



Atmospheric Micro- and Nanoplastics

A review of sampling and
analysis methods

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EES-2020-419

Master Programme Energy and
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Research report of Lawrence Aalders

Report: EES-2020-419

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ACKNOWLEDGEMENTS

As for almost all students around the world, the last year has been hectic, strange and sometimes even a bit scary for me. The COVID-19 pandemic has definitely impacted my work. Instead of writing this literature review, we actually wanted to experiment with sampling and analysis techniques, and arrangements were made to do multiple experiments. The pandemic prevented me from carrying out my research as envisioned beforehand. However, due to some quick thinking, we managed to turn the project around while still doing some experiments when restrictions eased a bit. Due to the pandemic, the project never reached its full potential. Still, I learned many things I would never have learned otherwise. In the end, I am happy with the final report and the experiences I gained while working on this project. I would like to thank prof. dr. Ulrike Dusek and dr. Dipayan Paul for their excellent supervision during the project. Working with both of you was great, and I could not have wished for better supervision during my first research project, even though the pandemic stood in our way. In addition, I like to thank ir. Jan Mulder for helping me in the lab whenever I needed help and for carrying out the experiments during the lock-down period. I also like to thank all the other people at the Center for Isotope Research (CIO) who made me feel welcome from day one. I would like to thank dr. Rupert Holzinger, dr. Dusan Materić, dr. Florian Meier, and Iris ten Have from Utrecht University for their cooperation and helping us with the project by providing us with relevant information and by doing the analysis of the samples. Finally, I thank my family and friends for their unconditional love and support during these strange times. I could not have done it without you.

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SUMMARY

Plastics have become so integrated into society that it is almost impossible to think of a world where they would not exist anymore. They are used so much because of their versatility and durability, earning them a place in almost each sector. However, with the widespread use of plastics also comes the problem of plastic waste. The increase in plastic waste over time and poor waste management have caused a substantial amount of plastic to end up in the environment, where they are prone to fragmentation and UV-degradation for example. This leads to the generation of micro- and nanoplastics, which are easily transported throughout the environment and can have adverse health effects due to their small size. Research has mostly been focusing on aquatic micro- and nanoplastics, but there is also the possibility of these plastics to end up in our atmosphere. Research into this aerial pathway is thus far limited by the absence of standardized research protocols or accurate sampling and analysis methods. Therefore, this thesis discusses how the sampling and analysis of atmospheric micro- and nanoplastics could be improved. In a review of the research field, it is shown what has previously been studied in the field, what has been found out already and what is still unknown. In the next section, sampling and analysis methods are discussed. It turns out that problems with sampling are mostly related to airborne micro- and nanoplastics; current sampling methods have no selectivity and are not able to accurately sample nanoplastics. With the analysis methods it is currently not possible to accurately quantify these plastics. In addition, analysing nanoplastics is out of the question, since observation is limited to the micrometre size range with current analysis methods. Alternative methods are discussed to overcome these problems. For the collection of micro- and nanoplastics, impaction sampling with a cascade impactor is suggested. In a few experiments, it is shown that such an impactor is potentially able to selectively sample nanoplastics, thereby reducing contamination and increasing efficiency in analysis. However, additional experiments have to be done to confirm the suitability of a cascade impactor for this field of research. To improve on existing analysis methods, a mass spectrometry method called Thermal Desorption-Proton Transfer Reaction-Mass Spectrometry (TD-PTR-MS) is suggested for the identification and quantification of particles. With this method, accurate analysis can be done in the nanogram range due to high sensitivity and low detection limits. However, information of sizes and shapes of individual particles are not provided, for which we need a complimentary analysis method. It is suggested that Infrared-Photoinduced Force Microscopy (IR-PiFM) would be a suitable complimentary analysis method, which not only provides information on the sizes and shapes of particles but is also able to determine the chemical composition of particles. Both analysis methods would be suitable for a complete analysis of microplastics, and more specifically nanoplastics as well. Experiments have to be done to prove the value of these methods in research of atmospheric micro- and nanoplastics before they can be applied in a standardized research protocol.

SAMENVATTING

Plastics zijn tegenwoordig zo geïntegreerd in de samenleving dat het bijna onmogelijk is om een wereld voor te stellen waarin ze niet meer zouden bestaan. Ze worden zo vaak gebruikt vanwege hun veelzijdigheid en levensduur, waardoor ze in bijna elke sector hun plaats hebben gevonden. Met het grootschalig gebruik van plastics komt echter ook het probleem van plastic afval. Door de toename van plastic afval in de loop der tijd én slecht afvalbeheer is er een aanzienlijke hoeveelheid plastic in het milieu terechtgekomen, waar het bijvoorbeeld vatbaar is voor fragmentatie en UV-degradatie. Dit leidt onder meer tot het ontstaan van micro- en nanoplastics, die gemakkelijk door het milieu worden getransporteerd en door hun kleine formaat nadelige gezondheidseffecten kunnen hebben. Onderzoek heeft zich vooral gericht op aquatische micro- en nanoplastics, maar het is bijvoorbeeld ook mogelijk dat deze plastics in onze atmosfeer terechtkomen. Onderzoek naar deze 'luchtroute' is tot dusver beperkt, onder andere door het ontbreken van gestandaardiseerde onderzoeksprotocollen of nauwkeurige bemonsterings- en analysemethoden. Dit proefschrift beschrijft hoe de monsternamen en analyse van atmosferische micro- en nanoplastics kan worden verbeterd. In een overzicht op het onderzoeksveld wordt aangetoond wat er eerder in het veld is onderzocht, wat er al is ontdekt en wat er nog onbekend is. In de volgende sectie worden bemonsterings- en analysemethoden besproken. Het blijkt dat er zich vooral problemen voordoen met de monsternamen van de door de lucht verspreide micro- en nanoplastics. De huidige bemonsteringsmethoden hebben geen selectiviteit en zijn niet in staat om nauwkeurig nanoplastics te bemonsteren. Met de huidige analysemethoden is het momenteel niet mogelijk om deze plastics nauwkeurig te kwantificeren. Bovendien is analyse van nanoplastics uitgesloten, aangezien observatie met de huidige analysemethoden beperkt is tot het micrometerbereik. Alternatieve methoden worden besproken om deze problemen op te lossen. Voor het verzamelen van micro- en nanoplastics wordt impactiebemonstering met een cascade-impactor aanbevolen. In enkele experimenten wordt aangetoond dat een dergelijke impactor in staat is om selectief nanoplastics te bemonsteren, waardoor contaminatie wordt verminderd en de analyse-efficiëntie toeneemt. Er moeten echter aanvullende experimenten worden gedaan om de geschiktheid van een cascade-impactor voor dit onderzoeksgebied aan te tonen. Om bestaande analysemethoden te verbeteren, wordt de massaspectrometriemethode Thermal Desorption-Proton Transfer Reaction-Mass Spectrometry (TD-PTR-MS) voorgesteld voor het identificeren en kwantificeren van plastic deeltjes. Met deze methode kan een nauwkeurige analyse worden uitgevoerd in het nanogrambereik, met name vanwege de hoge gevoeligheid en lage detectielimiet. Met deze methode wordt er echter geen informatie verstrekt over de afmeting en vorm van individuele plastic deeltjes, waarvoor een aanvullende analysemethode nodig is. Er wordt gesuggereerd dat Infrared-Photoinduced Force Microscopy (IR-PiFM) een geschikte aanvullende analysemethode kan zijn, die niet alleen informatie geeft over de grootte en vorm van deeltjes, maar die ook de chemische samenstelling van deeltjes kan bepalen. Beide analysemethoden zouden geschikt zijn voor een volledige analyse van microplastics, en meer specifiek ook van nanoplastics. Er moeten meer experimenten worden gedaan om de waarde van deze methoden in onderzoek naar atmosferische micro- en nanoplastics te bewijzen voordat ze kunnen worden toegepast in een gestandaardiseerd onderzoeksprotocol.

1. INTRODUCTION

1.1 Introduction to plastics

Plastics were introduced in the early 1900s. However, the mass production and use of plastics did not occur until the Second World War and after (Geyer *et al.*, 2017). Large parts of society were broken down due to the war and had to be build back up again to function properly. At that time, people needed a type of material that allowed for rapid and large-scale production of goods and secondary materials, and people saw that plastics had the right properties. Since then, there has been a continuous rapid growth in the production and use of plastics (Geyer *et al.*, 2017). Today, plastics have become integrated into our society to such extent that it is difficult to imagine a world without them. Almost every sector uses plastic or plastic materials to function, from the medical world and car manufacturing branch, to the packaging industry. The production of most man-made materials is surpassed by plastic production, with the exception of materials used in the construction sector (Geyer *et al.*, 2017).

But what are plastics exactly? Plastics are a group of materials that are, as the name says, **plastic**, which means they can be shaped into different products during a manufacturing process. Most plastics are made from fossil fuel sources like natural gas or crude oil, otherwise known as hydrocarbons. These hydrocarbons can come in the form of simple molecules, such as CH₄, or as longer, more complex molecules. Simple hydrocarbon **monomers** can be joined together to form long chain polymers that will then consist of repeating monomeric units. They consist of at least hydrogen and carbon, with typically an addition of several heteroatoms, such as oxygen, sulphur or nitrogen atoms (Woodford, 2019). After extraction from the source the hydrocarbons are separated in a refinery by fractional distillation, which is a process that separates molecules of different shapes, sizes and weights by using their difference in boiling point (Woodford, 2019). After condensation, the hydrocarbons have been separated in different, simpler fractions, which can then be used produce different types of plastics.

These simpler fractions are then linked together to form a long polymer chain through a process called polymerization. Depending on the type of monomer used the polymerization process results in a certain type of plastic (Woodford, 2019), like polyethylene (PE, (C₂H₄)_n), polystyrene (PS, (C₈H₈)_n) or polyethylene terephthalate (PET, (C₁₀H₈O₄)_n) to name a few. Notice that **poly** is in the name of almost all plastics, indicating that they are indeed formed through a polymerization process. Since there is a wide range of monomers available there is also a great variety of plastics derived from them, and they all have their own specific properties. Usually, plastics are characterized by properties like their thermal conductivity, tensile strength or hardness (Rodriguez, 1999). Thus, there are a lot of different types of plastics with their desirable and undesirable properties, depending on the end-use of the plastic. For example, for food packaging, plastic should be strong and waterproof to protect it during transport but should also be flexible to allow for easy storage. In general, the reason why plastics are used so frequently is due to their versatility and durability.

1.2 The global plastic problem

1.2.1 Plastic waste production

It is safe to say that society depends on plastic, maybe even more than we want. Almost everybody uses plastics daily, may it be directly by opening a packaged item or drinking from a bottle of water, or indirectly by using products that depend on plastics in the manufacturing stage. In fact, most of the plastics that are produced globally are destined to go to the packaging industry (Geyer *et al.*, 2017). There has been a global shift in the packaging industry from reusable packaging, to more and more single-use containers (Geyer *et al.*, 2017), which caused this industry to use even more plastics than it did in the past. The problem with single-use containers is as their name suggests; they are single-use

and can therefore not be used multiple times for the same purpose. This development has increased the share of plastics in the global municipal solid waste, from less than 1% in 1960 to about 10% in 2005 (*Jambeck et al., 2015*). This has inevitably put more pressure on waste management systems.

After the use stage there are basically three possibilities in the end-of-life stage for plastics. They can either be recycled, incinerated or disposed (*Geyer et al., 2017*). With recycling, different types of plastics are reprocessed into secondary material or plastics. However, these usually have a lower technical and economic value (*Geyer et al., 2017*), which makes it less usable and favourable than the production of new, primary plastics. With incineration or thermal destruction, plastics are collected and together burned in ovens till there is nothing left. Lastly, plastics can be disposed and put in landfills. This can either be done in a controlled way by putting the plastic waste in managed sanitary landfills, or by putting the plastics in uncontained open dumps, either in urban areas or the natural environment (*Geyer et al., 2017*). The amount of plastic waste generation is related to wealth, with high-income countries producing the most plastic waste. Although wealthier countries produce more plastic waste, they also have better waste management systems in place, due to the financial aspects of waste management (*Jambeck et al., 2015; Wilson, 2015*). Therefore, one would expect more landfilling and disposal of plastic waste in low-income countries, which is indeed the case.

Geyer et al. (2017) have done the first comprehensive global analysis of all mass-produced plastics ever made. In this analysis they have developed a material flow model by combining global data on plastic production, use and end-of-life. Their results show that from 1950 to 2015 about 8300 Mt of plastic has been produced cumulatively. Of this grand total, around 2500 Mt is (still) in use. *Geyer et al.* estimate that around 6300 Mt of plastic has entered the end-of-life stage, of which 800 Mt has been incinerated and 600 Mt has been recycled. This means that around 4900 Mt of plastic waste has been disposed and has either accumulated in controlled sanitary landfills, in uncontained open dumps, or in the natural environment (*Geyer et al., 2017*). It is not difficult to imagine that plastic waste from open dumps can easily get into the natural environment. *Geyer et al.* project that in 2050, following historical trends, about 9000 Mt of plastic will have been recycled, 12.000 Mt of plastic will have been incinerated, and 12.000 Mt will have been disposed and dumped in landfills or the natural environment. This increase in landfilling and dumping is especially concerning, because plastics can easily enter the natural environment from the landfills and open dumps.

1.2.2 Environmental pollution with plastic waste

Thus, one of the biggest environmental problems that society is dealing with currently is environmental pollution with plastic waste, and with the threat it poses to wildlife and in some cases even human life. Some of the earliest reports on plastic pollution were already back in the sixties and seventies, when *Kenyon & Kridler (1969)* reported plastic accumulation in the stomachs of albatrosses, while *Buchanan (1971)* reported consistently increasing synthetic fibre concentrations in water samples in the North Sea. Since then, research has come a long way and there have been numerous news items and reports showing the environmental pollution with plastic waste and waste in general (*Barnes et al., 2009*). A lot of developing countries are struggling to implement efficient waste management systems, and it is in these countries that we see a lot of open waste dumps. Even though waste management is less efficient in these countries, developed countries make more use of plastic products, and thus have more plastic waste to manage. Inevitably, a substantial amount of all the plastic that is used will end up in the environment. How exactly the plastics end up in the environment has been the subject of many studies the last couple of decades. However, there are essentially two processes that can happen to plastics. Either they accumulate or they fragment and degrade into smaller plastic particles. Although it is very important to model and study the spread and accumulation of larger plastics in the environment, we will be focussing more on the smaller plastic particles in the environment in this review. These particles are difficult to track and as a result more difficult to study.

1.2.2.1 Introducing micro- and nanoplastics

When talking about small plastic particles there is some terminology involved, especially when researchers are looking at the smallest of plastic particles. There has been a lot of debate amongst different research groups, but the main consensus now seems to be a differentiation on the basis of size. When talking about a **microplastics**, researchers generally talk about plastic particles equal to or smaller than 5 mm, and larger than 1 μm (Frias & Nash, 2018). If **nanoplastics** are mentioned, we are looking at plastic particles smaller than 1 μm (Gigault et al., 2018). Although there are some exceptions, it is usually on the basis of these cut-off sizes that small plastic particles are differentiated in micro- and nanoplastic studies.

Micro- and nanoplastics have two origins. In literature, micro- and nanoplastics are described as either **primary** or **secondary** (Waldschläger et al., 2020). Primary micro- and nanoplastics are produced with intended use. For example, in industry, plastic pellets are produced as precursor material for other plastic goods. These plastic pellets are usually smaller than 5 mm but can vary in size depending on the end-goal of transport and manufacturing. Because of their small size (and shape), plastic pellets are easily transported all over the world and can be stored in large amounts in factories. They are also produced in recycling processes (Waldschläger et al., 2020). After sorting, cleaning, and melting the different types of plastics, the plastic pellets are formed and can be used again for the manufacturing of new products. Besides plastic pellet production, micro- and nanoplastics are also produced for the use in personal care products, in which they either act as ingredients contributing to product stability and activity or as microbeads, which have a scrubbing effect and are usually found in products like toothpaste or body scrubs (Hernandez et al., 2017; Waldschläger et al., 2020).

Secondary micro- and nanoplastics are created from larger plastic pieces, which have been subjected to **fragmentation** and **degradation**. Even though plastics are usually extremely durable, these two processes occur simultaneously over time when plastics are exposed to the natural environment. Fragmentation occurs when plastics are subjected to mechanical forces that compromise the structural integrity of those plastics, which occurs at the beach with waves crashing down on the beach for example (Barnes et al., 2009). This results in the formation of micro- and nanoplastics. Usually, degradation occurs at the same time, which is the chemical decomposition of plastics. When plastics are exposed to sunlight, they undergo photo-oxidation, which cleaves bonds in the structure of the plastic and weakens the molecular structure. The molecular mass of the polymeric molecule is reduced, which in turn leads to brittleness and subsequent disintegration of the plastic (Browne et al., 2007). In literature the names of fragmentation and degradation are interchanged, but are however two different processes, even though they occur simultaneously.

A lot of secondary micro- and nanoplastics are formed on landfills and open dumps, where they are exposed to the environment. However, secondary micro- and nanoplastics can also be produced through other mechanisms. An important mechanism is the machine washing and drying of clothes. Nowadays, a lot of clothing is made from fabrics that incorporate plastics like polyester, nylon, and acrylic. Due to the tumbling action of a washing or drying machine, individual fibres can be released from the fabric, which can easily enter the environment via wastewater streams (Henry et al., 2019). Another important mechanism is the release of micro- and nanoplastics particles through tire abrasion. There are millions, if not billions, of vehicles driving around the world's highways and roads every day. Due to contact abrasion of the tires with the road, micro- and nanoplastics (in this case rubbers, which contain elastomers) are released into the environment (Sommer et al., 2018). Many more sources exist and have been studied, which are reviewed partially (amongst others) in a review paper by Waldschläger et al. (2020).

1.2.2.2 How do micro- and nanoplastics end up in the environment?

In the natural environment there are essentially three sub-environments we can distinguish, which are the aquatic (includes surface waters, seas and oceans), terrestrial, and aerial environment. Micro- and nanoplastics are transported to these environments and either persist for a long time or move to another environment. Another possibility is that micro- and nanoplastics can settle in an environment in so-called receptors of micro- and nanoplastics. *Waldschläger et al.* (2020) have made use of the source-pathway-receptor model to describe and model how micro- and nanoplastics are transported from the source through pathways and finally ending up at the receptors (**Figure 1**). But in order to better understand the different transport mechanisms, we have to know how micro- and nanoplastics end up in the environment in the first place. So, how do they end up in the environment?

