modal class of identified microplastics. Large particles appear to be filtered from the outlet, with particles larger than 100 µm representing 41% of all microplastics in the outlet water samples compared to 59 % in soil and sediment samples and 66% in the raw runoff water.

A microplastic abundance of 26.1 MP/L was measured in the raw runoff water collected on site. By comparison, the outlet of the BFS retrieved abundances of 0.71 MP L^{-1} and 11.8 MP L^{-1}, for an overall concentration of 4.1 MP L^{-1}. These represent concentrations of 0.31 mg MP g^{-1} in the raw runoff, and 1.7 µg MP g^{-1} at the outlet of the BFS, for 84% of difference in concentration. Removal rates of 94% were measured in an earlier studies on the same site for total suspended solids, which is in a similar order of magnitude (Flanagan et al., 2018).

These preliminary results are in similar orders of magnitude, but on the lower end of values measured in the literature (Cho et al., 2023; Treilles et al., 2021; Werbowski et al., 2021). This may be explained by differences in analytical methodology and targeted particles between this work and others studies, or by a lower level of microplastic contamination on the road where this runoff is collected. It is also possible that other factors, particularly the intensity of the rain events, affect the microplastic abundance in the runoff. The low number of samples collected prevents this quantification.

For the sake of comparison, 4 additional runoff samples were collected on a similar site in Nantes, and underwent the same treatment and analysis. In these samples, a median microplastic abundance of 12 MP L^{-1} was obtained.

4.4 Flux estimates

While the number of samples is limited, it is possible to extrapolate a yearly flux from the microplastic concentrations in the inlet and the outlet of the BFS. Table 12 summarizes the yearly precipitations from 2017 to 2022 at the Roissy-Charles de Gaulle meteorological station, the closest meteorological station available (Infoclimat, 2023; Meteo data, 2023).

TABLE 12: YEARLY PRECIPITATIONS AT THE ROISSY-CHARLES DE GAULLE METEOROLOGICAL STATION

Year	Precipitation (mm)
2016	674.1
2017	723.7
2018	736.9
2019	770.8
2020	691.9
2021	877.4
2022	548.7
mean	**724.9**

The mean of this cumulated rainfall can be used to estimate an average rainfall volume of 255 m^3 on the 352 m^2 of road drained by the BFS every year. This volume can be used to estimate the upper limit for the yearly flux of microplastics in the raw runoff:

$$\boldsymbol{Q_{runoff-max} = \overline{P_{2017-2022}} \times S \times c_{runoff}}$$

- $\boldsymbol{\overline{P_{2017-2022}}}$ is the average yearly rainfall on the BFS
- $\boldsymbol{S}$ is the surface area of the road drained by the BFS
- $\boldsymbol{c_{runoff}}$ is the microplastic concentration measured in runoff

This represents an upper limit of 6.7×10^6 MP yr^{-1}, or 80 g MP yr^{-1}. In earlier works on the same sites, an estimate of 38% of the yearly runoff was noted to overflow from the BFS directly into the overflow trench (Flanagan, 2018). As the microplastic content of overflowing runoff may not infiltrate in the BFS, this provides a lower limit of this yearly flux:

$$\boldsymbol{Q_{runoff-mon} = (1 - x_{overflow}) \times \overline{P_{2017-2022}} \times S \times c_{runoff}}$$

- $\boldsymbol{x_{overflow}}$ is the fraction of runoff that overflows before its microplastic content infiltrates into the BFS

This represents a flux of 4.1×10^6 MP yr^{-1}, or 49 g MP yr^{-1}.

An upper limit for the yearly flux of microplastics through the outlet of the BFS is obtained by considering that the totality of the runoff entering the BFS is evacuated through its outlet. This is represented in the following equation:

$$Q_{outlet-max} = \overline{P_{2017-2022}} \times S \times c_{outlet}$$

- c_{outlet} is the microplastic concentration at the outlet of the BFS.

This represents a flux of 1.6×10^6 MP yr^{-1}, or 0.5 g MP yr^{-1}. However, earlier works on the same site note that 20% of the runoff's volume is dissipated by the BFS through evapotranspiration (Flanagan, 2018). Considering this volume lost through evapotranspiration and the volume that overflows before it filters through the volume, a lower limit of the flux at the outlet can be estimated:

$$Q_{outlet-min} = (1 - x_{overflow}) \times (1 - x_{evapotranspiration}) \times \overline{P_{2017-2022}} \times S \times c_{outlet}$$

- $x_{evapotranspiration}$ is the fraction of runoff that is lost to evapotranspiration and does not leave through the outlet.

This represents a flux of 7.9×10^5 MP yr^{-1}, or 0.2 g MP yr^{-1}

In light of the extrapolation from these samples, the microplastic fluxes from the runoff and the outlet of the BFS are in the following ranges:

49 g MP yr^{-1} < Q_{runoff} < 80 g MP yr^{-1}

0.2 g MP yr^{-1} < Q_{outlet} < 0.5 g MP yr^{-1}

Though this estimate is not related to the microplastic mass balance of the BFS, another perspective is to assess the flux of microplastics from the runoff that are not filtered by the BFS and that is susceptible to infiltrate deeper into receiving environments. This is obtained by summing the flux of microplastics from the outlet of the BFS and the flux of microplastics that overflow from the runoff. Overall, this represents a flux of 3.3 MP $\times 10^6$ yr^{-1}, or 30 g MP yr^{-1}.