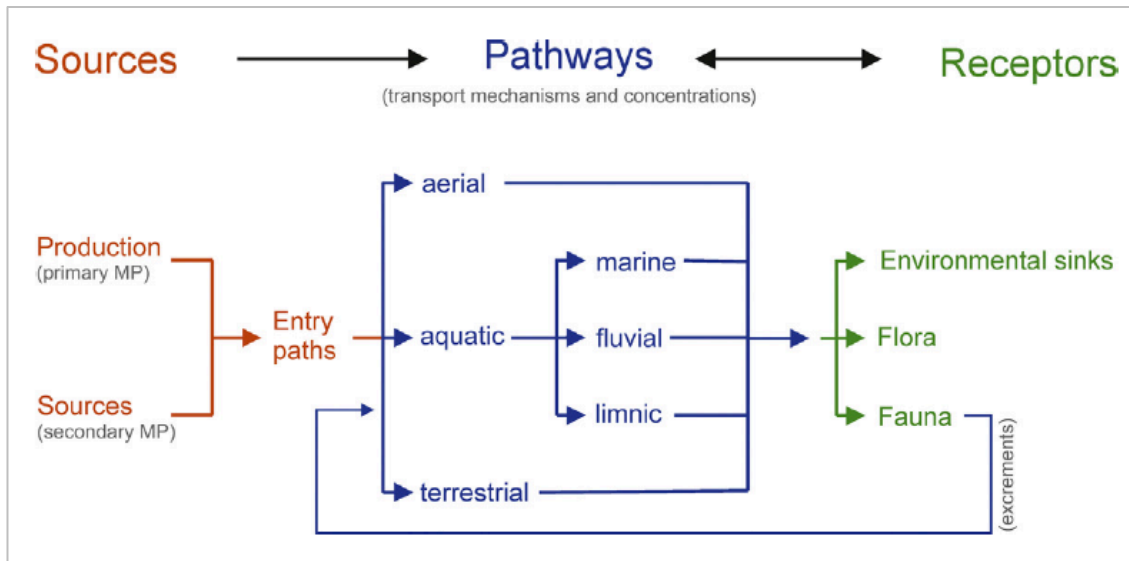


Figure 1: The source-pathway-receptor model as described by *Waldschläger et al.* (2020).

It seems that the main pathways for micro- and nanoplastics into the environment are wastewater treatment plants and sewage sludge (*Waldschläger et al., 2020*). Also, wind seems to be an important factor, because it can transport plastics from place to place. Wastewater treatment plants remove contaminants from wastewater and release the cleaned effluent back into the environment. However, it turns out that most of the micro- and nanoplastics present in the wastewater are retained in the effluent after treatment, which makes wastewater treatment plants a considerable source of micro and nanoplastics (*Magnusson & Norén, 2014; Talvitie et al., 2015*). This is most likely due to their small size and diameter, which allows them to pass through filters in the treatment process. Furthermore, wastewater is treated differently in different parts of the world, as stated in the World Water Development Report by the *United Nations* (2018). Only 20% of all the wastewater in the world is treated in wastewater treatment plants before it is allowed to flow back into surface waters. This means that most wastewater in the world potentially contains a considerable number of micro- and nanoplastics that end up in surface waters.

Sewage sludge seems to be another pathway of micro- and nanoplastics into the environment. Sewage sludge is the solid remains of wastewater after filtration during treatment. In many countries this sewage sludge is distributed amongst local and regional agriculture businesses and used as a fertilizer. However, some sewage sludge is landfilled or incinerated after which it has little or no economic value anymore. There are strict rules on the use of sewage sludge for agricultural purposes in many countries, because they may contain harmful concentrations of heavy metals or other contaminations (*Hudcová et al., 2019*), but there seems to be no restrictions on the micro- and nanoplastic content of sewage sludge (*Waldschläger et al., 2020*). There have been several studies that looked into the micro-

and nanoplastic deposition through the application of sewage sludge to agricultural fields as fertilizer, and it turns out that, in Europe at least, sewage sludge contributes significantly to micro- and nanoplastic pollution (Nizetto *et al.*, 2016). On agricultural fields where sewage sludge is used as fertilizer, wind and precipitation could transport redistribute the micro- and nanoplastics.

Redistribution of micro- and nanoplastics is especially the case for secondary micro- and nanoplastics. The machine washing and drying of clothing and home textiles and tire abrasion are just two of many possibilities for micro- and nanoplastics to enter the environment. The redistribution depends on the characteristics of the environment micro- and nanoplastics are transported into, but also on the properties of the micro- and nanoplastics. In aquatic environments the transport usually occurs through and depends on flow, but if the particle density is higher than the density of water (whether it be in a lake, river or ocean) sedimentation of the particle is most likely to occur (Waldschläger *et al.*, 2020). This way, the aquatic environment acts not only as a transporter of micro- and nanoplastics, but also as a reservoir on the long-term. In the terrestrial environment transport is influenced by natural and anthropogenic activity. It has been shown that micro- and nanoplastics are generally vertically transported by earthworms for example. Further transport occurs through precipitation, which depends on the particle size and shape (Waldschläger *et al.*, 2020). Anthropogenic activity like ploughing of agricultural fields or excavation at building sites could also be ways of transport in the terrestrial environment. In the aerial environment, wind is involved in the transport of micro- and nanoplastics. Atmospheric samples mainly contain synthetic textile fibres and road dust (Dris *et al.*, 2017), that get introduced into the atmosphere from households and traffic respectively. It has been shown that micro- and nanoplastics from the aerial environment are potentially a considerable source for the aquatic and terrestrial environments.

In studies by Allen *et al.* (2019) and Bergmann *et al.* (2019) that will be discussed in more detail later, it was shown that even in remote locations, such as the Arctic, Alps and Pyrenees, micro- and nanoplastics can fallout and settle on the surface. In these studies, snow samples were taken from different locations, and all contained some form of micro- and nanoplastics, whether it be fragments, films or fibres. These observations suggest that micro- and nanoplastics can indeed be transported over long distances in the atmosphere. The settling of micro- and nanoplastics even in remote locations raises questions about possible micro- and nanoplastic concentrations in the atmosphere and their fallout in more urban or suburban areas. However, as is evident from several review articles (Wagner & Reemtsma, 2019; Huang *et al.*, 2020; Waldschläger *et al.*, 2020; Zhang *et al.*, 2020), research into micro- and nanoplastics in the aerial environment is relatively scarce and there are many things still unknown. Therefore, to understand the 'behaviour' of micro- and nanoplastics in the atmosphere there is more research needed, which is also the reason that, I will focus on the aerial environment and atmospheric micro- and nanoplastics in this review. In addition, exposure to micro- and nanoplastics may have possible health effects for humans (and possibly animals).

1.3 Health effects of exposure to atmospheric micro- and nanoplastics

When looking at all routes of human exposure to micro- and nanoplastics, there are three possibilities for micro- and nanoplastics to be potentially toxic (Wright & Kelly, 2017; Revel *et al.*, 2018; Prata *et al.*, 2020; Yong *et al.*, 2020) (Figure 2). Micro- and nanoplastics can be ingested, which usually occurs when eating or drinking contaminated food and drinks. They can also be inhaled; atmospheric micro- and nanoplastics that get inhaled will get into the airways and lungs. Finally, exposure occurs through dermal contact. Although a less significant route of exposure, nanoplastics of < 100 nm could potentially transverse the dermal barrier (Revel *et al.*, 2018). Because we are focusing on atmospheric micro- and nanoplastics, the remainder of this section will focus on the health effects that occur through inhalation of micro- and nanoplastics.

There are multiple ways micro- and nanoplastics get introduced into the atmosphere, with households, traffic and resuspension of surface dust probably contributing the most to the total micro- and nanoplastic concentration in the atmosphere. However, it seems that humans are more likely exposed to micro- and nanoplastics in indoor environments (*Dris et al., 2017*), which is likely due to synthetic fibres from clothing and home textiles. It is estimated that humans are exposed to about 26 to 130 atmospheric microplastic particles on a daily basis (*Prata, 2018*). The total number of daily inhaled plastic particles would likely even be higher if nanoplastic particles are taken into account as well. Given that people nowadays spent a lot more time indoors than outdoors, they could be exposed to significant concentrations of micro- and nanoplastics. However, to the best of my knowledge, no present study till date has evaluated nanoplastic concentrations in either indoor or outdoor environments, which is mostly due to analytical limitations. Furthermore, there are differences in experimental procedures between research groups, which makes it difficult to compare studies. Although these complications make it challenging to judge to what extent nanoplastic particles may impact health, there is still evidence that both micro- and nanoplastic inhalation may have detrimental health effects.

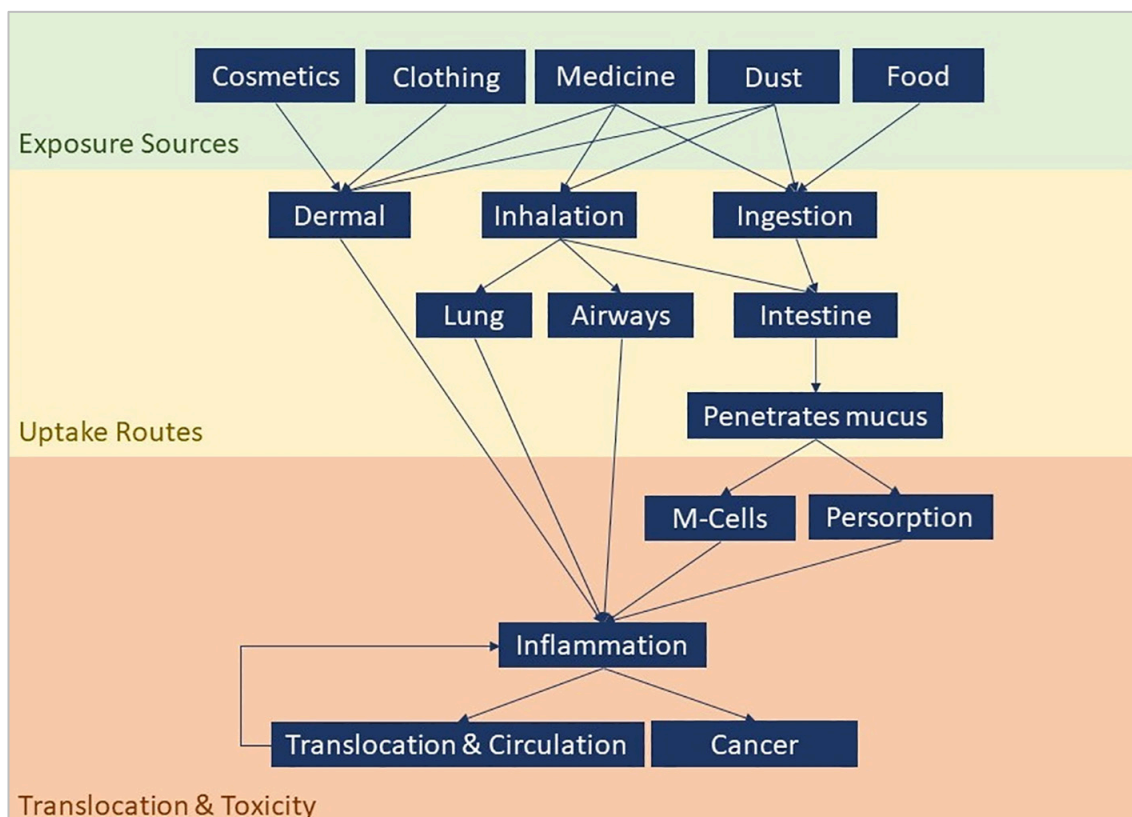


Figure 2: The pathways of exposure and toxicity for microplastics in humans (*Prata et al., 2020*).

Most of the current knowledge about atmospheric microplastic exposure was found after diseases occurred amongst industry workers, who are exposed daily to high concentrations of airborne microplastics (*Prata, 2018*). These diseases occurred in the synthetic textile industry, the flock industry and the vinyl chloride (VC) and polyvinyl chloride (PVC) industries, which all deal with some form of airborne microplastics (*Prata, 2018*). First of all, deposition of micro- and nanoplastics in the airways and lungs depends on the properties of the plastic particle. For example, PET has a higher density than PS. This makes it more likely that PS will reach deeper parts of the lungs, which has to do with the **aerodynamic equivalent diameter**. Additionally, the size of the plastic particle also determines deposition, with smaller particles (e.g. nanoplastics) being able to reach deeper parts of the lungs than larger particles (e.g. microplastics). So, how can micro- and nanoplastic inhalation lead to disease?

Upon inhalation of a plastic particle, the particle will get deposited in the airways and lungs, which, as described before, depends on particle properties. Deposition can occur via impaction, sedimentation, diffusion, or interception, also depending in which part of the airway and lungs the particle resides (Wright & Kelly, 2017; Prata, 2018). Naturally, the body wants to get rid of the plastic particle irritant. There are several clearance mechanisms for removal and translocation of particles in the airways and lungs, which include coughing, mucociliary action, macrophage action, and lymphatic transport (Prata, 2018; Prata et al., 2020). Smaller nanoplastics may even transport into the bloodstream and are thus able to induce toxicity in other organs or tissues (Prata, 2018). Fibres are more difficult to remove with this system due to their low mass-high surface area. Micro- and nanoplastics in the airways and lungs will have a large surface area, which induces the release of certain factors that eventually lead to chronic inflammation. This is known as **dust overload** (Donaldson et al., 2000), which usually occurs in areas where the atmosphere is heavily contaminated with inert pollutants and particles. Chronic inflammation induces a continuous release of pro-inflammatory factors and oxidative stress, and eventually leads to cancer related symptoms (Prata, 2018; Prata et al., 2020; Yong et al., 2020). Therefore, we can conclude that micro- and nanoplastics, just as much as 'regular' air pollutants, can have quite serious long-term health effects. However, it should be noted that the study of health effects of micro- and nanoplastic exposure is still an emerging field. Thus, a lot more research is needed to understand the details of exposure and toxicity pathways.

1.4 Problem setting and research questions

In the previous sections we have seen that plastic products have been around for quite some time already and that they cause serious environmental problems through plastic waste, with current examples being open dumps in low-income countries and the Great Pacific garbage patch. Furthermore, plastic waste can fragment and degrade after which micro- and nanoplastics are formed. These micro- and nanoplastics are not visible to the naked eye and therefore often remain undetected. This makes it likely that these plastic particles can invade the living space of humans and animals alike. It has been shown that exposure to these plastic particles could have detrimental health effects, thus making it important to understand sources and pathways of exposure. Previous research efforts have been made to do so. However, these efforts have not been divided equally amongst the sub-environments discussed earlier.

There have been more studies of micro- and nanoplastics in the aquatic and terrestrial environment than in the aerial environment. This is evident from the number of scientific publications; the majority of these publications address micro- and nanoplastic pollution in the aquatic environment (Barbosa et al., 2020). Oceans and seas are getting extra attention, since these act as a reservoir of micro- and nanoplastics. Thus, there is less known at the moment about micro- and nanoplastics in the aerial environment. The first proper study of microplastics in the atmosphere was carried out by the group of Dris et al. (2017), in which they quantitatively measured microplastics indoors and outdoors. Other groups have taken notice of their work and since then, several more studies have been published to study microplastic concentrations. However, these studies all seem to use different methodologies, sampling protocols, and analytical instruments.

This makes it difficult to compare studies. Besides differences in approach, current analytical instruments have some disadvantages. These lie in the sensitivity or cut-off value for the observation of an analytical method or in the ease of use, which will be explained in a later section. Nanoplastics especially are poorly researched, since current techniques make it difficult or almost impossible to analyse them. There is also a need for the standardization of sampling protocols, not only for better and more reliable results but more so because this allows for comparison, which is important to improve research in this field. The main question we would like to answer is: **“How can we improve research of atmospheric micro- and nanoplastics?”**. However, to figure out how sampling and analysis

can be improved from previous and current studies, we have to find out what has been done already and how exactly it can be improved. This leads us to the following research questions:

- 1) What is the *status quo* of the research into atmospheric micro- and nanoplastics?
- 2) Which sampling and analytical procedures are currently used and available, and what are their advantages and disadvantages in the context of micro- and nanoplastics?
- 3) How can we improve on existing sampling and analytical procedures and what would be the best alternative with current technologies?
- 4) Can we sample atmospheric micro- and nanoplastics using a novel sampling protocol?

In this paper, I will provide an overview of the previous and current studies of atmospheric micro- and nanoplastics. Then, I will uncover the advantages and disadvantages of current sampling and analytical methods and give a possible solution for a sampling and analysis protocol. In addition, I also show some preliminary data and results from a pilot study using a novel sampling method in the field of atmospheric micro- and nanoplastic research.

2. PREVIOUS RESEARCH OF ATMOSPHERIC MICRO- AND NANOPLASTICS

In this section, I will review the current and previous research in the field of atmospheric micro- and nanoplastics. The research group of *Dris et al.* were the first to report microplastic concentrations when directly sampling the atmosphere using active samplers. From then on, they have done more research in this field, and others have followed behind them. Different groups have tried to do their own experiments, trying to understand and measure micro- and nanoplastics. Since the study of atmospheric plastics is a relatively new field of research, these groups have used multiple different experimental protocols in terms of sampling and analysis. Therefore, I will review the atmospheric plastics studies and elaborate on the current knowns and unknowns in the field.

2.1 The beginning of a new field of research

In 2015, *Dris et al.* did a study in the area of Paris, France, in which they investigated micro-plastic contamination of the urban environment and of surface waters. Their findings confirmed that microplastics can indeed be found in different urban environments and that they are indeed present in sewage, fresh water, and atmospheric fallout. They concluded that atmospheric fallout could be a significant source of the fibres they found in the urban environment (*Dris et al., 2015*). However, they found that there were virtually no studies investigating atmospheric microplastics and the atmospheric fallout. Thus, they concluded that this was essentially the first evidence of atmospheric microplastic in the urban environment and that more studies are needed to investigate the sources and the effects of local and spatial characteristics. Therefore, they followed up with another study which they published in 2016.

This time they focussed solely on microplastics in the atmospheric compartment and were the first to do so at the time (*Dris et al., 2016*). They investigated the contribution of atmospheric fallout to plastic pollution by sampling atmospheric fallout at different locations just outside of the city of Paris, France. They did this in an urban and a more sub-urban location for about a year and about six months, respectively. At both sampling sites they found large amounts of fibres in the atmospheric fallout, which had not yet been reported in other literature (*Dris et al., 2016*). In the urban sampling site, the fibre content of the samples varied a lot, which indicates that there is a high annual variability. They also looked at different size ranges of the fibres (50 μm to 5000 μm) and found that the samples contained mostly fibres from the smallest size ranges (at least in the urban site) of 200 – 400 μm and 400 – 600 μm , whilst fibres from the larger size ranges were rarely observed (*Dris et al., 2016*). Fibres in the lowest size range of < 50 μm were not counted in the study, since they were very difficult to identify. They also found differences in the number of fibres between the two sampling sites, with the samples from the urban site containing more fibres (110 \pm 96 particles/m²/day) than the samples from the sub-urban site (53 \pm 38 particles/m²/day). This is likely due to population differences and anthropogenic activity, with a higher population density observed in and around the urban site (*Dris et al., 2016*). Further analysis of their samples was done in order to determine the proportion of synthetic and natural fibres in the samples and to chemically characterize them. They showed that about 29% of the total number of fibres were of synthetic origin and contained petrochemicals. Thus, this study showed that the atmospheric fallout is a significant source of microplastic pollution and that it cannot be neglected as a potential source. However, *Dris et al.* do underline that this was a pilot study and that the statistical power of their findings was not great, due to relatively short sampling times and the absence of more sampling sites. According to them, more specific studies were needed to confirm their observations and to investigate atmospheric fibre content.

Using their previously described pilot study as a steppingstone, *Dris et al.* set up a more elaborate study, which was published in 2017 (*Dris et al., 2017*). In this study they investigated microplastics, but in particular synthetic fibres. Firstly, they sampled the indoor and outdoor atmosphere to find out

about indoor and outdoor concentrations of synthetic fibres. Secondly, they collected indoor dust fallout to determine the synthetic fibre content of dust. Lastly, they took samples from regularly used vacuum cleaners. The sampling was carried out in two different, but roughly equally sized apartments (apartments A and B) and one office (workplace). These two spaces were considered to get an overview of the contamination in places where people are likely to spend most of their time (*Dris et al., 2017*). The atmosphere was only sampled when people were present in the respective rooms; the air samplers would be turned on whenever someone entered the room. Sampling took place for an entire year, since the researchers were also interested in the seasonal variation in the atmospheric concentration. In the size range of the fibres they studied (50 μm to 5000 μm), they found that all samples contained fibres; the indoor and outdoor atmosphere showed a similar size distribution, with most of the fibres present fitting into the smallest size ranges between 50 μm – 450 μm (*Dris et al., 2017*). Larger fibres were rare. This is likely due to their size; larger fibres settle more rapidly on surfaces, which is consistent with the findings in their pilot study (*Dris et al., 2017*).

Both the office (4.0 - 59.4 fibres/ m^3) and apartment A (2.5 - 18.2 fibres/ m^3) showed higher fibre concentrations than apartment B (1.1 - 16.3 fibres/ m^3). *Dris et al.* think this is due to differences in home textiles and doing the laundry; the floor was carpeted in apartment A and the people hanged their clothing to dry in the living room, which was avoided in apartment B due to a tumble dryer (*Dris et al., 2017*). Regarding the differences between the indoor and outdoor concentrations, the outdoor atmosphere (median of 0.9 fibres/ m^3) showed significantly lower concentrations of fibres than the indoor atmosphere (5.4 fibres/ m^3). The researchers expected this; the volume of the apartments and the office is obviously a lot smaller than the outdoor air volume. Thus, outdoor concentrations were lower due to a **dilution effect** (*Dris et al., 2017*). When looking at the deposition rate of the indoor dust they sampled, they found this was significantly higher (between 1600 - 11,000 fibres/day/ m^2) than the deposition rate of the outdoor atmospheric fallout in their 2016 study (2.1 - 355.4 fibres/day/ m^2), which again shows the significance of indoor contamination with fibres in microplastic studies. When *Dris et al.* examined the fibre content of the vacuum cleaner bags, they used data on dust deposition found by *Seifert et al.* (2000) to estimate the deposition rate of fibres in the apartments and office. When calculating this way, they found a fibre deposition rate of 2070 and 7300 fibres/day/ m^2 , which is consistent with their earlier findings using just the dust samplers.

When looking at the chemical composition of the fibres in their samples, they noticed that around two-thirds of all the fibres they examined were of natural origin, whereas the remaining one-third contained petrochemicals and are thus of man-made origin (*Dris et al., 2017*). They found different types of polymers, but the most recurring was polypropylene (PP). Most residential buildings and offices have many sources of this polymer since it is often used in carpets and furniture, thus finding predominantly PP in their samples makes sense. Though their pilot study (*Dris et al., 2016*) lacked in statistical power, the proportion of synthetic fibres found in the current study was similar. However, the type of polymers that were found is different between the studies. Their results do show that the contribution of synthetic fibres to indoor dust is significant and that people are exposed to these microfibrils on a daily basis (*Dris et al., 2017*). And as explained in the introduction, exposure to airborne micro- and nanoplastics could have significant health effects. Still, *Dris et al.* point out that there is still an uncertainty of the potential health effects, since the methods they used were not suitable to detect particles and fibres in the nanometre range. Furthermore, the indoor and outdoor concentrations of micro- and nanoplastics may have been a lot higher if particles and fibres in the nanometre range could have been detected as well. Thus, *Dris et al.* concluded that there was more research needed and that methods have to be developed that include nanometre sized particles and fibres in the total indoor and outdoor concentrations.

2.2 Expansion of the research field

Shortly after the study by *Dris et al.* (and their previous pilot study) was published, other research groups started to set up their own studies and have published papers on atmospheric micro- and nanoplastic research. Many of the published studies used similar experimental methods for sampling and analysis as *Dris et al.* However, there is not yet a clear, standardized protocol for sampling and there are different analysis techniques that can be used to quantify and characterize micro- and nanoplastics. Furthermore, most studies have been focussing on microplastics, but as we have seen, nanoplastics could potentially be more harmful due to their small size. Thus, finding analysis techniques and methods to identify and study nanoplastics become more important. In the following paragraph, we will discuss the published studies in a chronological order and elaborate on the sampling and analysis techniques that are used. After that, we will point out their advantages and disadvantages and why they should (not) be used to study atmospheric micro- and nanoplastics.

2.2.1 The earliest studies focussing on atmospheric micro- and nanoplastics

Dehghani et al. published a study in 2017. Contrary to the 2017 study by *Dris et al.* they wanted to look more at outdoor contamination of microplastics. They were specifically interested in deposited dust on street surfaces and their microplastic content and characteristics. Thus, they collected ten samples of street dust on multiple locations throughout the central district of Tehran, Iran. Sample collection was done using anti-static wooden brushes and they collected dust from about 30 m² on both sides of roads. Sub-samples of each location were mixed to obtain a bulk representative sample and contaminations like asphalt and stones were removed. Each sample was analysed for organic matter and subsequently treated and cleaned with a H₂O₂ solution, which has been found to be effective to remove the organic matter from samples (*Nuelle et al., 2014*). Microplastics were then separated from the dust in the samples using a **flotation method**, which uses a solution with a density lower than dust to float the microplastics to the surface of the sample solution. After filtration of the samples on filter paper, the samples were dried and transferred to petri-dishes. Three different analysis techniques were used in this study. First, they were analysed with a fluorescence microscope for identification, since most plastics contain pigments or dyes (*Dehghani et al., 2017*). Secondly, regular binocular microscopy was used for quantification and describe properties such as shape, size, colour and degradation stage. To describe the topography of the microplastics, they also used a scanning electron microscope (SEM) as their third and last analysis technique.

Since industry usually adds fluorescent pigments or dyes to plastics, they examined the particles with the fluorescence microscope. They found that the majority of particles were indeed fluorescent, meaning that they were microplastics. However, the researchers pointed out that it was difficult to obtain good results in this study, since the microplastic content of their samples was relatively low compared to other materials in the samples. Therefore, they used SEM analysis to identify the plastic particles more accurately (*Dehghani et al., 2017*). They observed smooth surface textures on the microplastics and found different shapes and sizes. Analysis also showed the presence of trace minerals, which indicate additive presence or surface adsorption of debris. Using the binocular microscope, they found a total of 2649 microplastics particles in the size range of < 100 µm - > 1000 µm in the ten dust samples they collected. The concentration of microplastics ranged from 83 ± 10 particles/30 gr dry dust to 605 ± 10 particles/30 gr dry dust. Sizes ranged from 100 µm up to 5 mm and most plastic particles (33.7%) were found in the 250 - 500 µm size range. *Dehghani et al.* also noticed that the number of particles in the lowest size range of < 100 µm were lowest but admit that underestimation could have played a role here, since these particles are not easily detected using light microscopy (*Dehghani et al., 2017*). The samples contained mostly microplastic granules (65.9%) or fibres (33.5%), with only a small contribution of spheres. Concluding, this study investigated the occurrence and abundance of microplastics in street dusts and was probably the first to do so at the time. However, analysis could be improved; fluorescence microscopy proved to be inefficient and with

SEM analysis they only examined a small number of their samples since is generally considered a time-consuming method. Visual quantification and characterization include human error, though serves its purpose as a preliminary examination. The detection cut-off size was 50 μm , making it impossible to investigate plastic particles below that limit and which leads to inaccuracies. The size range of < 50 μm is important in atmospheric micro- and nanoplastic research, since these particles are more easily re-suspended into the atmosphere and are thus most likely to be inhaled (*Dehghani et al., 2017*).

Around the same time, *Cai et al. (2017)* also published their research on microplastics. Instead of looking at street dusts, they took samples of the atmospheric fallout. They argue that deposited microplastics are important to study, since deposition plays an important role in the exchange of these particles between the aquatic, terrestrial and aerial environment (*Cai et al., 2017*). Samples were collected in three different urban sites in the city of Dongguan, China. The atmospheric fallout was continuously sampled with open-top, glass bottles at a height of 15 m, thus using a similar method as *Dris et al. (2016)*. Given that dry and wet deposition was monitored, the researchers recorded the volumes each time the samples were collected. Samples were filtered through glass fibre filters and were dried and stored in glass petri-dishes. Similar to *Dehghani et al. (2017)* they used three different methods for analysis. A digital microscope was used for initial identification of microplastics. To further identify microplastics in their samples, they used micro-Fourier Transform Infrared ($\mu\text{-FTIR}$) spectroscopy. This spectroscopy technique radiates a sample with an infrared beam, part of which is either absorbed by or transmitted through the sample. Depending on the chemical structure of the sample, some wavelengths of the beam are absorbed or transmitted, which result in a molecular 'fingerprint' of the sample. Each polymer has its own fingerprint, which make identification possible (*Thermo Fisher Scientific, 2020a*). To examine surface characteristics, *Cai et al.* analysed suspect sub-samples with SEM, since analysing all samples was not possible (*Cai et al., 2017*).

Their results are similar to those of *Dris et al. (2016)*. Visual analysis using the digital microscope revealed that the samples of the atmospheric fallout mainly contained microplastic fibres, which was later confirmed using $\mu\text{-FTIR}$ analysis. Beside the fibres, they found foams, fragments, and films, which probably all have different origins and sources. They found these in all samples, indicating that the lower atmospheric compartment is contaminated with microplastics (*Cai et al., 2017*). Concluding, re-suspension of microplastics from the surface is probably the main source of microplastics in the atmosphere, according to *Cai et al.* With the $\mu\text{-FTIR}$ analysis they found four kinds of polymers, of which cellulose was the most abundant (73%). However, this is due to fibres being the most abundant in their samples. During visual analysis, many fibres were overestimated as being microplastics and also consisted of cellulose, meaning that most of these fibres were natural fibres (*Cai et al., 2017*). Because they mostly found fibres in their samples, 20% of the fibres were randomly selected and detected with $\mu\text{-FTIR}$. About three-quarters of those detected fibres were found to contain no plastics. When looking at the other shapes of microplastics, around 85% of those were microplastics, thus making it clear that most fibres found in the atmosphere are usually of natural origin.

When averaged over the three sampling sites, *Cai et al.* found a particle concentration of 228 ± 43 particles/ m^2/day . The concentrations of microplastics were on average 36 ± 7 particles/ m^2/day . When comparing their results to the result found by *Dris et al. (2016)*, they found that the concentration of microplastics in Dongguan were close to the sub-urban site in Paris (53 ± 38 particles/ m^2/day) but were smaller than the urban site in Paris (110 ± 96 particles/ m^2/day), indicating that microplastic abundance between the two cities was in the same order of magnitude (*Cai et al., 2017*). Microplastic concentrations in Dongguan depended on population density and thus human activity; they found higher concentrations in the denser populated sampling sites and vice versa. SEM analysis to compare surface characteristics revealed that synthetic fibres are relatively homogenous and compact. Other particles showed many signs of abrasion and degradation, with grooves, pits and fractures showing on the particle surfaces. This study has shown that, even though the density of microplastics is higher than that of the air, they are capable of being suspended in the atmosphere. But this has to be confirmed

by air dynamics studies (Cai et al., 2017). Microplastics were found in all samples in different types, concentrations, shapes, sizes, and colours. They conclude that dust emission from the surface probably plays an important role in the transportation of microplastics between the aquatic, terrestrial, and aerial environment.

The first study after Dris et al. (2017) that sampled outdoor air directly was published by Abbasi et al. (2018). In addition to microplastics they specifically mention microrubbers in their study, which are a subtype of microplastic that have a distinctly different appearance and have different properties, characteristics and sources. Besides sampling the atmosphere for microplastics and microrubbers, they collected samples of street dust in a similar way like Dehghani et al. (2017) have. Sampling was done in Asaluyeh County, Iran at multiple different industrial and urban sites, collecting 15 street dust samples and 16 air samples. The air samples were collected using an ambient filter sampler that allowed the researchers to examine PM_{2.5}, PM₁₀, and total suspended particle levels. After sampling, the air samples were transferred to glass beakers, cleaned with H₂O₂, and separated from mineral dust using the flotation method also used by Dehghani et al. (2017). After drying the samples, they were identified using different types of microscopy (binocular, polarized light, and fluorescence microscopy) and a few microplastics from the street dust samples were selected for SEM analysis to examine topography and composition. In short, Abbasi et al. repeated the study by Dehghani et al. (2017) but added the ambient air samples and updated the approach for sampling and analysis.

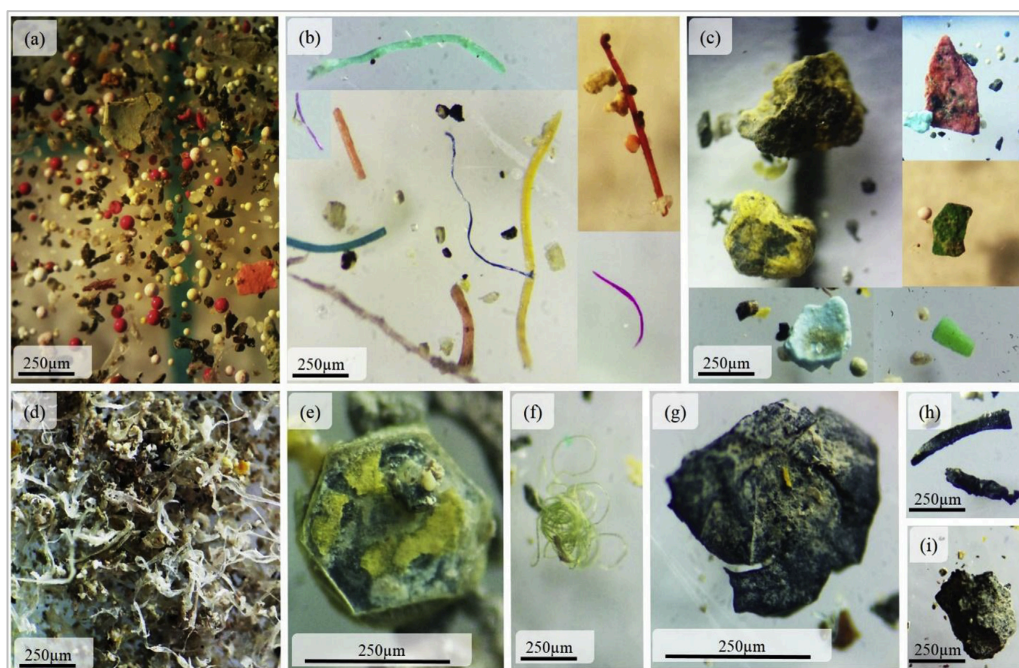


Figure 3: Optical microscope images of different types of microplastics and microrubbers as found by Abbasi et al. (2018) in street dusts.

Abbasi et al. found many different types of microplastics by using regular optical microscopy (Figure 3), which were also identified using fluorescence and polarized light microscopy. SEM analysis of the particles revealed surface characteristics similar to what Cai et al. (2017) found; particles showed smooth surfaces with grooves, pits, and flaking and thus showed evidence of abrasion and degradation. When quantifying and identifying the microplastics from the collected street dust samples, Abbasi et al. found a total of 13,132 microplastics and 3691 microrubbers. The highest concentrations of these particles were found in the samples from industrial regions (> 1000 per sample), whereas concentrations were lowest in samples from sites further away from the heart of the industrial region of the county (about 50 per sample). The distribution of microplastics and microrubbers was non-normal; the average number of microplastics and microrubbers was 900

particles/15 gr and 250 particles/15 gr of sample between the sampling sites. Microplastics were mostly spherical (74%) and film-like (14%), whereas microrubbers were mostly fragmented (61%) and fibre-like (36%), which was not significantly different between sampling sites (*Abbasi et al., 2018*). The size distribution of microplastics was also non-normal; about 75% of the particles found were in the size range of < 100 µm, with particles becoming less abundant when increasing the size ranges. This was particularly the case for the spherical particles and not so much for the other particle shapes, where size distribution was more normal.

Looking at the air samples, they found almost exclusively microplastic fibres during the eight-day sampling period in both locations. Microrubbers were also found, with most of those being either fragments or fibre-like. According to *Abbasi et al.* the design of the air sampler impacted the number of particles found in the smallest filter (PM_{2.5}). Furthermore, detection of particles less than 2.5 µm is very difficult, thus underestimation could have played a role. Also, the sampling of fibres is dependent on their orientation with respect to the inlet of the air sampler, which makes collection of these particles probably inaccurate. Therefore, the researchers only sampled PM₁₀ particles after the first few days of sampling PM_{2.5} particles. The concentration of microplastics in the air was similar between the industrial and urban sampling site, with concentrations of 0.76 and 0.63 particles/m³ respectively. When comparing street dusts and air samples we can see that street dusts contain all sorts of microplastics and microrubbers, whereas air samples contain mostly microplastic fibres. This is probably due to the low mass-high surface area of fibres. Thus, the results of this study show that street dusts mostly contain many different types of microplastics and that the atmosphere mostly contains microplastic fibres, results that were also found by *Dris et al. (2016)* and *Cai et al. (2017)*. Street dusts may be re-suspended and give rise to the large-scale transport of microplastics through the atmosphere. However, since only microplastic fibres were found in the air samples this is still uncertain, which is partly due to the detection size limit of the analysis techniques.

A study by *Kaya et al. (2018)* focussed on microplastic particles in the atmosphere. In the previous studies, researchers found mostly microplastic fibres in the air samples. *Kaya et al.* wanted to quantify the number of microplastic particles in areas where humans are easily exposed to suspended microplastics. To do this, they sampled suspended microplastics and microplastic fallout in soils on two locations (a bus terminal and university campus) in the Sakarya province of Turkey for a six-month period. Weather conditions at the time of sampling were also recorded, since they wanted to investigate the impact of these on the amount of microplastics in the air (*Kaya et al., 2018*). Air samples were collected using a vacuum pump and two filters (500 and 50 µm). Pre-treatment procedures of the air and soil samples were almost identical to the procedures by *Dehghani et al. (2017)*; cleaning with H₂O₂, density separation with the flotation method, centrifuging, and filtration on different filters. All samples were examined under a microscope and classified according to their colours and shapes. To determine the polymer composition, *Kaya et al.* used µ-FTIR analysis.