5 Macrolitter accumulation in the BFS

5.1 Presentation of the flux

Finally, the fragmentation of the macrolitter accumulating in the system represents a third potentially major source of microplastics. In a 2022 study by Ledieu *et al.*, macrolitter accumulation was monitored over the course of a year in a high-traffic highway (Ledieu et al., 2022). The majority of the identified debris consisted in plastic materials, with sources including both deliberate litter and accidental leaks. These debris may fragment due to contact with traffic, mechanical erosion, or be damaged by the yearly mowing of the vegetation growing in the BFS. Macrolitter fragmentation remains a poorly understood topic. Some weathering studies have been conducted to assess the factors that are susceptible to damage plastic debris and product microplastics, but these studies remain qualitative and cannot provide reliable assessments of the microplastic production from the fragmentation of larger debris (Andrady, 2022).

5.2 Macrolitter accumulation monitoring in the BFS

5.2.1 Sampling methods

In order to assess their potential as a microplastic source in the soils of the BFS, the macrolitter accumulation was monitored on the BFS. Two successive monitoring campaigns were conducted between June 2021 and March 2023. After a complete clean-up of the site to define a baseline condition, the first campaign was conducted from June 2021 to June 2022. The second campaign was conducted from June 2022 to June 2023. A total of 5 samples were collected in each campaign, with delays between samples ranging from 23 to 87 days.

During both campaigns, two parts of the sites were sampled separately: a first portion that consisted in the BFS up to the road, and a second portion further away from the BFS, in the overflow trench. All visible debris were collected by hand and stored in plastic bags for their analysis.

5.2.2 Treatment and analysis

All samples underwent the same treatment and analytical procedure following their collection. First, all debris collected were rinsed with water, and left to dry at ambient temperature.

After they were dried, all debris from a sample were sorted by function and placed on a table for analysis, as shown on Figure 53a. Debris were then weighed and categorised using the DCSMM-OSPAR (Convention for the Protection of the Marine Environment of the North-East Atlantic) classification (MSFD Technical Subgroup on Marine Litter., 2013). It is a standardised macrolitter classification based on the materials of the debris (plastic, metal, glass, etc.) and their function before they were discarded.

In the second campaign, the samples were also characterized chemically in addition to the use of the OSPAR classification. Indeed, while the OSPAR classification is useful to link the macrolitter to their original sources, the identification and quantification of microplastics is largely based on the chemical identification of their polymer. Analysing the composition of the macrolitter can help to link the plastic fraction of the macrolitter and the microplastics present in the soils.

Plastic debris were analysed using a Nicolet iS5 ATR-FTIR (Thermo Scientific, USA). Figure 53b shows the ATR-FTIR used for analyses. 16 scans were conducted for each spectrum. After they were collected, the spectra were compared to both the Thermo Scientific libraries and library developed by the research group. Spectra that had a similarity score > 80% were considered a match, and spectra with a similarity score between 50% and 80% were manually confirmed by comparing the peaks before they were considered a match.

5.2.3 Characterization of the accumulated macrolitter

In addition to the OSPAR classification which is largely based on the function of the debris characterized, the type of material composing the debris was noted during their characterization. Figure 52 represents the distribution of materials accumulated in the samples collected. Plastic was the dominant material in all samples, representing 79% of all objects characterized and