The atmospheric fallout samples contained an average of 8 microplastic particles after a 30-minute sampling period. They also found what was expected beforehand; microplastic fibres were more abundant than other microplastic particles. With µ-FTIR analysis they mostly found polyamide and polyesters. However, even though µ-FTIR analysis is usually very reliable, the percentage match of their results with the spectral library was not high. Concluding, *Kaya et al.* underline that their results do not reflect all the microplastics present in the air. This is firstly due to the small sizes of particles they examined, giving them inaccurate results. Secondly, sampling of microplastics seems to be very dependent on weather events, which makes it impossible to predict or model the number of microplastics in the air at a certain location. But other variables exist as well, like population density, human activity, traffic, and urbanization (*Kaya et al., 2018*). However, their results do show that the air contains at least a background amount of microplastics, which shows the need to consider them in air pollution studies. And since identification of the smallest microplastic particles is difficult with current techniques, they highlight the need for the development of better analysis protocols.

2.2.2 The field takes flight

In 2019, five papers were published in the field of atmospheric micro- and nanoplastics. *K. Liu et al.* (2019) researched the distribution of airborne microplastics in Shanghai, China. Meanwhile, *C. Liu et al.* (2019) published an extensive study on microplastics in dust. In this study, they collected urban dust samples (indoor and outdoor) in 39 cities throughout China. With the publication by *Allen et al.* (2019) we see the first real signs of atmospheric transport of microplastics, since they found microplastics in a remote location. *Klein & Fisher* (2019) studied microplastics in the atmospheric fallout on six sampling sites of metropolitan Hamburg, Germany. A study by *Bergmann et al.* (2019) showed that microplastics even prevail in the Arctic, highlighting that atmospheric transport and deposition could indeed be important pathways of microplastics pollution. Finally, *Wright et al.* (2019) published their results on atmospheric plastics in central London, England. This variety in studies shows that research in atmospheric micro- and nanoplastics is very diverse. Whilst sampling of atmospheric fallout and dust collection gives us a temporal and spatial dependent overview of contamination, atmospheric concentrations of plastic particles can give us an overview of general air pollution levels in a given area or region and can help to trace air pollution sources. *K. Liu et al.* (2019) tried to study exactly that in their research.

They argue that the sources and spatial distributions of atmospheric microplastics are poorly understood and that most studies that use passive samplers are inaccurate and often underestimate microplastic concentrations (*K. Liu et al.*, 2019). To understand the sources, transportation and distribution of atmospheric microplastics, they used active, non-selective samplers to collect microplastics in four different monitoring stations, their locations ranging from more coastal to more urban and sub-urban areas. These different locations could give the researchers an insight in the horizontal distribution of atmospheric microplastics. Additionally, they tried to get insights in the vertical distribution by sampling at different heights in one of the more centrally located sampling stations (1.7 m, 33 m, and 80 m). Unlike other studies, the flow rate of their sampler was a lot higher (100 ± 0.1 L/min), which allowed them to sample a relatively high volume of air in a shorter amount of time. Analysis was done using a stereomicroscope (for quantification and size determination) and μ -FTIR (for detection of suspected microplastics).

In all but one of the collected samples they found microplastics, which proves again that microplastics are indeed present in the atmosphere. The mean contamination levels in Shanghai ($0.93/\text{m}^3$) were comparable to those observed in Paris ($0.9/\text{m}^3$) by *Dris et al.* (2017), which is due to the same local differences in population density or human activity described in previous papers. The highest concentrations of microplastics were found in the urban area ($4.18/\text{m}^3$), whereas the lowest concentration was found in the coastal sampling station ($0/\text{m}^3$). This is due to the dilution effect; clean ocean air mixes with the contaminated, inland air, which decreases concentrations significantly (*K. Liu et al.*, 2019). Overall, the level of human activity is the most significant factor that determines atmospheric microplastic concentration here. On the sampling site where they measured the concentration of microplastics vertically, they found that the highest concentrations ($1.48/\text{m}^3$) at the lowest height of 1.7 m, with lower concentrations at 33 m and 80 m ($0.99/\text{m}^3$ and $0.9/\text{m}^3$, respectively). However, statistical analysis revealed that there were no significant differences between the concentrations found at the different heights, which is probably caused by mixing of air.

Consistent with the previously described studies of *Cai et al.* (2017), *Dehghani et al.* (2017), *Abbasi et al.* (2018), and *Kaya et al.* (2018), *K. Liu et al.* found mostly microplastic fibres in their samples (67%). They did find fragments (30%) and granules (3%) but found no foams and films. Sizes of the observed microplastics ranged from about 23 μm to 9555 μm , with an average size of 582.2 μm . At the vertical sampling site, they found slightly bigger microplastics on the lowest level (mean 597.5 μm) than on the middle level (mean 176.2 μm). What is interesting though, is that they found an average particle size of 830 μm at the highest level of 80 m. This probably has something to do with the proportion of fibres

in their samples at that height (77.78% at 80 m vs. 72.09% at 1.7 m), with the biggest fibres reaching higher altitudes due to their low mass-high surface area. They also found many different polymers in the air samples. Other investigations into microplastics revealed that urban wastewater might be a significant source, and *K. Liu et al.* state that the similarity between the microplastics found in the air samples and wastewater samples indicate a strong connection between the two sources (*K. Liu et al., 2019*). Additionally, the researchers explain that production of synthetic fibres is the highest in Asia than anywhere else in the world, since roughly 81% of the world's synthetic fibres are produced there. This might be an explanation for the large proportion of synthetic fibres in their samples. Besides, high production of other textiles in Asia, made from either natural or man-made materials, explains the other fibres in their samples. Furthermore, as a local custom, people in Shanghai mostly hang their clothes, sheets and other textiles to dry outside their home on balconies, which results in even more microfibrils being produced, since mechanical abrasion, photo-oxidation, and thermal degradation act on these textiles due to wind, UV- and solar radiation (*K. Liu et al., 2019*).

To conclude, *K. Liu et al.* have shown that there is a spatial, horizontal distribution of atmospheric microplastics in Shanghai, since their results show that there is a gradient of microplastic concentrations from urban to coastal areas. Furthermore, their results show that a vertical distribution might also exist, but this remains to be tested. When comparing their results with other studies there are similarities in chemical composition and particle characteristics, which indicates that atmospheric microplastics are omnipresent in different parts of the world. Given that transport of these microplastics can easily occur, they could be a significant source of pollution for the terrestrial and aquatic environment, even though microplastic concentrations between different parts of the world differ (*K. Liu et al., 2019*). In this study, the drying of clothing and other textiles outdoors is a significant factor of microplastic pollution, that derives from cultural and local norms. Thus, this research shows that atmospheric microplastic pollution is highly dependent on, not only factors such as population density, but also human activity, industry and local customs.

A study by *C. Liu et al.* (2019) investigated microplastics in outdoor and indoor dust samples, and more specifically the presence of polyethylene terephthalate (PET) and polycarbonate (PC) microplastics, which are two widely used polymers. This study is interesting in two ways, in that 1) they wanted to investigate the spatial distribution of PET and PC across mainland China, and 2) they wanted to compare the results of different analysis techniques, including the use of a mass spectrometry method. Both had not been investigated before in the field of atmospheric micro- and nanoplastics. Collection and pre-treatment were done using similar methods as previous studies in different households; dust samples were collected outdoors (on windowsills and balconies) and indoors (in bedrooms and living rooms) using a brush and they used the same flotation method as *Dris et al.* (2017) and *Dehghani et al.* (2017). Although they did include a pre-cleaning step by removing visible contaminations, they did not include cleaning with H₂O₂ as other studies did. Sample analysis was done using the commonly used light microscope and μ -FTIR, as well as a liquid chromatography-tandem mass spectrometry technique (LC-MS/MS), which they developed in another study (*Wang et al., 2017*). This technique uses a depolymerization process that splits the PET and PC polymers into their building blocks before analysis.

In all the samples from across China, *C. Liu et al.* found PET in both outdoor and indoor dust. Outdoor dust samples contained a median concentration of 2780 mg/kg of dust, whereas indoor concentrations were quite a lot higher, with a median of 26,800 mg/kg of dust (*C. Liu et al., 2019*). PC was found in about 72% of the outdoor dust samples, and in about three-quarters of the indoor samples, with a median concentration of 2.0 mg/kg and 4.6 mg/kg of dust respectively (*C. Liu et al., 2019*). When dividing the samples into Northern and Southern China, they observed a slight regional distribution with the highest concentrations in Southern China, but this was not statistically significant. PET microplastic concentrations were higher in areas with high income and population density than in areas with low income and population density, indicating a positive correlation. Also, the researchers

found that the shorter the amount of time between sampling and the last rainfall, the higher the PET concentration, which shows that micro- and nanoplastics are possibly deposited by precipitation events. Examination of the microplastic shapes was done using 30 selected samples from both outdoors and indoors; ten samples with the highest concentrations, ten with middle concentrations, and ten with the lowest concentrations of PET (C. Liu et al., 2019). They mostly found fibres in their samples, with a proportion of 73.7% outdoors and 88.0% indoors. Indoors, a range of 17-620 fibres/mg was observed, which are similar results as Dris et al. (2017) who found 190-670 fibres/mg. Indoor granules ranged from 6-184 particles/mg. Outdoors, they found a range of 7-431 fibres/mg and 0-100 particles/mg. For their μ -FTIR analysis, they randomly selected 50 fibres and 20 granules from both Northern and Southern China for further analysis. About half of the fibres from Southern China were synthetic (46%) and included six types of polymers. Of the North Chinese fibres, 19 were of synthetic origin and four different polymer types. In regard to the granules, they found 8 and 5 granules in Southern and Northern China, respectively, with a total of 5 and 4 different polymer types (C. Liu et al., 2019).

In total, they found higher concentrations of PET in both outdoor and indoor dusts than PC, which is likely due to the production of these polymers in China; PET production is about 30 times higher than PC production (C. Liu et al., 2019). They found a positive correlation in the concentration of PET and the abundance of fibres in dusts, meaning that the contribution of PET to fibres in dusts is probably significant. Of the fibres found indoors 40-50% were synthetic polymers, which is a bit higher than the results of Dris et al. (2017). They found no PC in dusts using μ -FTIR analysis. However, when analysing the dust samples with LC-MS/MS they found PC microplastics about 74% of the samples, which shows that the LC-MS/MS has a higher sensitivity than the μ -FTIR analysis. It should be mentioned that this analysis protocol with the LC-MS/MS was designed specifically for the detection of PET and PC, thus it cannot be used for the detection of other polymer types (C. Liu et al., 2019). However, the researchers think development of mass spectrometry techniques for microplastic detection is a step in the right direction. Furthermore, C. Liu et al. end with a call to action to study nanoplastics as well.

Allen et al. (2019) provided us with the first signs of atmospheric transport of microplastics. They argued that, if microplastics can be found in air and fallout samples, they can easily be transported through the atmosphere and deposited by gravity or weather events. If microplastics were to be found even in remote locations, it would be strong evidence for atmospheric transport of microplastics. Therefore, they chose to sample dry and wet atmospheric deposition in a remote area of the Pyrenees mountains. Sampling took about five months, with samples being collected each month. They used two types of passive fallout collectors, which provided them with a duplicate sample for each period (Allen et al., 2019). Prior to the analysis, all ten samples were filtered, cleaned with H₂O₂, separated using the flotation method, and then vacuum dried on fresh filters. All the samples were then visually examined with a stereo microscope for counting and particle characteristics. However, white and transparent particles were excluded, which may have led to an underestimation. To confirm whether or not plastics were indeed present and to determine the chemical composition of the particles, the researchers used Raman spectroscopy. In short, Raman is a spectroscopy technique that measures light scattering of a sample after it has been illuminated and excited with a monochromatic laser light. Different frequencies are scattered back depending on the molecules and their bonds, which, just like FTIR, provides the researcher with a unique spectrum or 'fingerprint' of a sample (Thermo Fisher Scientific, 2020b). This analysis technique has been used before in the field of aquatic micro- and nanoplastics, but this was the first time it was used in the atmospheric context.

Their analysis showed that fragments, fibres and films were present in each sample, with an average of 365 particles/m²/day. The data showed that rain- and snowfall strongly correlate with the number of microplastic particles, indicating that more atmospheric microplastics will deposit when it rains or snows. The intensity and the number of weather events positively correlate with microplastic deposition, whereas the duration of these weather events was negatively correlated. Thus, event

occurrence and intensity, and not duration, positively affect microplastic deposition (Allen et al., 2019). These and other results from previous studies like Dris et al. (2017) show that precipitation events promote microplastic fallout. Previous studies have also shown that, in a particle size distribution, most deposited microplastics found were in the lowest size ranges, which is no different to what Allen et al. found. They found microplastics in a range of $> 25 \mu\text{m}$ and $< 2600 \mu\text{m}$. The majority of the fragments they found were in the $< 50 \mu\text{m}$ range. With fibres we see a similar trend; most of the fibres were between $100\text{-}200 \mu\text{m}$ and $200\text{-}300 \mu\text{m}$ in length. A modification of their fibre length scale allowed Allen et al. to compare the average fibre length of their study with previous studies. Now, most of the fibres they found fitted in a $50\text{-}700 \mu\text{m}$ range, thus showing similar results to Cai et al. (2017), who found most between $200\text{-}700 \mu\text{m}$ and Dris et al. (2016), who found most between $200\text{-}600 \mu\text{m}$.

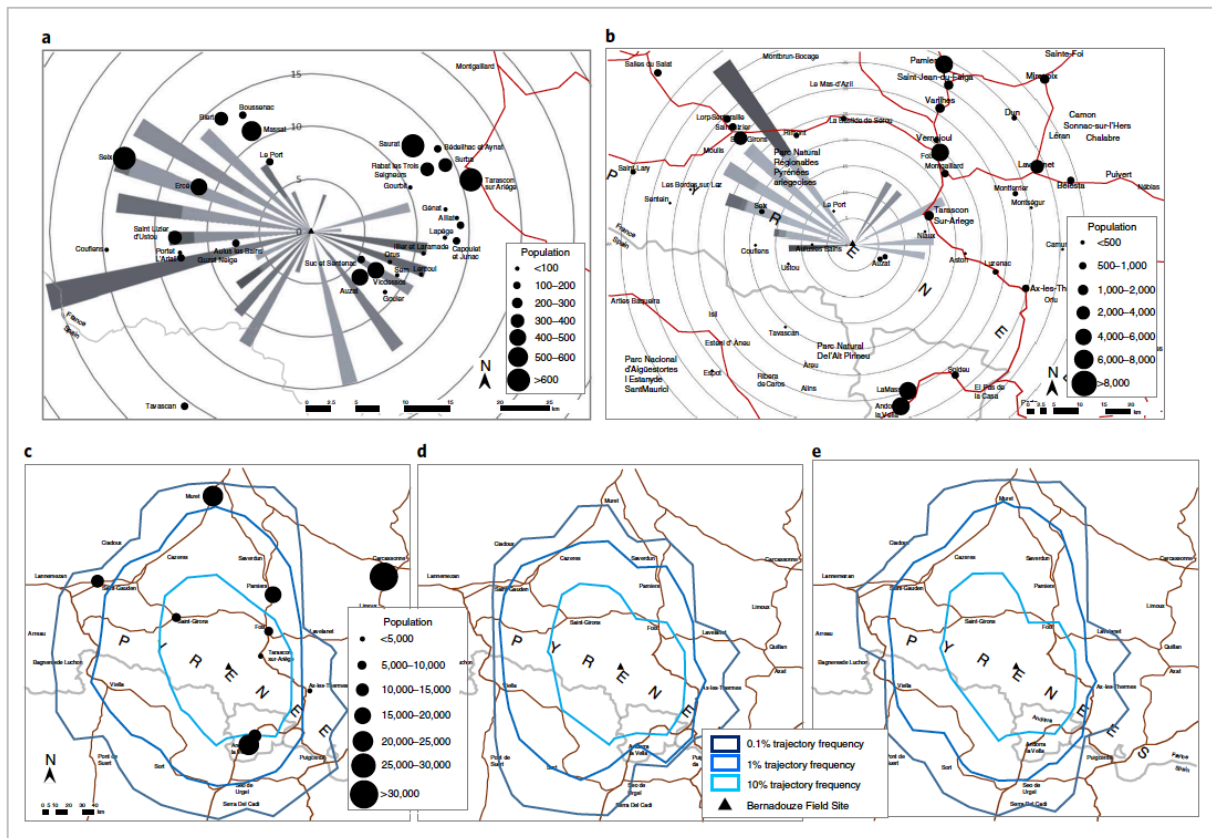


Figure 4: Example of microplastic transport trajectories, based on the recorded meteorology and the HYSPLIT4 back trajectory modelling. We see (a) rain and snow event trajectory calculations and (b) trajectories of wind events. With the HYSPLIT4 software, (c-e) back trajectories could be modelled for (c) wind, (d) rainfall, and (e) snowfall events (Allen et al., 2019).

Their Raman analysis showed that PS and PE were the most predominant polymers in the deposition samples. PS and PE are most commonly used in packaging materials and are often single use, thus making it no surprise to see these polymers in their samples (Allen et al., 2019). Besides PS and PE, they found PP, PET, and PVC. The sampling location that Allen et al. have chosen for this study is very different from the sampling locations in previous studies, since this is the first study that sampled microplastics in such a remote location. In this study, an average of $365 \text{ particles}/\text{m}^2/\text{day}$ were found. Dris et al. (2016) found an average of 110 ± 96 and $53 \pm 38 \text{ particles}/\text{m}^2/\text{day}$ in Paris, whereas Cai et al. (2017) found $228 \pm 43 \text{ particles}/\text{m}^2/\text{day}$ in Dongguan, which are both large cities. When excluding the particles sizes that were not counted in the Paris and Dongguan studies, the microplastic fragment abundance in the study by Allen et al. (2019) are comparable with the city averages. Similarly, when looking at the data for fibres in the same way, microplastic fibre abundances were slightly lower, but comparable to the city averages (Allen et al., 2019).

Additionally, *Allen et al.* did a microplastic source and transport analysis in this study, which has never been done before in the field. They used the HYSPLIT4 back trajectory model to investigate the transport of air parcels to the sampling site. An example from the study of *Allen et al.* is shown in **Figure 4**. With data on wind speed, trajectory and other meteorological data, an estimation can be made of the path of air parcels to the sampling site, thus roughly indicating where microplastics could have originated from. The assessment revealed a microplastic source area extending about 95 km away from the sampling site. When an air parcel travels towards the sampling site, it has the potential to pick up microplastic emissions from other towns and cities, which can be deposited at the sampling site. To conclude, this study shows that microplastic deposition can be significant even in remote locations. Furthermore, the researchers proved that at least local and regional sources of microplastics can be transported through the atmosphere to remote locations.