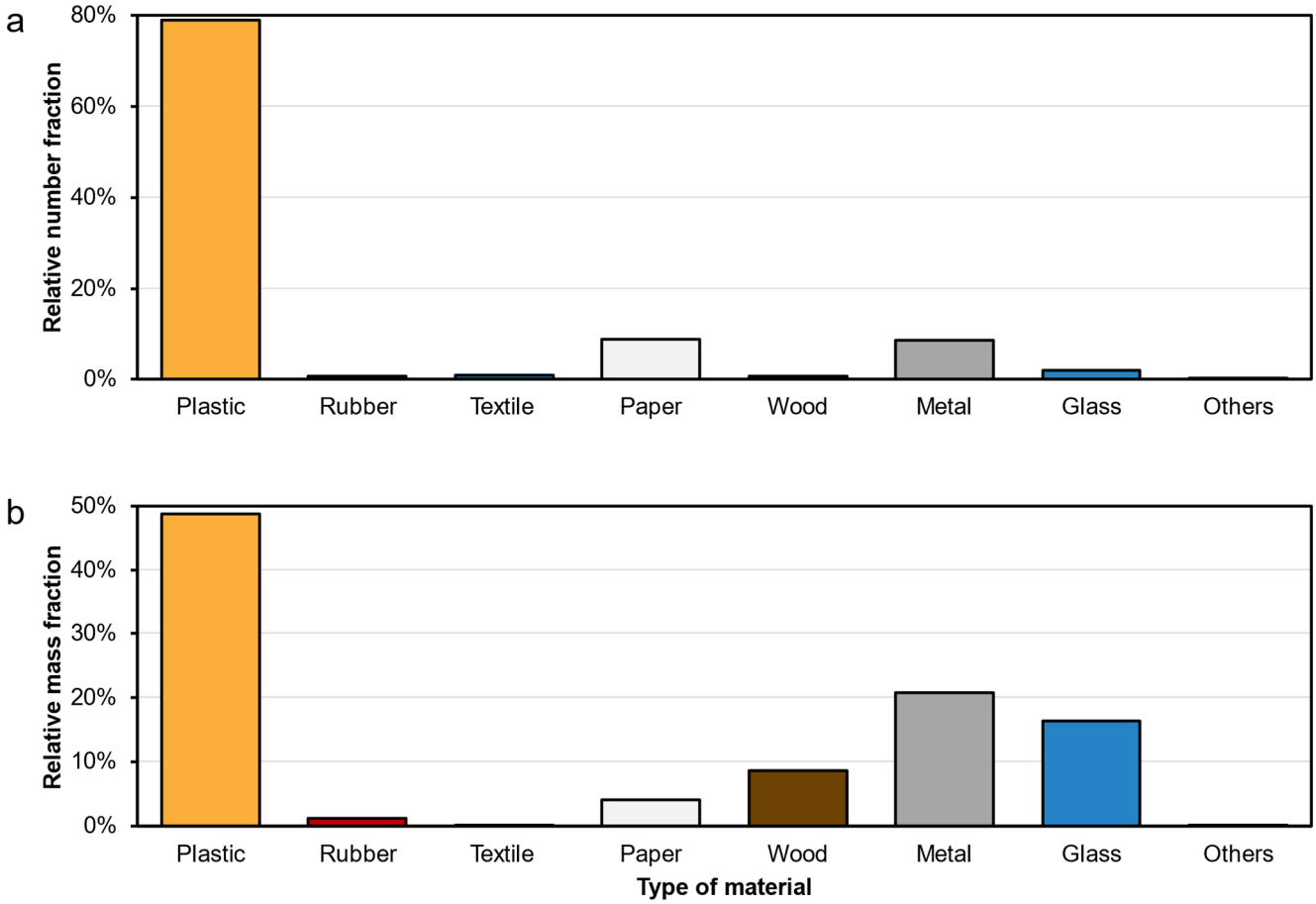

FIGURE 52: DISTRIBUTION IN NUMBER (A) AND IN MASS (B) OF MATERIALS IN THE MACROLITTER ACCUMULATED OVER THE TWO CAMPAIGNS

49% of the mass of macrolitter collected. The majority of metal and glass items retrieved were cans and bottles. They were typically less common than plastic items but more massive, resulting in a higher mass fraction than their number fraction. While some of the rubber items may be partly composed of SBR or BR, they represent a small fraction of the macrolitter identified on site and are likely to be a negligible fraction of the SBR+BR identified in the soil and sediment samples.

a b

FIGURE 53A - REPRESENTATION OF THE SORTING AND CHARACTERIZATION OF A SAMPLE B- ILLUSTRATION OF THE ATR-FTIR USED IN THE SECOND CAMPAIGN

5.2.4 Macrolitter accumulation on the Compans BFS

A mass of 15.5 kg of debris were collected over the two separate monitoring campaign, for a total of 1,348 individual items. These are separated in 8.9 kg and 386 elements in the initial collection collected, 3.1 kg and 387 elements in the first campaign, and 3.6 kg and 412 elements in the second campaign. In order to assess the overall accumulation of debris on the BFS, the results are represented as an accumulation rate over the sampling period, in number and mass of debris per day.

Figure 54 represents the macrolitter accumulation rates over the two sampling periods. Accumulation rates in numbers of items range from 0.86 to 2.66 items d^{-1}. In mass, these accumulation rates range from 3.1 to 40.4 g d^{-1}, with a median of 10.5 g d^{-1}. As shown on Figure 54, accumulation rates in mass and in numbers are not particularly correlated. The highest accumulation rates in appear to be related to the accumulation of debris from single events such as road incidents, when a few items of large mass are added to the system at once.

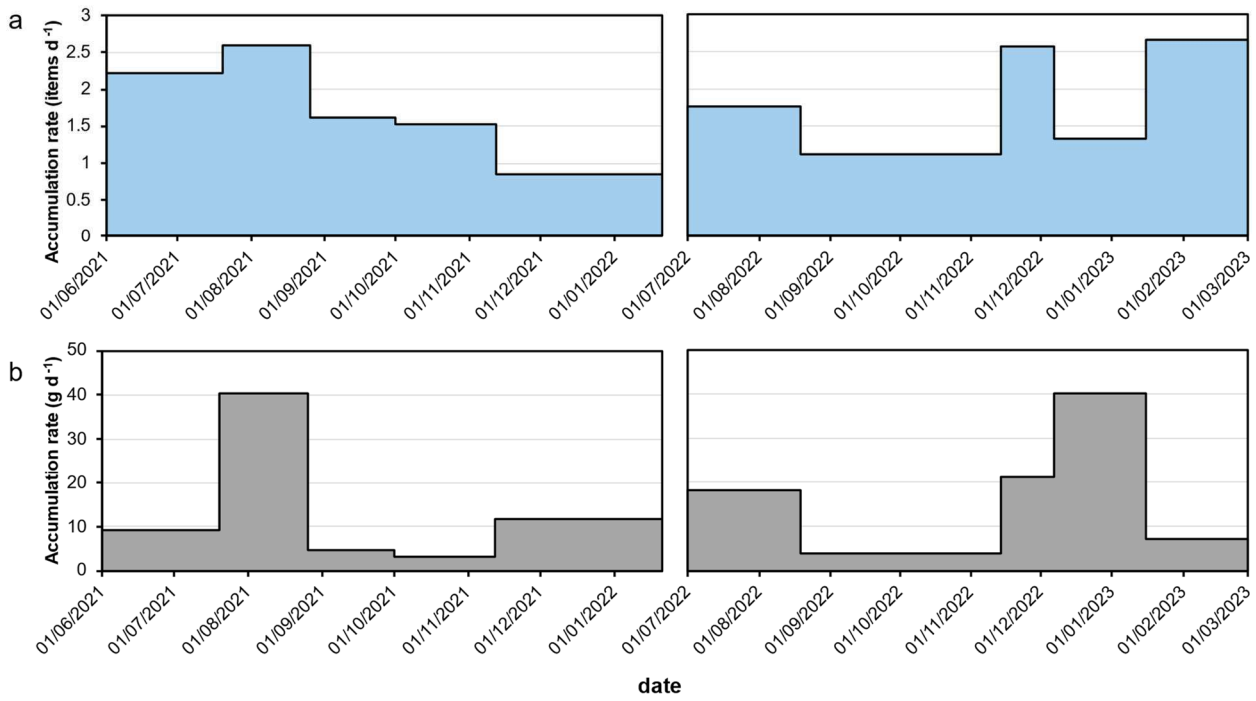

FIGURE 54: MACROLITTER ACCUMULATION RATES IN NUMBER (A) AND IN MASS (B) IN THE COMPANS BFS

5.3 Estimate of a yearly macrolitter accumulation flux

For each campaign, the mean daily macrolitter accumulation is converted to a yearly accumulation rate. This represents an accumulation rate of 5.1 kg yr^{-1} during the first campaign, and 6.6 kg yr^{-1} during the second monitoring campaign. Finally, it is possible to extrapolate a yearly accumulation rate from the first sample collected at the beginning of the first campaign. This sample was collected in June 2021, and the BFS was constructed in March 2016. Considering the 8.9 kg of debris collected on that first period, this represents an average accumulation rate of 1.7 kg yr^{-1} during the initial 5-year period.

The difference between the average accumulation rate in the macrolitter monitoring campaigns, and the accumulation rate inferred from the first sample collection suggests the existence of a macrolitter sink out of the site. Some of the possible outlets include, as previously mentioned, the fragmentation of the debris into smaller particles including microplastics. It is also likely that some of the macrolitter is not accumulated on site, but rather temporarily deposited before it is transported further away by the wind or other unobserved processes.

The mean accumulation rate obtained from all macrolitter samples collected is considered the overall macrolitter flux into the BFS system $Q_{macrolitter}$.

$$\mathbf{Q_{macrolitter} = 5.5\ kg\ yr^{-1}}$$

In order to complete the mass balance of the BFS, a microplastic fragmentation rate must be obtained from this macrolitter accumulation. It can be represented by the following:

$$\boldsymbol{Q_{fragmentation} = \tau_{fragmentation} \times x_{plastic} \times Q_{macrolitter}}$$

- $\boldsymbol{\tau_{fragmentation}}$ is the yearly fraction of the plastic fraction of macrolitter that are fragmented into microplastics.
- $\boldsymbol{x_{plastic}}$ is the fraction of macrolitter accumulated that is plastic.

Unfortunately, neither available data nor the information found on the literature can provide estimates for $\boldsymbol{\tau_{fragmentation}}$. However, $\boldsymbol{x_{plastic}}$ was obtained in the macrolitter accumulation monitoring campaigns. An estimate of the yearly influx of the plastic fraction of macrolitter can be obtained:

$$\boldsymbol{Q_{plastic} = x_{plastic} \times Q_{macrolitter}}$$

$$\boldsymbol{Q_{plastic}} \mathbf{= 3.08\ kg\ yr^{-1}}$$

6 Final discussion – Mass balance estimates

6.1 Working hypotheses

Several assumptions must be made in order to model the mass balance of microplastics in the BFS using the available data.

In chapter 3, an estimate of the microplastic stock in the BFS was obtained by extrapolating the microplastic abundances and concentrations. The vertical distribution of microplastics in the soil also showed a very limited presence of microplastics in the deeper soils. This suggests it is a reasonable assumption to consider the soils of the BFS were free of microplastics when it was first constructed in 2016, and that its current stock of microplastics is due to a continuous accumulation.

The vertical profile also suggested that microplastic and TRWP infiltration is limited. By exclusively considering the sediment and surface soil layers of the BFS in the mass balance,

the outlet of the system can be ignored. These surface layers represent respectively 92% and 90% of the overall mass of microplastics and TRWP in the BFS.

Finally, as discussed earlier, $\tau_{fragmentation}$ cannot be directly estimated, which prevents the estimation of the yearly microplastic flux produced from the fragmentation of macrolitter accumulated on site. This unknown will be discussed to close the mass balance.

6.2 Mass balance estimate for microplastics into the BFS

In this chapter, estimates of the yearly influx of microplastics from the road runoff into the BFS were obtained. A similar yearly influx can be estimated from atmospheric deposition.

Using these fluxes, it is possible to assess the balance of microplastics in the BFS system. As mentioned in previous works conducted in the BFS, the current setup was constructed in March 2016 (Flanagan, 2018; Kanso, 2021). The soil sampling campaign presented in chapter 3 was conducted in December 2022, leaving 6.75 years of accumulation. Considering a continuous accumulation on the surface, this allows to estimate the following:

$$Q_{total} = \frac{M_{surfce}}{t}$$

- $M_{surface}$ is the total stock of microplastics on the surface of the BFS
- t is the total period of accumulation.