A publication by *Klein & Fisher (2019)* added to the previous studies that investigated the atmospheric fallout of microplastics. They investigated the abundance and regional differences of deposition in Hamburg, Germany (*Klein & Fisher, 2019*). In this study they sampled atmospheric fallout for twelve weeks using passive fallout collectors in six different sampling sites, three of which were urban and three were rural. They took 200 ml from each sample for analysis and then calculated back to the entire volume recorded. Samples were cleaned using a NaClO solution (in a similar way samples are cleaned with H₂O₂) and filtered onto cellulose filters. After transferring them into a petri-dish, the researchers stained the filters using a **Nile Red dye**. Identification and quantification of microplastics is made easier and more accurate when using this dye and makes it more efficient to distinguish them from organic material (*Tamminga et al., 2016; Klein & Fisher, 2019*). The stained filters were then analysed using a fluorescence microscope for identification and quantification. Any plastics on the stained filters will appear bright yellow or white, whereas organic material will appear orange or red, thus showing the ease of identification. From each sampling site, six particles were analysed with Raman spectroscopy for polymer composition. Besides normal sampling, a laboratory and procedural blank were also considered as a quality control and for background contamination, and with which the results were corrected.

They found a range of 5 – 164 particles per sample, with the highest average of particles found in the sampling site in a fir forest area (rural; 109.4 ± 19.2 particles per sample). Closely second and third were the samples from an open field (rural; 76.5 ± 49.8 particles per sample) and a beech/oak forest (rural; 70.9 ± 31.6 particles per sample). The samples from the urban sites showed lower average particle counts than the rural sites, with averages of 56.4 ± 43.6 particles, 51.2 ± 31.6 particles, and 29.1 ± 14.9 particles per sample. On average they found 214.6 particles/m²/day in the urban sites and 395.5 particles/m²/day in the rural sites (*Klein & Fisher, 2019*). Most of the particles were fragments (95%), with the remainder being mostly fibres. They considered three size ranges: < 63 µm, 63-300 µm, and > 300 µm. The fragments were mostly in the size range of < 63 µm, with decreasing numbers going up in the size ranges. On the contrary, most of the fibres were in the biggest size range, with decreasing numbers going down in the size ranges. With the Raman spectroscopy analysis, they found four types of polymers, with PE and PET being the most abundant amongst the fragments and fibres, respectively.

Klein & Fisher underline that in quantifying microplastics, it is a challenge to distinguish between organic, inorganic, and microplastic particles. Even though the Nile Red staining procedure has a disadvantage (it dissolves PS), it makes the distinction between particles more efficient (*Klein & Fisher, 2019*) and thus less time-consuming and expensive. Regarding the influence of weather, their results showed that microplastic abundance is related to wind speed and direction. However, unlike other studies, they found no relation between the number of precipitation events and abundance. The rural sites were most polluted, with the forest sites showing higher microplastic abundance. *Klein & Fisher* explain that this is due to a **comb-out effect**; microplastics floating in the atmosphere get filtered out by trees and plants, which could then be deposited due to the effects of gravity, wind or precipitation. An explanation for the high microplastic abundance at the open field site comes from the proximity of

this site to a highway (Klein & Fisher, 2019). To conclude, Klein & Fisher have shown that the use of a staining dye in combination with fluorescence microscopy is useful to distinguish between organic and inorganic particles, which makes identification and quantification of microplastics more efficient. Although they did not find any relation of microplastic abundance and weather events, their results indicate a relation between wind speed and direction, which was also found by Allen *et al.* (2019).

One of the more interesting papers from 2019 comes from Bergmann *et al.* (2019). In their research, they took snow samples at various different locations in the Arctic, the Alps, and Bremen, Germany. There have been signs of microplastic contamination in the Arctic; surface waters turned out to contain higher concentrations of microplastics than the global average, even though samples were taken in remote location (Bergmann *et al.*, 2019). The researchers suggest that atmospheric transport of microplastics could explain why the Arctic shows such high levels of microplastics pollution, which has also been suggested by previous studies. Snow samples were collected on ice floes in the Arctic Fram Strait, on Svalbard, on the Isle of Heligoland, in the Bavarian Alps, and in the city of Bremen. They made sure only to sample freshly deposited snow from the surface. The concentrations were determined and expressed as the number of particles per litre of melted snow. These were obtained with FlowCAM analysis, which is a real-time microscopy technique for particle analysis that usually serves its purpose in aquatic studies (Bergmann *et al.*, 2019). With this technique, particles and microplastics down to a size of 11 μm could be identified and quantified in this study. The snow samples were also filtered on aluminium oxide filters for further analysis with μ -FTIR spectroscopy. They used a different, automated method with the μ -FTIR, which prevented them from identifying microplastic fibres reliably. Thus, they also used a stereomicroscope to examine only fibres on the filters.

Unlike other studies, Bergmann *et al.* did not distinguish between different microplastics, like fragments, granules, or films. Only microfibrils were considered different from the general microplastics, but they could also not distinguish between microplastic fibres and other fibres since their techniques did not allow for that. Thus, Bergmann *et al.* only distinguished between microplastics and microfibrils. They found microplastics in almost all samples, with a range of 20-154,000 particles/L for microplastics and 43-10,200 particles/L for microfibrils. Microplastic and microfibril concentrations in snow samples from Europe ($24,600 \pm 18,600$ particles/L and 1431 ± 325 fibres/L) were significantly higher than those from the ice floes (1760 ± 1580 particles/L and 1380 ± 1100 fibres/L). However, the concentrations from ice floes were still substantial, given that these are so far up North (Bergmann *et al.*, 2019). There was one ice floe sample that was suspected of being contaminated, hence the high average concentration. However, removal of this sample from the data set brought the average concentration on the ice floes down to 180 ± 70 particles/L, which is still substantial contamination (Bergmann *et al.*, 2019). The microplastics ranged in size from 11-475 μm , with 80% of them being $< 25 \mu\text{m}$. Almost all (98%) of the particles were $< 100 \mu\text{m}$, with numbers decreasing when size increases. Fibres ranged from 65-14,314 μm , of which 31% were $< 500 \mu\text{m}$. Again, numbers decreased when size increases and the average length of European fibres was longer than Arctic fibres.

Given that the studied area was so diverse (from Europe to the Arctic), they found nineteen different polymers with the μ -FTIR analysis. Interestingly, the average number of different polymers was higher in European samples (8.63 ± 0.80 polymer types) than in Arctic samples (5.14 ± 0.79 polymer types), which is most likely due to higher population densities and human activity in the direct vicinity. Furthermore, the polymer composition of European and Arctic samples was significantly different (Bergmann *et al.*, 2019) and some polymers (e.g. PVC, PC, and PLA) were only found in Arctic sampling sites. Thus, even though the Arctic sampling sites are so remote, microplastics and microfibrils can still be found. Bergmann *et al.* compare atmospheric transport of microplastics with that of mercury (Hg), which can be found in high concentrations in Arctic wildlife (Bergmann *et al.*, 2019). According to them, there are three main wind streams that bring air masses from different continents to the Arctic; air masses that travel long distances and pass over densely populated areas that act as microplastic sources. This could bring the microplastics to the Arctic, causing the high concentrations Bergmann *et*

al. observed in their snow samples. Besides particle concentrations, particle sizes found in the Arctic were mostly in the smallest size range. Even smaller particles than found by *Bergmann et al.* possibly exist as well, but the detection limit of current techniques does not yet allow for a full investigation for particles below 11 μm . Furthermore, smaller particles might escape deposition with precipitation events due to their small size and are thus more likely to reside in the atmosphere at all times. Therefore, taking air samples might be a better way to study the smallest microplastics.

The final paper we will discuss in this section was published by *Wright et al.* (2019). At the time of writing, it was also the most recent paper in the field of atmospheric micro- and nanoplastics. This study added to the limited knowledge about micro- and nanoplastics by examining the presence of microplastics in the atmospheric fallout of London, England. They took atmospheric deposition samples using passive fallout collectors, which were placed on the roof of a building about 50 m in height. These samples were collected twice a week for a total of four weeks. A pre-concentration procedure was carried out prior to analysis by filtering the samples multiple times on filters using a vacuum pump, after which they were cleaned with a methanol solution and filtered on new filters. The researchers used Nile Red dye to stain the particles on the filter, similar to the study of *Klein & Fisher* (2019). The identification and quantification of suspected microplastics was done with fluorescence microscopy and particles were sized using ImageJ software. $\mu\text{-FTIR}$ analysis was used to analyse the chemical composition of the particles. Finally, *Wright et al.* explored local geographical sources and transport using microplastic characteristics, such as shape, aerodynamic equivalent diameter and density. Using data on air pollution and wind speed and direction, they used the HYSPLIT software (also used by *Allen et al.*, 2019) to incorporate a back-trajectory analysis in their study.

In total *Wright et al.* collected eight deposition samples. Microplastics were found in all samples, with fibrous particles being significantly more abundant than non-fibrous (i.e. fragments or granules) particles. They found a range of 510-925 microplastic fibres/ m^2/day , with an average of 712 ± 162 microplastic fibres. Other, non-fibrous microplastics were found in a range of 12-99 particles/ m^2/day , with an average of 59 ± 32 particles/ m^2/day . Overall, atmospheric deposition of microplastics was calculated to have an average of 771 ± 167 particles/ m^2/day . Sizes of microplastics were on average $905 \pm 641 \mu\text{m}$ and $164 \pm 167 \mu\text{m}$ for microplastic fibres and particles, respectively. For both types of microplastics, the researchers found that microplastic abundance increased when sizes decreased, suggesting that there are shorter and smaller fibres and particles present in the atmosphere (*Wright et al.* 2019). However, these smaller microplastic fibres and particles were not included in the results, since the cut-off size of the $\mu\text{-FTIR}$ did not allow for accurate analysis. Although not all particles could be analysed using $\mu\text{-FTIR}$, they found that 17% of the fibres were composed of petrochemicals, thus identifying them as microplastic fibres. Most of the fibres present were characterized as cellulose-fibres, which suggests that most fibres in the atmosphere are of natural origin. Of the microplastic particles, about two-thirds were identified as fragments, one-quarter as films, and the remainder as either granules or foams.

For an accurate analysis of the back-trajectory and long-range transport of the microplastic particles, *Wright et al.* calculated the time the particles were suspended in the atmosphere by determining the settling velocities of the microplastics. *Wright et al.* were the first in the field to do this for microplastics specifically, since *Allen et al.* (2019) based their calculations on the settling of dust particles. Based on the most frequent diameter and polymer density of the microplastics fibres and particles *Wright et al.* found, they calculated the aerodynamic equivalent diameter, which is the diameter of a spherical particle that has a density of 1000 kg/m^3 (or 1) and that has the same settling velocity as the particle of interest (i.e. the microplastic fibres or particles) (*Hinds, 1999*). Using the aerodynamic equivalent diameter of the microplastic fibres and particles they could determine the **settling velocity** of the microplastics, which is the terminal velocity with which particles that are suspended in the atmosphere settle on the Earth's surface (*Hinds, 1999*). With this data, they could run the HYSPLIT model to evaluate the back-trajectory and long-range transport. They found that microplastic fibres and

particles would have travelled for about 60 km and 12 km, respectively. The low mass-high surface area of fibres probably explains the longer trajectory, since they are easily suspended in the atmosphere. They also found a relation of wind speed and direction and microplastic deposition; for microplastic particles, deposition increased when the wind speed increased and was from the South-West. A similar relation with wind speed was found for microplastic fibres (*Wright et al., 2019*). However, when winds were from the North-West, fibre deposition also seemed to increase, thus indicating that microplastic fibres and particles had different origins. The source area of fibres was modelled to range between 640 and 8700 km², whereas the source area of particles ranged between 186 and 875 km². This difference is likely due to the settling velocities they found; microplastic fibres were less prone to settling than particles, which means they could travel in the atmosphere over a longer distance and area (*Wright et al., 2019*).

With this study, *Wright et al.* confirmed findings in previous studies; fibre abundance was significantly higher than particle abundance, a decrease in microplastic sizes increases abundance, and smaller microplastics could not be detected due to constraints of the analytical procedures. With the μ -FTIR analysis they mostly found polyacrylonitrile (PAN) fibres, otherwise known as acrylic. Given that the sampling took place in the winter months finding mostly PAN fibres is logical, since it is used a lot in knitted clothing (i.e. winter clothing) (*Wright et al., 2019*). The influence of North-Western winds on fibre abundance could be explained by a commercial area North-West of the sampling site, in which many people travel during the day. Concluding, *Wright et al.* found higher microplastic deposition rates than in previous studies and found no influences of meteorological parameters. They state that cities are therefore a source of atmospheric microplastics to the surrounding environment, however exact data on sources and transport is lacking and should be investigated more.

2.3 What can be learned from these previous studies?

2.3.1 Sampling of atmospheric plastics and their significance

We have seen in the previous section that there are a few different ways to study atmospheric micro- and nanoplastics. From the thirteen studies that have been published in the field thus far, ten focussed on atmospheric fallout, deposition and dusts, whereas only three focussed on airborne, suspended microplastics. When studying deposition and dusts, we can explain more about the pollution of the direct environment of the sampling site with micro- and nanoplastics. Deposition is usually expressed as a number of particles/m²/day, whereas dust concentrations are expressed as a number of particles/mg of dust. Thus, when sampling micro- and nanoplastics in deposition or dusts, we get time and space dependent results. Having accurate numbers on the rate of deposition could help to determine local or regional air pollution. However, when looking at air pollution specifically, sampling micro- and nanoplastics directly from the atmosphere would be more insightful. Usually, air pollution data is reported as mean concentrations per m³ of air volume or as the amount of $\mu\text{g}/\text{m}^3$. When measuring airborne micro- and nanoplastics this way, comparison with more traditional air pollutants, like CO₂ or NO₂ of which we know a lot more, becomes more useful. It gives us a direct overview of the amount people are likely to inhale on a daily or annual basis.

2.3.2 Known and hypothesized pathways of micro- and nanoplastics

Allen et al. (2019) and *Bergmann et al. (2019)* have proven with their research that atmospheric transport of microplastics over longer distances is possible, due to micro- and nanoplastics being present in remote locations. Microplastics (and possibly nanoplastics) have been directly sampled from the atmosphere (*Dris et al., 2017; Abbasi et al., 2018; K. Liu et al., 2019*), thus making it likely that micro- and nanoplastics are indeed transported in the atmosphere. There are two ways micro- and nanoplastics can enter the atmosphere: either by direct emissions from human activity or by resuspension of particles from the surface. Cities are suggested to be a source of airborne micro- and nanoplastics pollution to the surrounding environments. It was suggested by *Waldschläger et al. (2020)*

that the terrestrial and aquatic environments act as a reservoir of micro- and nanoplastic particles, since different studies have found micro- and nanoplastics in the terrestrial and aquatic environment. Thus, it seems that micro- and nanoplastics get introduced into the atmosphere in populated areas with human activity (i.e. cities or towns) and get transported to surrounding areas by wind, where they either remain suspended or get deposited on the Earth's surface or in rivers, lakes, or oceans. The known and hypothesized pathways are summarized in **Figure 5**.

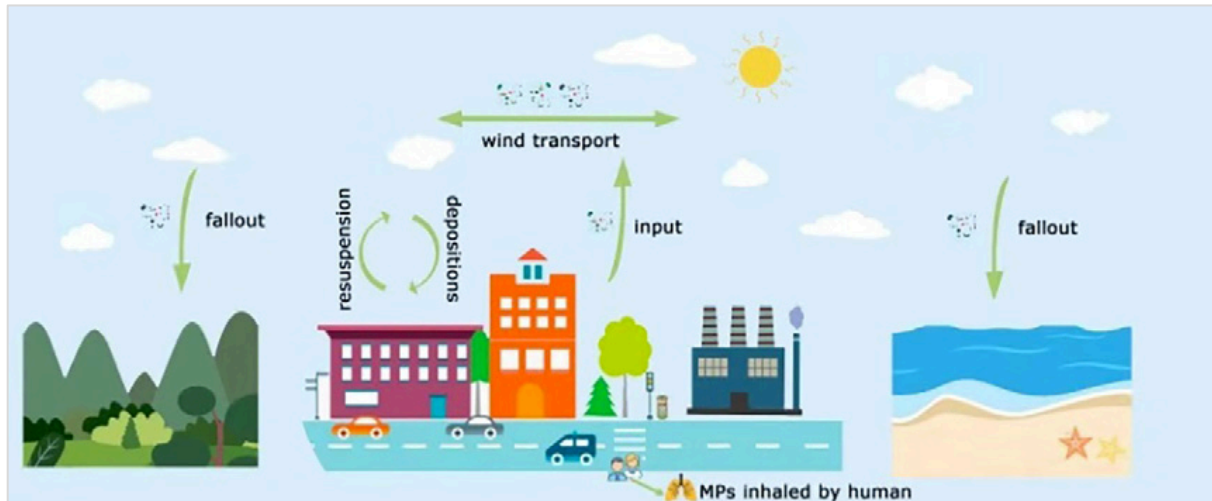


Figure 5: Summarizing pathways of micro- and nanoplastics in the environment (Chen et al., 2020).

2.3.3 Concentrations of micro- and nanoplastics

We cannot say much about micro- and nanoplastic concentrations at the moment. Sure, it was shown that air and fallout samples in different parts of the world all contain microplastics in different concentrations. Evidence suggests that microplastic concentrations are spatially distributed, with higher concentrations in urban environments than in remote areas. Sampling campaigns in sub-urban (Dris et al., 2016), coastal (K. Liu et al., 2019) or remote areas (Allen et al., 2019; Bergmann et al., 2019) have shown that microplastic concentrations are generally lower there than in densely populated, urban areas, thus showing a correlation between human activity and microplastic pollution. A vertical distribution was also observed (K. Liu et al., 2019), but this was not statistically significant. However, it is likely that micro- and nanoplastic concentrations become lower with increasing altitude. Concentrations around the world are influenced by different factors but are still comparable, since they fall in similar ranges. However, we have seen that identification and quantification of the smallest particles (< 50 μm) is often not possible. Bergmann et al. (2019) admit that 11 μm was their detection limit, whereas Abbassi et al. (2018) consider 2 μm as a minimum detectable size. Additionally, the results of most studies show that microplastic numbers increase when the size of these microplastics decreases. Thus, the detection limit of current analysis techniques makes the examination of atmospheric micro- and nanoplastics difficult and inaccurate. Furthermore, stereomicroscopes are often used as a first step for identification and quantification. The use of regular microscopy introduces even more inaccuracies in the analysis, since, firstly, it is difficult to differentiate between micro- and nanoplastics and organic particles, and secondly, because it requires a researcher to do the analysis, which gives rise to human error. Thus, both over- and underestimation are likely to have influenced the results in studies that made use of regular microscopy. A Nile Red staining procedure in combination with fluorescence microscopy has been used to make differentiation between organic and inorganic particles easier (Klein & Fisher, 2019; Wright et al., 2019), but the detectable sizes remain limited to micrometre sized particles. Concluding, microplastic concentrations have been estimated to some extent, however these are inaccurate due to the limitations in the analysis process and the missing knowledge about nanoplastic concentrations.