A total mass of 2.04 kg of microplastics accumulated in the surface of the BFS since it was constructed. Only considering accumulation and no vertical migration, a flux of 340 g yr^{-1} or 3.14×10^7 MP yr^{-1} is necessary to account to the stock.

$$\mathbf{Q_{total} = 340\ g\ MP\ yr^{-1}}$$

Table 13 summarizes the yearly flux of microplastics necessary to account for the microplastic stock in the BFS, the yearly fluxes of microplastics from the two sources identified, and an extrapolation of the total accumulation since the construction of the BFS. The yearly flux of microplastic from atmospheric compartment into the BFS is only in the orders of 1g yr^{-1}, two orders of magnitude below this estimate. Similarly, the flux of microplastics from runoff into the BFS ranges from 49 to 80 g yr^{-1}, not enough to account for the total stock.

TABLE 13: SUMMARY OF THE DIFFERENT MICROPLASTIC FLUXES IN THE BFS

	Yearly influx		**Accumulation 2016 - 2022**	
	MP yr^{-1}	**kg yr^{-1}**	**MP number**	**mass (kg)**
Entire BFS	4.26×10^7	0.37	2.88×10^8	2.22
Surface soil and sediment only	3.14×10^7	0.34	2.12×10^8	2.04
Atmospheric deposition	2.02×10^5	0.0011	1.36×10^6	0.0077
Road runoff (upper limit)	6.66×10^6	0.080	4.5×10^7	0.54
Road runoff (lower limit)	4.13×10^6	0.049	2.79×10^7	0.33
Plastic fraction of the macrolitter		3.08		20.7

The macrolitter accumulation monitoring conducted suggest an average accumulation rate of 5.84 kg yr^{-1}. On average, the plastic fraction of this macrolitter represents an accumulation rate of 3.08 kg yr^{-1}. In order for macrolitter to represent a microplastic source on a similar order of magnitude as road runoff, 2.6% in mass of the plastic fraction of macrolitter accumulated each year must fragment into microplastics. In order for macrolitter to represent the entirety of the remaining source of microplastics in the BFS, 9.4% in mass of the plastic fraction of macrolitter accumulated each year must fragment into microplastics.

While these fractions appear particularly high, two factors from this site are susceptible to increase the macrolitter degradation. Firstly, the heavy traffic surrounding the site means debris left on the road are likely to be damaged by passing vehicle and fragment faster. Secondly, the vegetation growing in the BFS is mowed on a yearly basis. The product of this vegetation is left in place and not exported, meaning any item that was damaged by the mowing is susceptible to staying on site.

Three scenarios are possible for the sources to match the accumulation of microplastics in the surface of the BFS. Firstly, it is possible that a major microplastic source was missed in this mass balance, representing the majority of the microplastic input in the BFS. While this is possible, it is hard to assess.

Secondly, the microplastic abundance in the runoff may be highly underestimated. In order for runoff to account for all of the microplastic accumulation, the mean abundances should be an order of magnitude above the abundances measured here. While these values are found in the literature, they typically represent the highest possible abundances rather than an average (Cho et al., 2023; Lange et al., 2021). Additionally, it is possible that microplastic transfer in runoff are subject to a first flushing phenomenon, with higher abundances at the beginning of a rain event and lower at the end of rain event (Treilles et al., 2021). In order to better assess runoff as a microplastic source in the BFS system, runoff abundances should be measured sequentially throughout precipitation events.

The third possibility is that the remaining flux necessary to account for the microplastic accumulation in the surface of the BFS is accounted for by the fragmentation of the plastic fraction of macrolitter accumulated on site. Such a fragmentation rate would largely be driven by the accelerated fragmentation of plastic litter by traffic, and by the yearly mowing and crushing of vegetation on site. Macrolitter fragmentation would then represent the dominant microplastic source in the BFS system by an order of magnitude.

6.3 Estimates for TRWP input into the BFS

As shown in chapter 3, the estimates of the TRWP stock in the BFS are one to two orders of magnitude higher than the estimates for microplastics. Similarly to microplastics, 90% of the TRWP stock in the system is in the road accumulated sediment and the surface soil layers.

Based on the range of compositions of the TRWP, Table 14 summarizes the yearly TRWP flux necessary to account for the microplastic stock in the BFS, or in its surface layers.

As discussed on chapter 3, based on the potential composition of TRWP (U.S. Tire Manufacturers Association, 2020), the total mass of TRWP that accumulated in the surface of the BFS since its construction ranges from 39.7 to 173.1 kg. Exclusively considering a continuous accumulation, this represents a yearly flux of 5.88 to 25.6 kg yr^{-1}. Un fortunately, no TRWP concentrations were obtained in runoff samples or atmospheric deposition samples. Consequently, both sources are considered together when discussing the TRWP input into the BFS, as they are two secondary pathways for TRWP produced from traffic.

$$\mathbf{39.7\ kg < M_{TRWP\text{-}BFS} < 173.1\ kg}$$

$$\mathbf{5.88\ kg\ yr^{-1} < Q_{TRWP\text{-}BFS} < 25.6\ kg\ yr^{-1}}$$

- $M_{TRWP\text{-}BFS}$ is the total mass of TRWP that accumulated on the surface of the BFS over its period of activity
- $Q_{TRWP\text{-}BFS}$ is the yearly TRWP flux necessary to account for this stock

TABLE 14: SUMMARY OF THE TRWP FLUX IN THE BFS

	Yearly influx (kg yr^{-1})		Accumulation 2016 – 2022 (kg)	
	Lower bound	**Upper bound**	**Lower bound**	**Upper bound**
Entire BFS	6.49	28.3	43.8	191.3
Surface soil and sediment only	5.88	25.6	39.7	173.1

As discussed in chapter 3, the highway next to the BFS is passed by an average of 11,000 vehicles d^{-1} in each direction. Considering the 32 m of length of the BFS, the yearly TRWP flux into the BFS can be converted into a TRWP flux per vehicles per length of road.

$$Q_{vehicle} = \frac{Q_{TRWP-BFS}}{\boldsymbol{l_{BFS}} \times \boldsymbol{n_{vehicle}}}$$

- $\boldsymbol{l_{BFS}}$ is the length of the BFS
- $\boldsymbol{n_{vehicle}}$ is the average daily traffic on the road next to the BFS

s represents a TRWP flux ranging between 45 and 199 ng vehicle^{-1} km^{-1}.

In a 2024 study, De Oliveira *et al.* measured *in situ* the TRWP production rate of an adapted vehicle. The tyre wear loss ranged from 11 to 29 mg vehicle^{-1} km^{-1} (De Oliveira et al., 2024). The production rate of the SBR+BR fraction of TRWP ranged from 0.5 to 14.3 µg vehicle^{-1} km^{-1}, with a production rate of 10 µg vehicle^{-1} km^{-1} in a highway road. According to the authors, these concentrations could range in TRWP production rates of 32 to 78 µg vehicle^{-1} km^{-1}.

In chapter 3, SBR+BR to TRWP conversion rates estimates ranged from 5.5% (considering heavy-duty vehicle tyres with a lower SBR+BR fraction, and a 50% mineral incrustation fraction) to 24% (considering exclusively passenger tyres with no mineral incrustation. Using the same conversion factors and the SBR+BR emission rates of the 2024 De Olivera *et al.* study, the TRWP production rate in highway roads would range from 41 to 181 µg vehicle^{-1} km^{-1} (De Oliveira et al., 2024). In other studies, TRWP productions ranged from the orders of 44 to 104 mg vehicle^{-1} km^{-1} (Yan et al., 2021), to much higher values in the orders of the mg vehicle^{-1} km^{-1} (Aatmeeyata et al., 2009).

In all these studies, the TRWP production rates estimates are at least 2 orders of magnitude superior to the TRWP flux into the BFS necessary to account for the estimated stock in the surface soil layers. This suggests that the TRWP production in the road next to the BFS is more than sufficient to explain the high concentrations measured on site, with ~1% in mass of the produced TRWP accumulating in the nearby soil. However, these results also indicate that the BFS in itself is not sufficient to mitigate TRWP emissions in the environment, as only a small fraction of the particles are trapped in its soils.

7 Discussion and limits of these results

Figure 55 summarizes the results presented in this mass balance. Considering a continuous accumulation since its creation, the surface of the BFS traps 5.88 to 25.6 kg TRWP yr^{-1} emitted from the surrounding traffic. In this model, the system receives 1.1 g MP yr^{-1} directly from atmospheric deposition, 80 g MP yr^{-1} from road runoff infiltration, and up to 260 g MP yr^{-1} from the fragmentation of macrolitter accumulating on the site. The majority of these particles remains trapped on the surface, with less than 10% seeping in to the deeper soil layers of the BFS. A very limited flux in the orders of 0.2 g MP yr^{-1} leaves the site through the outlet and is susceptible to further infiltration.

Though several major results were obtained from these mass balances, they remain first-order estimates with clear limits in their methods and scope. The runoff results are based on a low