2.3.4 Micro- and nanoplastic characteristics

There are a few differences between the microplastics that can be found in air and deposition/dust samples. First of all, microplastics in air samples are mostly fibrous. *Dris et al.* (2017) focussed their study on microplastic fibres specifically and found that about one-third of all the fibres found indoors were microplastics. *Abbassi et al.* (2018) sampled the outdoor air and found almost exclusively microplastic fibres. In Shanghai, *K. Liu et al.* (2019) found both microplastic fibres and particles. About two-thirds of all the microplastics were fibres, with the remainder being fragments and granules. When looking at deposition/dusts, there is a larger variety of microplastic shapes. There are microplastic fibres present in deposition/dusts in varying proportions (*Dris et al.*, 2016; *Cai et al.*, 2017; *Wright et al.*, 2019). However, most studies show a higher abundance of fragments, granules, or films (*Abbassi et al.*, 2018; *Allen et al.*, 2019; *Klein & Fisher*, 2019). Thus, air samples contain mostly microplastic fibres, whereas deposition/dust samples show a more diverse assortment of microplastics. This is due to the low mass-high surface area of microplastic fibres, which makes them more susceptible to (re)suspension than microplastic particles. Since we found no reports of nanoplastics in air or deposition/dust samples yet, it is difficult to say something about nanosized particles in these samples. However, it is hypothesized that nanoplastics would be more abundant in air samples. Due to their small diameter and lower settling velocities, nanoplastics could escape deposition by precipitation events and are thus more likely to be suspended in the atmosphere. Additionally, if nanoplastics do get deposited, resuspension of these particles is more likely to occur, since the weight of nanoplastics particles is lower than microplastic particles.

We already looked at size distributions of microplastics in the atmosphere in the previous sections. In most studies, the size distributions were skewed; the smaller the particle size range, the higher the number of microplastics observed. This size distribution of microplastics is observed in both air samples and deposition/dust samples. Microplastic fibres are most abundant in the smallest size ranges, although there are present in all size ranges up to 5000 μm in most studies. Larger microplastic particles ($> 1000 \mu\text{m}$) have also been found, but they are not as abundant as larger microplastic fibres. Most studies also reported a high abundance of microplastics smaller than 50 μm , thus making it likely that small microplastics and possibly nanoplastics are the most abundant in samples. When looking at microplastic colours, there is a clear difference between fibres and particles. Microplastics fibres are mostly white/transparent or black/blue, which is likely due to abrasion of clothing or textiles. With microplastic particles we see more diverse colours, since particles can be created from more plastic sources than fibres. Regarding the chemical composition of microplastics, there are not many differences between air and deposition/dust samples. Since microplastic fibres are most abundant in air samples, polymer types associated with clothing and textiles (e.g. polyesters, nylon) were found the most. Fibres are also found in deposition/dust samples. Thus, we see a more diverse assortment of polymer types in these types of samples.

2.3.5 Factors that influence micro- and nanoplastic abundance

There are a few factors that affect microplastics abundances in air and deposition/dust samples. Research suggests that meteorological parameters, like precipitation, wind speed and direction or temperature influence deposition. *Dris et al.* (2017) showed that fibre abundance in urban Paris was five times higher during precipitation events, suggesting a wash-down function of precipitation. A similar correlation of abundance with rain or snow events was observed in the study by *Allen et al.* (2019) in the Pyrenees. Interestingly, the number of precipitation events and their intensity have a bigger influence on microplastic deposition than their duration. Most likely, the fibres are already washed out and therefore the duration of the event would not matter anymore. Airborne microplastics are also influenced by wind direction. Although a significant relationship was not found, *both Abbassi et al.* (2018) and *K. Liu et al.* (2019) found an effect of wind direction on microplastic abundance. *Klein & Fisher* (2019) did find a significant correlation and found that Southerly winds increased microplastic abundance in comparison to the more dominant westerly winds. Southern winds in Hamburg would

indicate microplastic transport from other parts of Germany to the sampling site, whereas the more dominant Western winds would be transporting relatively cleaner air from the North Sea. Wind direction thus seems to be related with population density and human activity, since sampling sites downwind of industrial and urban areas show higher microplastic abundance. Although *Klein & Fisher* (2019) found a higher concentration in forested areas due to a comb-out effect, urban samples generally contain more microplastics than sub-urban samples (*Dris et al., 2016; K. Liu et al., 2019*), showing again that population density and human activity affect microplastic abundances. Concluding, microplastic abundances in air and deposition/dust samples are likely affected by precipitation events, wind speed and direction, population density, and human activity. More studies are necessary to investigate the influence of other meteorological parameters, like temperature or humidity, on micro- and nanoplastic concentrations.

3. REVIEW OF SAMPLING AND ANALYSIS METHODS

In the previous section we reviewed all studies that have been done in the field of atmospheric micro- and nanoplastic thus far. We have seen different sampling methods and analysis techniques in these studies and most of them seem adequate to sample micro- and nanoplastics. However, there is currently no standardized method or procedure when it comes to sampling and analysis, which makes comparison amongst the different studies difficult. Almost all studies highlight the need for this standardization of sampling and analysis, since it improves the clarity of the results, guarantees the quality of the results, and increases productivity during the analysis of samples. Given that there are different options when choosing a suitable approach to study atmospheric micro- and nanoplastics, in the following section we review and discuss current sampling and analysis techniques that have been used. Advantages and disadvantages are discussed and then a new, improved sampling method and analysis procedures are highlighted.

3.1 Sampling methods

There are several ways to sample atmospheric micro- and nanoplastics. Researchers can sample deposited micro- and nanoplastics in the form of atmospheric fallout or dusts or as airborne micro- and nanoplastics. Between these, we can also make a distinction between active or passive and indoor or outdoor sampling. First, the options for sampling indoor micro- and nanoplastics. Indoor air has only been sampled once (*Dris et al., 2017*), which was done using a standalone sampling pump. These kinds of pumps usually pump air with a fixed flowrate through a quartz fibre filter. Thus, the filter allows air to pass through, but particles get deposited on the surface of the filter. Depending on the flowrate and the sampling time, the sampled air volume can be calculated and then the micro- and nanoplastic concentrations can be found as n particles/ m^3 or $\mu g/m^3$. Indoor deposited micro- and nanoplastics have been sampled in the same study by *Dris et al. (2016)* by exposing a quartz fibre filter in a petri-dish to the indoor atmosphere. Dust collection is another way to sample deposited micro- and nanoplastics, for both indoor and outdoor studies of micro- and nanoplastics. To collect dusts from surfaces, usually hog bristle brushes are used (*C. Liu et al., 2019*). It is important that the brush and the sample container are anti-static to prevent the dust from clinging to the brush and the sides of the container. An advantage of this method is that it is very low-tech and therefore low on costs. However, a disadvantage is the collection of a lot of unwanted particles, which almost always requires the sample to be treated in the lab to remove the unwanted particles prior to analysis.

Outdoor collection of airborne micro- and nanoplastics is similar to the method used indoors. *Dris et al. (2017)* used the same stand-alone sampling pump with a quartz fibre filter for outdoors as they did indoors. *K. Liu et al. (2019)* used a similar suspended particulate sampler, although the flowrate of their sampler was set much higher (100L/min) compared to the 8L/min by *Dris et al. (2017)*. Both studies used the same type of quartz fibre filter to collect particles. *Abbassi et al. (2018)* used a different suspended particulate sampler (**Figure 6**). This sampler is capable to take sequential air samples by changing filters automatically. Additionally, it has an inlet that is size-selective, which enables researchers to look at particles from different size ranges when required (total suspended particulates, PM_{10} , and $PM_{2.5}$). This is an advantage that an automatic, size-selective sampler has over non-selective samplers; when the $PM_{2.5}$ inlet is open for example, only particles of 2.5 μm and smaller are collected on the filter. Thus, larger particles won't get collected on that filter, which reduces contamination of the sample with particles researchers are not interested in. However, the inlet may also have an impact on the results, since not all fibres are collected for example. Depending on the flow inside the sampler and the orientation of the fibres relative to the inlet some fibres might not get sampled. Still, the compatibility of a size-selective sampler with micro- and nanoplastics sampling has to be thoroughly tested, since analysis of micro- and nanoplastics is currently limited to micrometre sizes (*Abbassi et al., 2018; Bergmann et al., 2019*).

Collecting outdoor samples of atmospheric fallout/deposition is very different from indoor sampling. First of all, weather can influence the sampling and makes simply exposing a quartz fibre filter to the atmosphere like *Dris et al. (2017)* almost impossible. The total atmospheric fallout, which includes dry and wet deposition, is therefore sampled using an open funnel with an attached bottle or glass beaker, as first introduced by *Dris et al. (2015)*. Plastics that fallout of the atmosphere get collected by the funnel and are either transported down the funnel into the collection bottle or stick to the side of the funnel. Rain and/or snow gets collected as well with this method, and therefore researchers usually record the amount of water in the bottle when samples are periodically collected. The advantage of this method is that it collects the total atmospheric fallout, which gives you a direct indication of the pollution of the surrounding area. One of the disadvantages is that some particles get stuck to the inside of the funnel. A rinsing procedure is required to clean the sides of the funnel and to collect the particles in the bottle (*Enyoh et al., 2019*). From this, inaccuracies may arise, because during rinsing the sample is susceptible to contamination. That brings us to the second disadvantage, which is the collection of unwanted organic or inorganic particles, such as pollen or sand for example. Since the total atmospheric fallout is collected, other particles are collected as well. After collection, the samples have to be treated in the lab to remove these unwanted particles. Collection of airborne micro- and nanoplastics is also susceptible to contamination. However, active samplers would be less prone to contamination since heavier and bigger particles might escape collection.



Figure 6: From left to right, Deltanova GH300 Air Sampler (*Dris et al., 2017*), TECORA, ECHO PM Sampler (*Abbassi et al., 2018*) and Palmex Rain Sampler (*Allen et al., 2019*).

3.2 Treatment of samples

There are three steps we can distinguish when it comes to treatment of samples prior to analysis. After collection the samples are pre-treated first, which is usually a simple step of sieving, decantation or filtration to reduce the volume of a sample. This depends on the type of study and the sampling methods used and is sometimes not even necessary, like we have seen with *Dris et al. (2017)* for example. When the samples are pre-treated, they are usually filtered on quartz fibre filters or polytetrafluoroethylene (PTFE) filters, which are both standard filter types in this type of particle research. To remove unwanted particles, it is possible to remove them through density separation. A solution with a density higher than most polymer types is added to the sample, which causes the micro- and nanoplastics to float towards the surface, hence the name **flotation method** that was mentioned before. *Dris et al. (2017)* used a zinc chloride ($ZnCl_2$) solution with a density of 1.6 gr/cm^3 , but a sodium

iodide (NaI) solution with a similar density can also be used, as shown by *Abbassi et al.* (2018). After another filtration step to remove the flotation medium, samples can be further treated to remove additional unwanted material that may interfere with analysis, which can be both organic and inorganic. There are multiple ways to do this, but in the field of atmospheric micro- and nanoplastics a H₂O₂ solution is mostly used. Finally, the samples are rinsed with distilled water, filtered on another filter and dried before analysis.

3.3 Analytical procedures and techniques

3.3.1 Visual identification with microscopy

The most used technique to visually identify microplastics is the use of a (binocular) microscope. Probably all labs around the world have access to a microscope, since it is cheap, easy to use, and a fast way to get a view of any microplastic presence. There are a few variants to the common microscope that were used. Polarized light microscopy was used by *Abbassi et al.* (2018) to identify and quantify microplastics, as well as a fluorescence microscopy step, which uses a light source with a specific wavelength to illuminate a sample. This type of microscopy was also used by *Klein & Fisher* (2019) and *Wright et al.* (2019), with the addition of a Nile Red staining dye as an improvement for sorting organic and inorganic particles. However, in the beginning of this paragraph, I intentionally left out the word *nanoplastics*, since these techniques and methods are only suitable for the detection of microplastics. When it comes to studying nanoplastics as well, these techniques and methods all fall short, since detection is limited to the micrometre size range. Furthermore, it is recommended to only use them for the identification and quantification of microplastics down to 500 µm (*Renner et al.*, 2018). There is also a high chance of false positives (especially when the samples are not treated prior to analysis), since the identification usually depends on the researcher's judgement. Lastly, chemical characterization is not possible with these techniques and thus other analytical techniques are needed. These techniques and methods would still be useful as a quick and easy initial identification and detection step to confirm the presence of microplastics prior to a further, more thorough analysis. Scanning electron microscopy (SEM) could potentially be used for the identification and quantification of nanosized particles. However, the use of SEM for this application would be impractical, since the preparation of a sample for SEM-analysis is complex and time consuming. Due to the clear and high-magnification images it can provide, SEM would be far more useful to study surface characteristics of plastics, which has been done before (*Dehghani et al.*, 2017; *Cai et al.*, 2017; *Abbassi et al.*, 2018).

3.3.2 Chemical characterisation using spectroscopic techniques

It is important to study the chemical characterisation of micro- and nanoplastics to determine which types of polymers may be present in atmospheric samples. Based on what we know about which types are used in different plastic products, we can make conclusions about where the micro- and nanoplastics in a sample might have originated from and from which type of plastic products. This chemical characterisation is almost impossible to do with visual techniques alone, which is why a second analysis method is necessary in virtually all studies. To this end, spectroscopic techniques like FTIR (and to a lesser extent Raman) are used quite frequently in micro- and nanoplastics research.

3.3.2.1 Fourier Transform Infrared (FTIR) spectroscopy

FTIR is the most used spectroscopy technique to identify and characterize microplastics thus far. It has been used almost since the start of the field of atmospheric micro- and nanoplastics (*Dris et al.*, 2016). With µ-FTIR the specific chemical bonds in the microplastics can be studied very accurately according to a fingerprint it generates of the particle during analysis. In FTIR, a sample is radiated with an infrared beam, part of which is either absorbed by or transmitted through the sample. Depending on the chemical structure and functional groups of the particles in the sample, some wavelengths of the broadband infrared beam are absorbed while the rest is transmitted. This results in a molecular

fingerprint of the sample, since it can be detected which wavelengths are absorbed and transmitted. A schematic overview of FTIR and an example of such an infrared spectrum is shown in **Figure 7**. Each type of plastic has its own fingerprint, which makes it possible to differentiate between multiple types of plastics in a sample after matching with a compound database (for more details on FTIR principles, refer to *Thermo Fisher Scientific, 2020a*). With μ -FTIR it is currently possible to analyse microplastics down to a size of 11 μm , which is a detection limit that is determined by the diameter of the infrared beam (*Bergmann et al., 2018*). Furthermore, the analysis is non-destructive, which means that a sample can be analysed multiple times if needed. There are some disadvantages when using μ -FTIR to study micro- and nanoplastics. First of all, the detection size limit is determined by the diameter of the infrared beam. Therefore, it is currently possible to sample microplastics down to a size of 11 μm , thus analysing nanoplastics is still not possible with μ -FTIR. Besides the detection size limit, the μ -FTIR instrument is very expensive, which makes it not the most ideal instrument to use in a standardized analysis protocol for micro- and nanoplastics (*Shim et al., 2017*). Not all labs in the world will have access to such an expensive instrument. Lastly, to examine each individual particle is very time consuming, which is why most studies randomly select sub-samples for further analysis. Routine analysis with μ -FTIR is thus not advised, however, this will not be an issue if researchers want a more thorough analysis of suspected microplastics (*Shim et al., 2017*). There are more issues with FTIR that are too detailed and don't fall within the scope of this review, which can be found in the review by *Shim et al. (2017)* and *Renner et al. (2018)*.

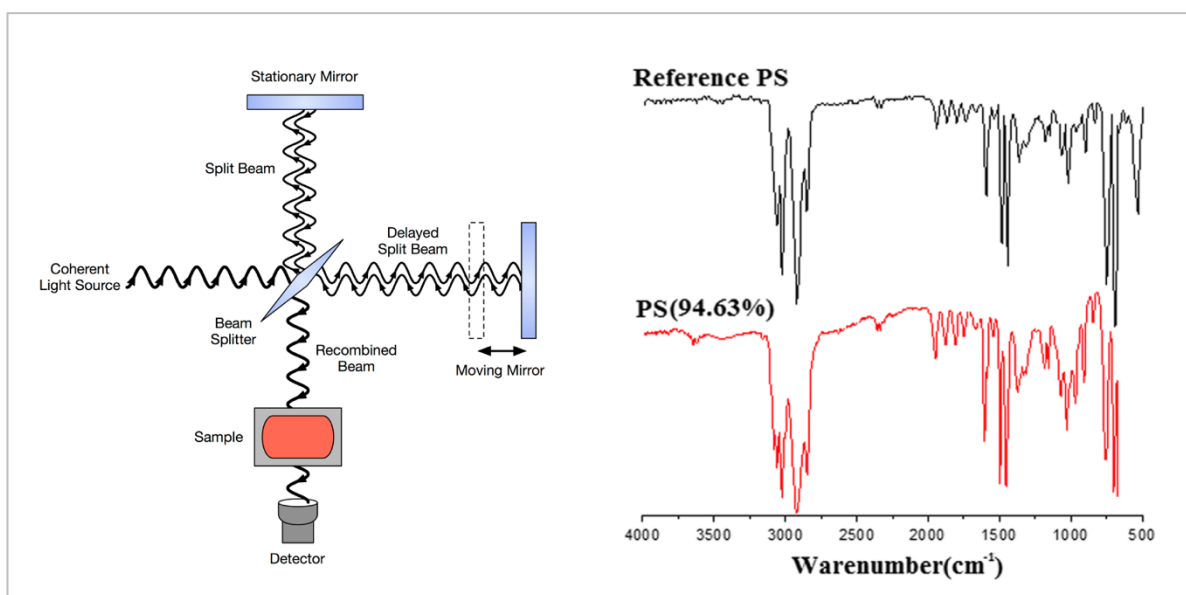


Figure 7: Schematic overview of FTIR spectroscopy (*Sanchonx, 2011*) and an example of an IR-spectrum of polystyrene (PS) compared to its reference IR-spectrum (*Cai et al., 2017*).

3.3.2.2 Raman spectroscopy

Raman spectroscopy is a similar technique to FTIR in that it returns a unique fingerprint of a sample. However, the principle behind Raman is very different to FTIR. With Raman, a monochromatic light source illuminates the sample, the energy of which can be absorbed, transmitted, reflected, or scattered. Scattered light can either be in the form of elastic collisions of the light with the sample, which is called Rayleigh scattering, or from inelastic collisions, which is called Raman scattering (*Thermo Fisher Scientific, 2020b*). The Rayleigh scattered light has the same frequency as the light source, but the Raman scattered light does not. Raman scattered light depends on the bonds in the molecules of the sample; the detected Raman scattered light has different frequencies that correspond to the vibrational frequencies of these bonds (*Thermo Fisher Scientific, 2020b*). Each type of molecule, or polymer in this case, has different molecular bonds. These frequencies are then matched with a

database to determine the functional groups and subsequently the type of plastic in the sample (for more details on Raman principles, refer to *Thermo Fisher Scientific, 2020b*). It is possible with Raman to identify plastics with a polymer profile similarly to FTIR. Furthermore, it is also capable to do a non-destructive chemical analysis, without the need for a contact mode (*Shim et al., 2017*). The analysis with Raman is however very expensive, since it requires expensive instrumentation, and it is even more time-consuming than FTIR in some cases. However, one advantage Raman spectroscopy has over FTIR is that it is capable of detecting particles down to a couple of micrometres, which is also limited by the diameter of the laser beam (*Shim et al., 2017*). Thus, it seems that Raman may be a better alternative for μ -FTIR when studying microplastics. However, in practice we see that Raman spectroscopy is seldomly used because it is more time consuming than FTIR (*Renner et al., 2018*). Thus, for routine micro- and nanoplastic analysis, Raman spectroscopy would not be very suitable.

3.3.3 Other techniques used for analysis of micro- and nanoplastics

In the study by *C. Liu et al. (2019)* we have seen the first use of a mass spectrometry technique in the field of atmospheric micro- and nanoplastics. The method they used is called liquid chromatography-tandem mass spectrometry or LC-MS/MS. With mass spectrometry, ions are analysed on the basis of their mass-to-charge (or m/z) ratio (*Thermo Fisher Scientific, 2020c*). Prior to analysis, molecules in the sample are first ionized by an ionization source. After ionization they are accelerated in vacuum through electric and magnetic fields, where the ions are deflected and separated. The radius of their path to the detector is then detected and calculated and it is this radius that is a function of the mass of the ions (*Thermo Fisher Scientific, 2020c*). A software programme will then generate the spectral data, which can be analysed and matched to a database to determine which compounds were present in a sample. A simple overview of mass spectrometry is shown in **Figure 8**.

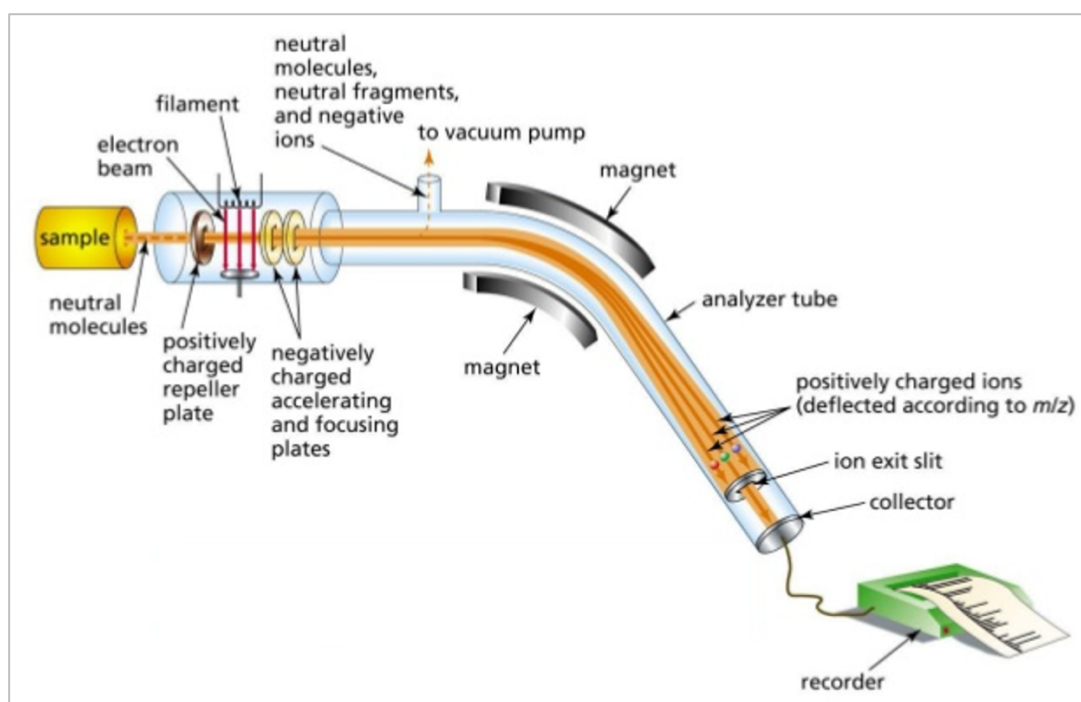


Figure 8: Simple schematic overview of mass spectrometry and its components, showing how particles are detected and analysed according to their m/z ratio (*Soderberg, 2020*).

In the case of *C. Liu et al. (2019)*, the components in the sample mixture were separated using liquid chromatography (LC), which is one of many different separation methods used in mass spectrometry analysis (for more details on liquid chromatography, refer to *Thermo Fisher Scientific, 2020d*). *C. Liu et al. (2019)* developed their own version of this technique to specifically identify the building blocks of PET and PC in their samples. Quantifying micro- and nanoplastics this way will not return a number of

particles, but instead a concentration of $\mu\text{g}/\text{kg}$ (in the study of *C. Liu et al. (2019)* at least). However, mass spectrometry will analyse a sample in bulk (so-called bulk analysis) and therefore information about size or shape will not be provided with this analysis (*Shim et al., 2017*). Furthermore, mass spectrometry usually requires expensive instrumentation. However, the sensitivity and accuracy it can provide will be useful when analysing micro- and (especially) nanoplastics (*Shim et al., 2017; Renner et al., 2018*). It will be especially interesting when it is used as a complementary step before or after spectroscopic analysis with $\mu\text{-FTIR}$ for example. That way the total dataset would include concentrations of micro- and nanoplastics, which are provided by mass spectrometry, and shapes and sizes, which are provided by a spectroscopic technique.

3.4 Promising sampling and analysis methods

3.4.1 Sampling using a high-volume cascade impactor

As we have seen, sampling of airborne micro- and nanoplastics is mostly being done with standalone air samplers (*Dris et al., 2017; K. Liu et al., 2019*) or with suspended particulate matter (PM) samplers (*Abbassi et al., 2018*). In regard to the standalone air samplers, these will collect all particles (both organic and inorganic) on just one filter. When sampling for a short amount of time, this will likely not cause any problems further on during analysis. However, when larger volumes of air are being sampled a higher number of particles will collect on a single filter, which will almost certainly require a treatment to remove any contamination or unwanted particles. While most treatment procedures are currently relatively standardized, treating these filter samples (like explained in section 3.2) will require multiple days to complete. Preferably, such a long treatment step would be best avoided, especially when the aim is a routine sampling and analysis of airborne micro- and nanoplastics.

To minimize the presence of unwanted particles, a suspended PM sampler will provide a solution. The suspended PM sampler as used by *Abbassi et al. (2018)* has a size-selective inlet, which prevents particles larger than the cut-off size from being collected on the filter. By using such a sampler, *Abbassi et al.* could independently sample total suspended, PM_{10} , and $\text{PM}_{2.5}$ particles. During their analysis, they found that relatively few particles were collected on the $\text{PM}_{2.5}$ samples, which was due to the aerodynamic diameter of the sampler inlet. They mentioned that their minimum detectable size was $2\ \mu\text{m}$ and that the number of particles smaller than $2.5\ \mu\text{m}$ might have been underestimated. They correctly note that collection of fibres depends on the orientation of the fibres relative to the inlet, and that they may either get collected or trapped. However, since they omitted their $\text{PM}_{2.5}$ data this was not further researched. Still, it seems promising to already separate particles during sampling, which will decrease subsequent treatment times and will reduce inaccuracies in identification and quantification during analysis. There exists another sampling device that has not been used before to sample micro- and nanoplastics, which, similar to the suspended PM sampler, collects and separates particles in different size ranges and does so even in the nanosized range. This device is also known as a high volume, cascade impactor.

An impactor is an air sampler and collector that relies on impaction to collect particles on a downstream filter. In **Figure 9** you can see a schematic overview of an impactor. Air is drawn in at the main inlet by a vacuum pump and guided through an impaction nozzle. The particles that are drawn in travel along the jet streamlines towards the impaction plate, which in turn deflects the air flow from the nozzle at exactly 90 degrees. The particles in the jet streamlines will either be able to make this turn around the impaction plate or not. Particles that do not, will get impacted on the impaction plate. This depends on the *inertia* of the particles, which is the resistance of a particle to a change in its velocity or direction. The impactor is calibrated in such a way that particles with a certain inertia can escape impaction (usually the smaller particles), whereas other particles will get impacted and collected (usually the bigger particles). Depending on the design of the impactor, particles up to a certain diameter can be collected.

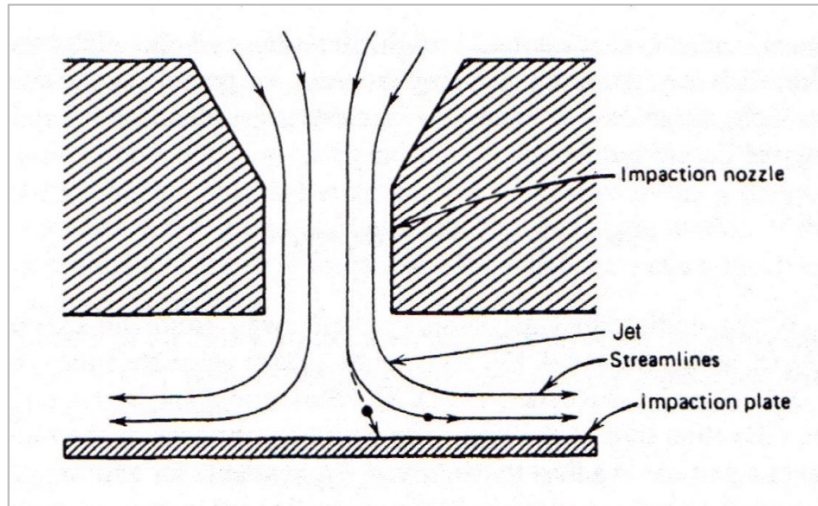


Figure 9: Schematic overview of a particle impactor (Hinds, 1999).

In **Figure 10** you can see a commercially available and schematic representation of a cascade impactor, which is essentially an assembly of multiple impactors in different stages. These kinds of impactors are designed in such a way that the biggest particles are collected in the top stages of the cascade impactor and the smallest particles are collected in the bottom stages. This is made possible by the design of the stages; the cut-off diameter can be reduced in each stage by decreasing the diameter of the nozzles but increasing them in number to allow for a constant flow rate (shown in the schematic overview of **Figure 10**). Thus, the cut-off diameter for particle impaction decreases with each stage. Therefore, the filters from each stage will collect a range of particles, which is made possible due to the calibration of the impactor. In theory, each stage will collect all particles bigger than its cut-off diameter. The cascade impactor also has a downstream after filter, or back-up filter, where all particles are collected that have escaped impaction in one of the stages. Thus, the one big advantage a cascade impactor has over traditional suspended particulate samplers is the automatic separation of particles based on their diameter. This sampling method is used quite frequently in aerosol research and it seems promising to use in airborne micro- and nanoplastic research. However, its application still has to be tested.

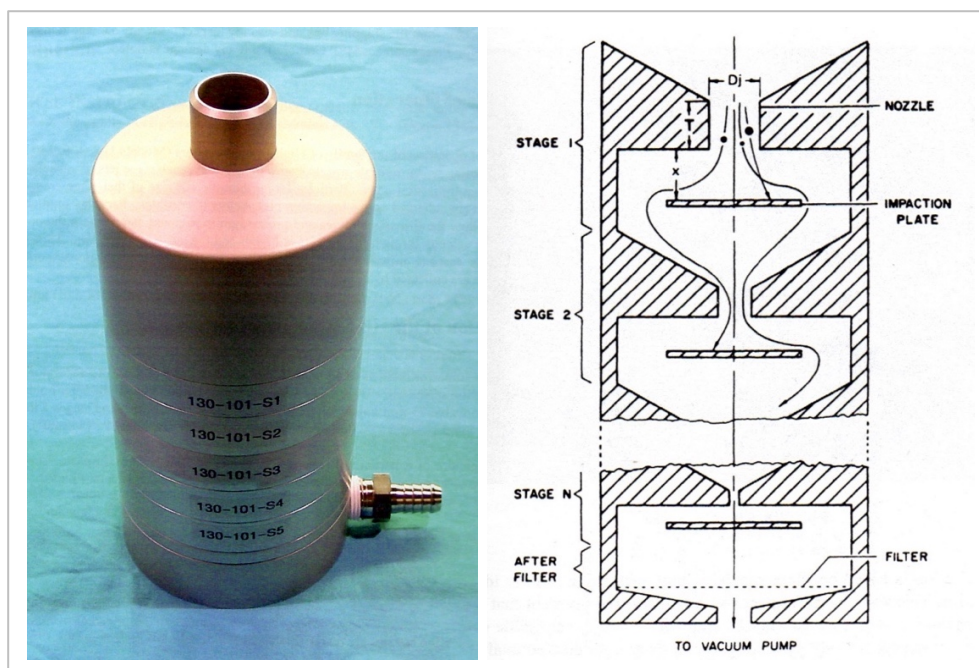


Figure 10: Picture of a commercially available cascade impactor (Copley Scientific, Model 130) and a schematic overview (Hinds, 1999).

3.4.2 Thermal Desorption-Proton Transfer Reaction-Mass Spectrometry (TD-PTR-MS)

We discussed why a mass spectrometry technique would be useful for the analysis of micro- and nanoplastics in section 3.3.3, especially in terms of sensitivity and accuracy. Moreover, human risk assessment will make more sense when concentrations are used ($\mu\text{g}/\text{kg}$), instead of using data on the number of particles inhaled or ingested. Recent advancements in mass spectrometry development may have provided researchers in the field of atmospheric micro- and nanoplastics a solution for identification and quantification (Zhang *et al.*, 2020). To get clear results from a spectrometric analysis, you would normally need a decent number of particles of adequate size (Zhang *et al.*, 2020). That was until recently, when Materić *et al.* (2020) presented a mass spectrometry method that has a higher sensitivity compared with previous mass spectrometry techniques. Their method is called TD-PTR-MS, which stands for thermal desorption-proton transfer reaction-mass spectrometry, which was developed back in 2010 (Holzinger *et al.*, 2010). With this method, the sample is first thermally desorbed in an oven, which means the particles in the sample are released from the sample carrier (i.e. the filter). Afterwards, the desorbed particles are guided to the PTR ionization unit, which, in this case, uses H_3O^+ -ions to ionize the particles. Then the ions are separated with a time-of-flight mass analyser and detected (Lindinger *et al.*, 1998). Finally, mass spectra are generated and the compounds in the sample can be identified. The TD-PTR-MS method was first developed to do online sampling and analysis of organic aerosols (Holzinger *et al.*, 2010) and was later used to analyse dissolved organic matter (Materić *et al.*, 2017). Furthermore, an offline TD-PTR-MS was developed to study organic aerosols from filter samples to enable long-term aerosol measurements (Timkovsky *et al.*, 2015).

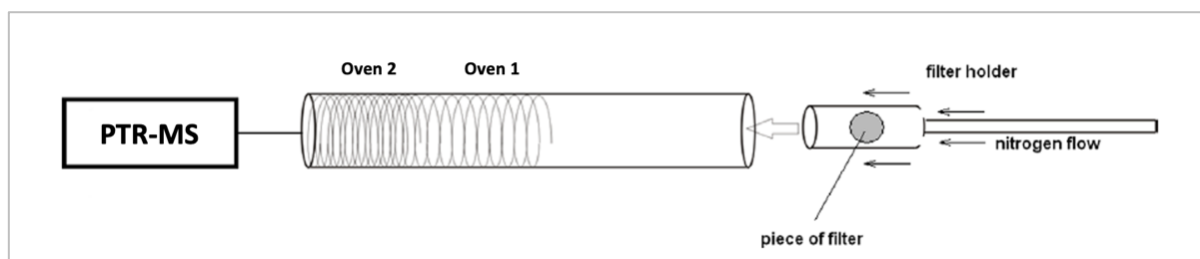


Figure 11: Offline setup of the TD-PTR-MS method (adapted from Timkovsky *et al.*, 2015).

At first, the TD-PTR-MS was coupled with an aerosol inlet (Holzinger *et al.*, 2010) to allow for on-site (or online) sampling and analysis of organic aerosols. However, Timkovsky *et al.* (2015) recognized that uncoupling the sampling and analysis of organic aerosols would be more cost effective, as opposed to bringing an expensive piece of equipment into the field for an extended amount of time. They tested if offline sampling of organic aerosols on quartz fibre filters would provide the same results with the TD-PTR-MS as the online sampling and analysis protocol. With offline sampling, aerosols are sampled on a filter, stored, and brought to the lab for analysis. The offline TD-PTR-MS method includes two ovens, in which the aerosols are thermally desorbed from the filter samples and then analysed. And indeed, the measurements with the offline method (Figure 11), corresponded well within the levels of uncertainty with the online TD-PTR-MS method (Timkovsky *et al.*, 2015). Thus, this specific offline method could work well with the cascade impactor. Sampling with the cascade impactor can take place at different locations, after which the filters can be stored (usually at -18 degrees Celsius). Then, analysis with the offline TD-PTR-MS method would take place, which will result in the concentrations of polymers in the different size ranges in the cascade impactor. A sample treatment step or pre-concentration step will not be necessary due to the higher sensitivity of the PTR-MS, which saves a lot of time in routine analyses of airborne micro- and nanoplastics. More importantly, the sensitivity of the TD-PTR-MS methods closes the gap between the chemical characterization and quantification in the nanogram range (Materić *et al.*, 2020). However, Materić *et al.* (2020) also note that a complementary analysis technique is needed to provide information about the size and shape of the micro- and nanoplastics, which will result in an even more detailed overview of micro- and nanoplastics contamination of the environment.

3.4.3 Infrared-Photoinduced Force Microscopy (IR-PiFM)

From the previous section it becomes obvious that there should be a complementary analysis technique that provides information about the size and shape of the micro- and nanoplastics. Although recent advances in μ -FTIR and μ -Raman have been proven to be very reliable for microplastic analysis, it was not possible to analyse sub-micron particles. For both techniques, the smallest sizes that have been published are 11 μm for μ -FTIR and 10 μm for Raman spectroscopy (Zhang *et al.*, 2020). However, in recent years the development of atomic force microscopy (AFM) coupled with either IR or Raman spectroscopy has come forwards as a potential method for the analysis of nanoplastics (Shim *et al.*, 2017). With AFM it is possible to image almost any surface type using a sharp and very small tip that is raster scanned across the surface of a sample and that measures the atomic forces at the tip-sample interface (Nanoscience Instruments, 2020). The position of the tip is monitored to allow for a constant force at this interface. This occurs through a laser beam deflection system, in which the tip is connected to a cantilever that is in turn illuminated by a laser beam. The deflection of the laser beam by the cantilever is detected and the forces at the tip-sample interface can be calculated by taking into account the stiffness of the cantilever and its position shift (Nanoscience Instruments, 2020). Imaging can occur through multiple modes (contact, tapping, or non-contact modes), but for the sake of simplicity we will not discuss these here. AFM is most frequently used to image the surface of an object and to determine the topography of this surface at a nanometre range. A basic schematic overview of the working principle of AFM is shown in Figure 12.