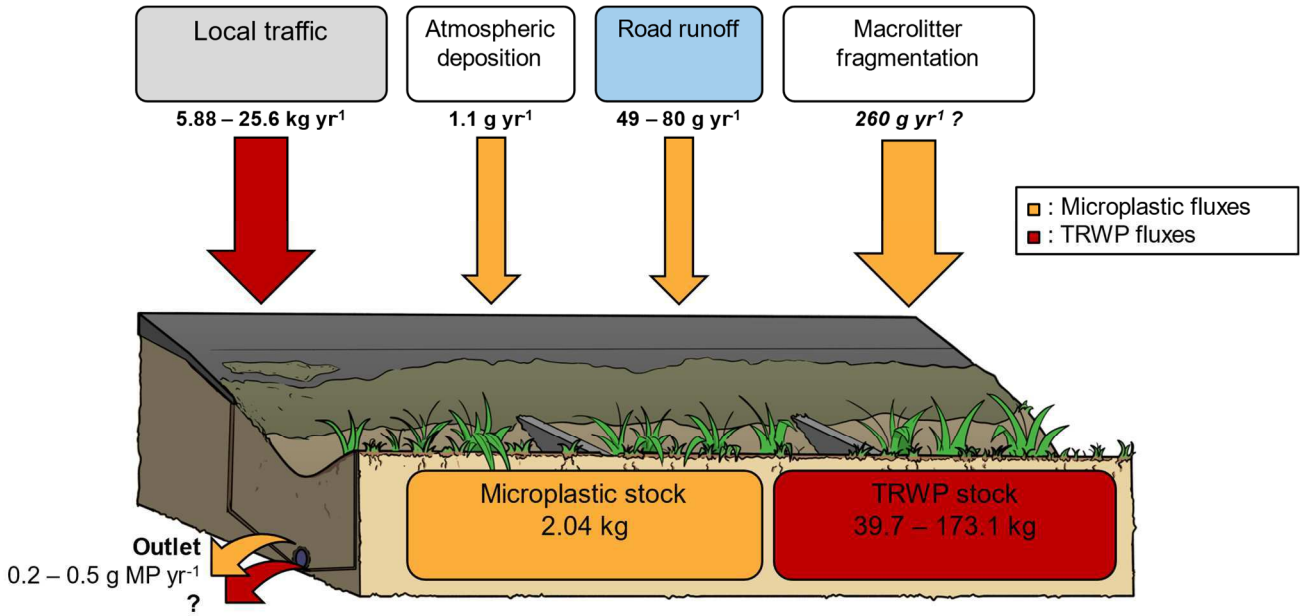

FIGURE 55: SUMMARY OF THE MASS BALANCE FOR MICROPLASTICS AND TRWP IN THE SURFACE OF THE BFS

number of samples, which prevented the assessment of the variability of microplastic fluxes from runoff into the BFS. Further sampling on site is expected to improve the robustness of these fluxes. Similarly, the atmospheric deposition data used was collected on a site far away from the BFS, and deposition rates are likely to be different. However, these results were considered sufficient to assess orders of magnitude of microplastic sources. Even if atmospheric deposition rates on the BFS were 1 or 2 orders of magnitude above the deposition rates used in this work, they would remain negligible compared to runoff or macrolitter fragmentation.

Finally, in order to assess the link between macrolitter and microplastic accumulation on site, the chemical composition of the plastic fraction of collected debris remains to be analysed.

Conclusion

Take-home messages

Methodological insights

The critical insight on literature conducted in Chapter 1 first highlighted that while some elements of common agreement exist in the literature, a lack of visibility and a high degree of variety remains from the very definitions used to the methodologies. While the size definitions for microplastics are agreed on, chemical definitions of what it constitutes are often implicit and unclear. Similarly, common denominators exist in the methods used to sample, prepare and analyse microplastic samples. Yet, clear differences remain in the exact practices selected.

Scientific methods are expected to depend on the objectives of a study and its targeted samples, as well as the available materials. Thus, the objective for the future should not necessarily be to standardize all practices. However, in order for the scientific community to grasp and build upon the results of a study, all methodological choices should be clearly expressed. Protocols and definitions should be discussed with as much clarity as possible, including the practices ensuring the quality assurance and quality control of the results.

The microplastic quantification strategy selected for this PhD was a fully automated imaging micro-FTIR analysis, followed by a post-treatment using the freeware SiMPle. This choice of method appeared to avoid the majority of experimenter-related biases for microplastic analysis, and enables the comparability of raw-results with future studies. However, it is a costly analytical procedure, that cannot be conducted in all laboratories. It also doesn't allow certain types of analyses, notably the focus on small microfibres.

Key findings of this work

In chapter 2, urban activity was shown to represent one of the major factors affecting atmospheric deposition. Notably, an 82% reduction in microplastic atmospheric deposition was measured at the same urban site during periods of decreased urban activity and traffic. This suggests a possibly immediate effect of temporal changes in activity on atmospheric microplastics.

Furthermore, a comparison with identical methodologies of atmospheric deposition of microplastics in urban and rural sites retrieved significantly lower deposition rates and different deposition characteristics in rural settings. This may imply that while a long-distance transport

of microplastics by the atmosphere is possible, it remains limited and local sources remain dominant. This suggests an overall low residence time of larger microplastics in the atmospheric compartment.

No clear effect of precipitations nor wind were observed in the campaigns conducted. While an effect of these parameters is observed in some specific situations in the literature, this is far from systematic. This does not imply that meteorological parameters do not affect atmospheric microplastics transport and deposition. Rather, it suggests that current methodologies based on passive sampling of bulk atmospheric deposition at a large temporal scale are not sufficient to assess the effect of these parameters. Passive monitoring with a small surface area for a long time allows to note small spatial effects, but averages out effects that occur on a small temporal scale.

Chapter 3 focused on microplastics and TRWP spatial and vertical distribution in the soils of a BFS on the side of a high traffic highway. Both types of particles appeared to behave similarly, displaying similar concentration profiles, though TRWP contamination was significantly higher than microplastic contamination in the site. Contamination was horizontally homogeneous, suggesting a diffuse input into the BFS. Concentrations were however significantly higher in the surface layers, with 90% of the total microplastic and TRWP stocks accumulating in the first 5 cm of soil. This suggests that the infiltration of microplastics and TRWP in the deeper soil layers occurs but is limited. It is likely that the suspended particles accumulating in the BFS create a less porous surface that limits the infiltration of microplastics. This also implies that the BFS is efficient at limiting the transfer of microplastics and TRWP from runoff into the environment. The overall stock of TRWP was particularly high, with up to 173 kg of particles accumulating in just the surface layers of a 32 m-long system over a period of 5 years.

In chapter 4, the potential inputs of microplastics and TRWP in the BFS were estimated and compared to one another. A first-order mass balance of microplastics in the soils of the BFS showed that atmospheric deposition likely represents a negligible source (<1%) of microplastics compared to runoff or macrolitter fragmentation. Runoff is likely insufficient to account for the entirety of the microplastic input into the site (~10%), suggesting macrolitter fragmentation is the dominant source of microplastics in the BFS. This is likely reinforced by the semi-regular mowing of all vegetation on site as well as the local heavy traffic.

Though no estimate of the relative contributions of the different sources of TRWP in the BFS was made here, the total accumulation of TRWP in the site is two to three orders of magnitude

lower than literature estimates of the TRWP production rates for a site with this level of traffic. This suggests that the majority of TRWP produced by traffic does not end up in the soils of the BFS. The TRWP that do end up in the soils of the BFS accumulate and are not released. In spite of levels of contamination reaching 1% in mass on the surface, this type of site is not sufficient to mitigate the contamination of the environment by TRWP emitted by traffic.

Limits of this work

The findings highlighted in this work lead to an array of perspective. Ranging from short to longer term, the first of these perspectives are insights in ways to improve the confidence in these findings.

In the shortest term, several improvements can be made to the work conducted here. In the study of the impact of urban activity on the atmospheric compartment, more rural samples should be collected in coupled sampling campaigns with urban settings.

The main limit of the mass-balance conducted in chapter 4 is the low number and indirect access to sampling values. Firstly, while it is likely that atmospheric deposition represents a negligible of the microplastic input in the BFS, monitoring bulk atmospheric deposition on site would help confirm this order of magnitude. Secondly, more runoff samples must be collected in order to assure that the only sample collected did not lead to a significant underestimate of the microplastic contribution from runoff in the BFS. Finally, a way to better constrain the contribution of macrolitter fragmentation into the site is to directly compare the chemical composition of the accumulated debris and the microplastics found on site.

The assessment of the microplastic stock in the BFS, and thus the estimate of the necessary microplastic fluxes to account for this total stock, were based on a one-off soil sampling campaign. A second row of soil core sampling 2 to 3 years later could help determine the microplastic accumulation rate.

Perspectives

Further studies

In addition to these elements aimed at directly improving this work, these results and their limits open the road to further research. In order to better assess the role of precipitations in the transfer

of microplastics, methodological adjustments must be conducted to specifically target microplastic contamination in rain samples. It is likely that there is a washout effect of microplastic transport in rain or runoff, with significantly higher concentrations at the beginning of a precipitation event than towards the end. Sequential sampling methods can be developed to selectively collect separate fractions of a rain event, either from atmospheric deposition or from stormwater runoff.

Further studies can also complement the results obtained here by assessing different time scales. Atmospheric deposition studies with a focus on small-scale spatial variability should be conducted by placing multiple samplers next to one another. Inversely, studies on microplastics and TRWP accumulation on the roadside soils could be conducted on longer sites, and on multiple SUDS surrounded by varying levels of traffic, to better understand the overall role of traffic and site parameters on microplastic transfer into soils.

For the results obtained here to contribute to the understanding of microplastic contamination and transfer pathways, they need to be built upon and confirmed by the scientific community. In environments affected by major meteorological events such as an alternation between a dry and a wet season, atmospheric deposition of microplastics are already established to be affected by precipitations (Purwiyanto et al., 2022). Further comparative studies of the effects of urban activity and meteorological parameters on atmospheric deposition of microplastics must be conducted in multiple environments. Studies on atmospheric deposition of particles that were not assessed here such as TRWP or microfibres must be conducted. Modelling studies must be conducted using atmospheric deposition data that were obtained in this work.

Broader knowledge gaps remaining

The works presented in this PhD provided data to contribute to the understanding of the major sources, transfer dynamics, and fate of microplastics in an urban setting. The results obtained and discussions conducted highlight broader gaps in knowledge remaining.

The sources, transfer dynamics, and fate of microplastics in urban environments are still poorly understood. The exact role of traffic as a direct or indirect microplastic source remains to be constrained. Other urban microplastic sources are just as much an issue. The diffuse abrasion of plastic materials in urban environments, in particular, is often considered a potential major source of microplastics in the environments, particularly into the atmospheric compartment.

However, such a source is hard to directly measure, and can only be estimated through in-depth modelling.

Similarly, the fate of microplastics in urban environments remains to be constrained. While early studies suggested the majority of microplastics eventually end up in the ocean, it seems soils are much more of a major microplastic sink than first considered. Yet, the fate of microplastics once they reach the soils is unclear. They may permanently accumulate in soils, but they may also infiltrate until they reach the aquifers. They may also slowly continue to fragment into smaller pieces down to the nano- scale. It is likely that some soils act as permanent sinks while others facilitate infiltration.

Finally, the relation between macrolitter, micro-nanoplastics and other contaminants are a major point of scientific and societal interest that must be studied. Plastic pollution can be seen as a continuum of sizes from the macroscopic to the nano- scale, of typologies from textile fibres to tyre wear particles, and of chemical compositions. Currently, the relations between macrolitter and microplastics remain poorly understood. The fragmentation process of macrolitter into microplastics is studied on a qualitative level but is not sufficient to provide rates of microplastic production beside theoretical fragmentation rates (Andrady, 2022; Y. Li et al., 2023). Further research coupling macro-and microplastic quantification in multiple environments can contribute to a better assessment of their source as microplastic sources.

In order to better understand their source, fate, and consequences, microplastics studies should be coupled with the study of other micropollutants. In particular, microplastics are susceptible to adsorb and transport micropollutants, and to release their additives in the form of potentially harmful leachates (Do et al., 2022; Fu et al., 2021; Li et al., 2018; Luo et al., 2020). Some of these additives, in particular TRWP additives, are relatively specific to some emission sources, and can be used as a proxy to better understand the sources and fate of microplastics and TRWP (Rauert et al., 2022).

The recent development of novel chemical entities as one of the planetary boundaries, one that is likely already operating outside of its safety space, encourages the joint study of microplastics and associated contaminants (Persson et al., 2022; Steffen et al., 2015).

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