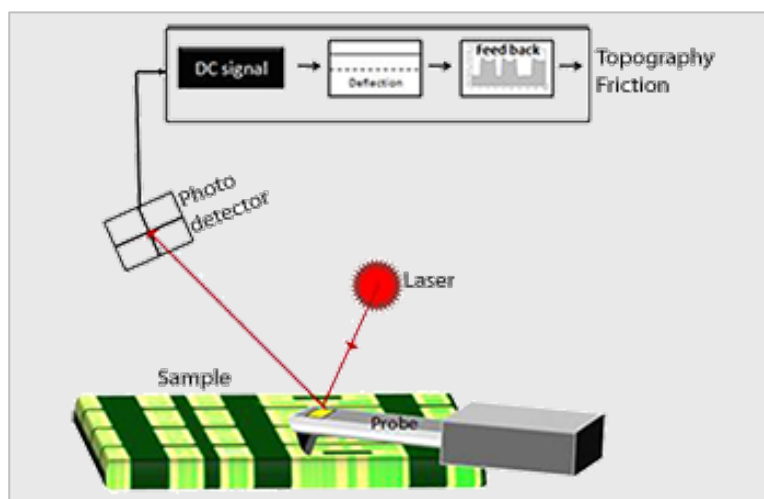


Figure 12: Basic schematic overview of AFM (Nanoscience Instruments, 2020).

When coupling an AFM with a FTIR or Raman spectroscopy technique it is also possible to determine the chemical composition of samples or objects. If Raman is coupled with AFM, the same object is scanned at the same time or independently with both separate techniques, but if AFM is coupled with FTIR, both techniques are merged into a single technique (Shim *et al.*, 2017). With AFM-IR, the sample is illuminated with an infrared laser, which causes the sample to thermally expand due to the absorption of the infrared. This causes the AFM cantilever to oscillate, which is detected and analysed with Fourier transform, and from which IR absorption spectra and absorption images can be determined (Dazzi *et al.*, 2015). With this technique it is possible to achieve spatial resolutions of 50 – 100 nm (Dazzi *et al.*, 2012), thus making it interesting for the analysis and characterization of particles in the nanometre range. There exists another variation of this technique, which is called Infrared-Photoinduced Force Microscopy (IR-PiFM).

This method “detects photo-induced molecular polarizability of samples down to the molecular level by mechanical detection of the force gradient of the interaction between the optically driven dipoles in the sample and a metal coated AFM tip” (Molecular Vista, 2020). This means that if the sample is

illuminated by a light source, there will be a photo-induced force as a result of the dipole-dipole attraction between the sample and the AFM tip. From the reflection of the cantilever and the photoinduced forces, the IR-PiFM technique is able to both image the topography of the sample and determine the chemical components in the sample (Nowak *et al.*, 2016). According to *Molecular Vista* (2020), the uniqueness of the IR-PiFM technique lies in the excitation with near-field and detection of the response in near-field, which allows for easier and more robust analysis when comparing with other nano-IR techniques. Shim *et al.* (2017) mention that analysis of a single nanoplastic with AFM-IR, and in this case IR-PiFM (Figure 13), would be very time-consuming, since it is difficult to find a single nanoplastic particle in an unknown sample. However, this is where the analysis may profit from choosing a suitable sampling technique, in our case the cascade impactor. Each stage in the impactor contains a specific number of nozzles through which particles travel. The lowest stages have the smallest diameter nozzles, which also results in a very localized impactation of particles on the impaction substrate. Thus, this should make it easier to locate even nanoplastics in the sample.

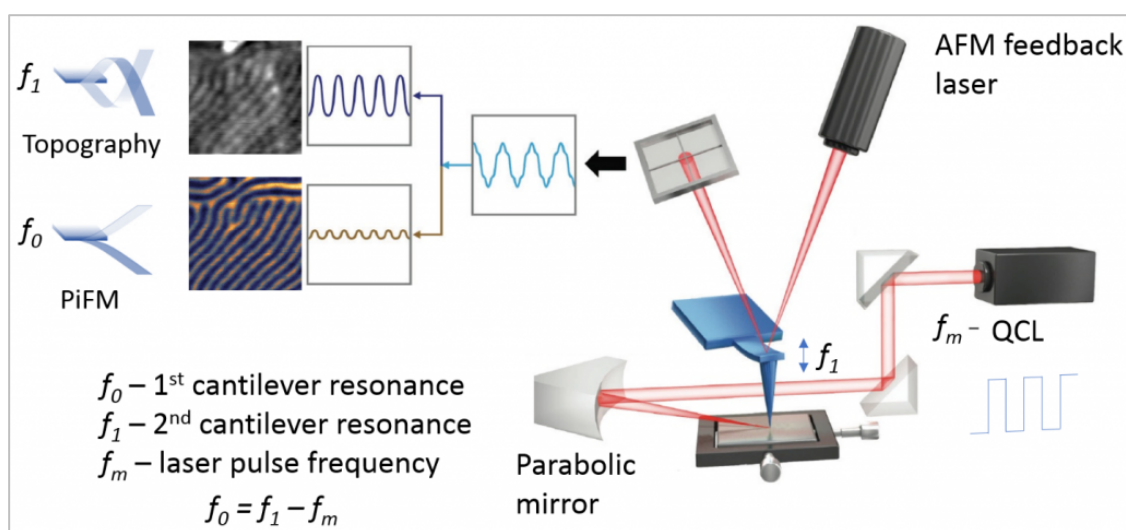


Figure 13: Schematic overview of the IR-PiFM technique (*Molecular Vista*, 2020).

The use of IR-PiFM for analysis will result in an output image as shown in Figure 14. Just as with regular AFM, the deflection of the cantilever is monitored by the AFM feedback laser. If any deflection is occurring, this will show in a signal with which the topography of the sample or particles can be determined, which is shown in the top left of Figure 14. The secondary laser in the IR-PiFM method is pointed at the sample just below the AFM tip. This will create photo-induced forces at the tip-sample interface, which is the second part of the IR-PiFM signal with which the chemical composition can be determined. These photo-induced forces are shown in the top right of Figure 14, which are translated into the spectrum shown in the same figure. The peaks in this spectrum correspond to individual function groups. By using a database and an algorithm, these functional groups can be allocated to different molecules, or polymers in this case. After determining a percentage match of the sample with the database, the polymer can be identified, which, in the case of Figure 14, was polyurethane (PU). With IR-PiFM, individual micro- and nanoplastics can be accurately analysed. Although analysis will be quite time-consuming, the sensitivity and observation size limit of this method will make it stand out compared to FTIR for example.

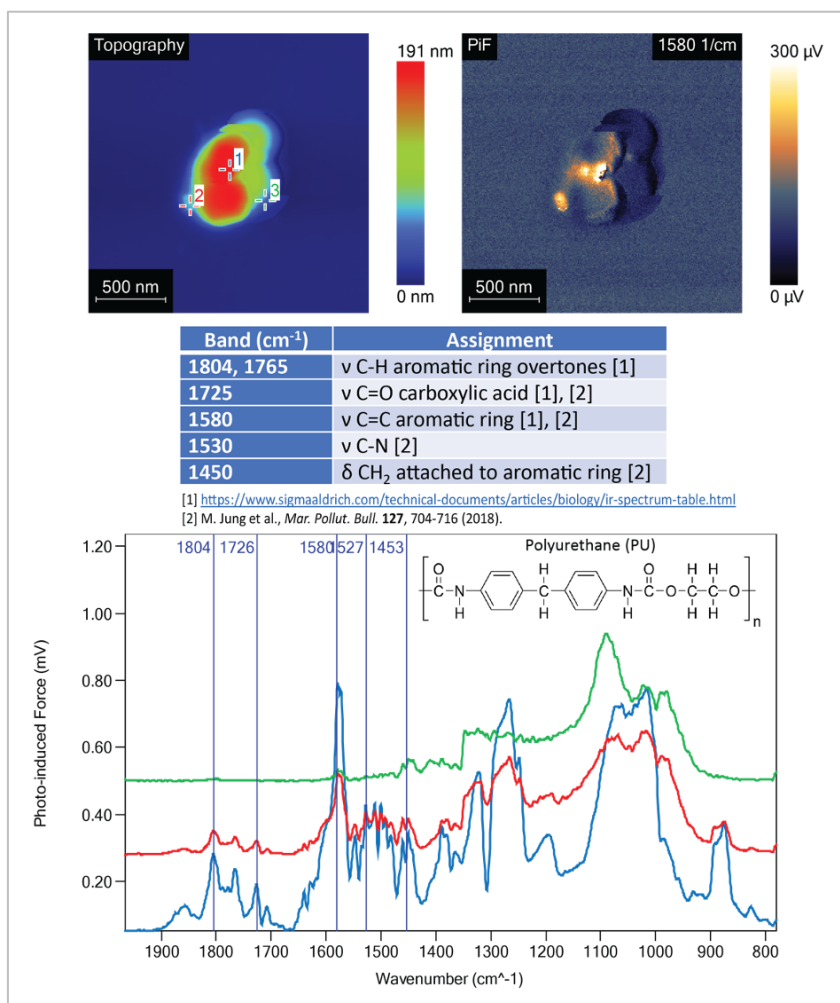


Figure 14: IR-PiFM output image for a polyurethane (PU) particle. Shown top left is the topography image, shown top right are the photo-induced forces that are measured. The peaks in the spectrum correspond to different functional groups of the PU molecule in the sample.

4. PRELIMINARY SAMPLING AND ANALYSIS OF MICRO- AND NANOPLASTICS

4.1 Sampling in a 3D-printer room

In a small experiment, we wanted to test the suitability of the cascade impactor for atmospheric micro- and nanoplastic research. Firstly, we needed to find a reliable source of micro- and nanoplastics. In the introduction we already mentioned the formation of secondary micro- and nanoplastics from machine washing and drying of clothing and through tire abrasion. Since it was not possible for us to sample in a laundry room or near a road at the time, we looked at other in-house options for our experiment. We found another department that has a room with 3D-printers (*Ultimaker S3*), in which we were allowed to sample. These 3D-printers work by heating and melting the plastic, or **filament**, of choice and extruding it through a nozzle onto the print surface. It has been shown in several studies that extrusion type 3D-printers emit fine and ultrafine particles and compounds. These emissions usually arise when the filament is heated to a semi-molten state before it is deposited on the print surface.

During the heating process, particles and so-called **volatile organic compounds** (VOCs) are released (*Zhang et al., 2017*). VOCs are a large group of carbon-based compounds which have a high vapor pressure, which basically means that they easily evaporated. They are usually emitted as gases from liquids or solids, such as certain types of paint, cleaning agents, glues, and even cosmetics (*US Environmental Protection Agency, 2020*). In certain concentrations they can be harmful to humans, which is another concern when investigating 3D-printers, but not the aim of our pilot study. In this case we are more interested in the particles released during the 3D-printing process. It has been well-documented that 3D-printers actually emit significant amounts of particles, which are mostly in the lowest size-ranges of < 100 nm (*Kim et al., 2015; Zhang et al., 2017; Azimi et al., 2016; Gu et al., 2019*). Thus, it is evident that 3D-printers are indeed a source of nanoparticles and that we would be able to sample nanoparticles and possibly even nanoplastics with the cascade-impactor. Therefore, we proceeded with our plan to start an experiment in the 3D-printer room.

4.2 Experimental procedures and setup

We selected a 3D-printer room inside one of our own University's buildings. The room was occasionally occupied with several students and staff members, but they were asked not to get in the vicinity of the experimental setup. We used an Ultimaker S3 3D-printer for this experiment and used polylactic acid (PLA) as the filament to print the object. We programmed the 3D-printer to print an object that required the extrusion tip of the printer to move around over a large area, hoping we would get as much micro- and nanoplastic formation as possible. The impactor was placed adjacent to the 3D-printer at a distance of 1 m, measuring the direct release of micro- and nanoplastics of the 3D-printer (*Figure 4-1*). Each stage in the impactor, as well as the back-up filter, was loaded with clean quartz fibre filters (*Pall Life Sciences*). During the experiments, we also used multiple air quality monitors (*Dylos DC1700 AQMs*), which are able to detect particles present in the atmosphere in time intervals and gave us an overview of contamination levels in the room at any given moment. We used these air quality monitors as a quality control check to see whether the contamination in the 3D-printer room was different between the two experiments.

The air around the 3D-printer was sampled twice; one time when the 3D-printer was operating and printing an object and one time when the 3D-printer was off. This way we could assess the release of micro- and nanoplastics from the 3D-printer itself by comparing the background contamination of the second experiment with the first experiment. Sampling times were similar in both cases (about 10.5 hours). A standalone LCP5 vacuum pump from (*Copley Scientific*) was used in combination with the cascade impactor to sample the air. Flow rate was set at 100 ± 0.1 L/min to comply with the calibration of the cascade impactor, thus sampling about 63 m³ of air both times. Afterwards, we wanted to do a

preliminary analysis before we further analysed our samples, and thus determined the total carbon (TC) content on the quartz fibre filters from both samplings. This analysis was done with a SUNSET analyser (*Sunset Laboratory Inc.*), which is an instrument that is used in aerosol organic carbon (OC) and elemental carbon (EC) analysis. By combining the OC and EC signals of the SUNSET we obtained the TC concentrations on the filters. An equally sized sub-sample was taken from each of the filters for the analysis.

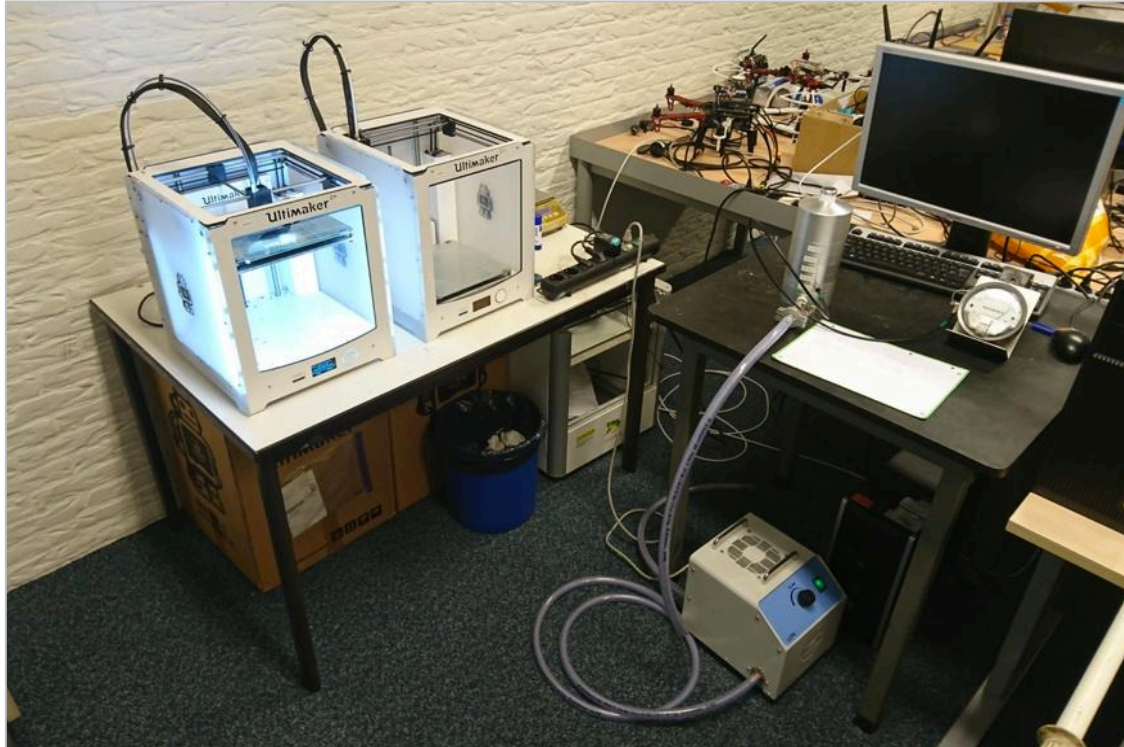


Figure 15: Experimental setup in the 3D-printer room. From left to right, the 3D-printer, the cascade impactor and vacuum pump.

Care was taken to work as cleanly as possible. The cascade impactor parts were cleaned several times before the experiment using acetone and rinsing and wiping off with 99% alcohol and lint-free paper towels afterwards. If needed, all components of the impactor were cleaned in an ultrasonic water bath, which is necessary to clean all the jets of the cascade impactor stages thoroughly. Before installing the filters on the impactor plates, the jets of each of the stages were blown through with compressed air a final time to prevent blockage of the jets. The quartz fibre filters were cleaned with a standardized protocol, in which they were burned clean for 2.5 hours in a 600 degrees Celsius oven. Afterwards, the clean filters were put in clean (and pre-baked) aluminium foil packets and stored in a freezer at -18 degrees Celsius awaiting further use. The filters were always installed in the cascade impactor inside a fume hood to prevent dust contamination. Samples were stored in clean (and pre-baked) aluminium foil packets and stored in the freezer again at -18 degrees Celsius, right until they were analysed.

4.3 Results

During both sampling experiments, we sampled the atmosphere in the 3D-printer room for about 10.5 hours. With the calibration and flow rate of the cascade impactor at 100 ± 0.1 L/min, this translates into a total of 63 m³ of air sampled. A quick visual inspection before the filters were stored confirmed that the cascade impactor did indeed sample particles in all of the stages in both experiments. Analysis with the SUNSET analyser gave us the TC concentrations on all the filters. In the bigger size ranges (0.25-0.44, 0.44-0.77, 0.77-1.44, 1.44-2.5, and > 2.5 μ m) there were no significant differences found between the 3D-printer ON and OFF experiments, which is what we expected from our literature

research about 3D-printer particle formation. Only the final stage, which was the back-up filter ($< 0.25 \mu\text{m}$), we found an almost three times higher concentration in the 3D-printer ON experiment compared with the OFF experiment (Figure 4-2), indicating that particle release from 3D-printers in this size range is significant. Since our sample size is very small, we did not run any statistical analysis, since that requires more samples and repetitions. However, this difference is still quite significant, especially when compared to the other size ranges. For the quality control of our experiments, we examined the data from the Dylos AQMs. We found no differences in air quality between the 3D-printer ON and OFF experiments. The small and insignificant decrease in air quality we did find in the data when the 3D-printer was running was not likely due to the release of fine particles from the 3D-printer itself, since the Dylos AQM only measures particles down to 500 nm. Thus, we concluded that the air quality on both sampling days was similar and had no influence on our experiment.

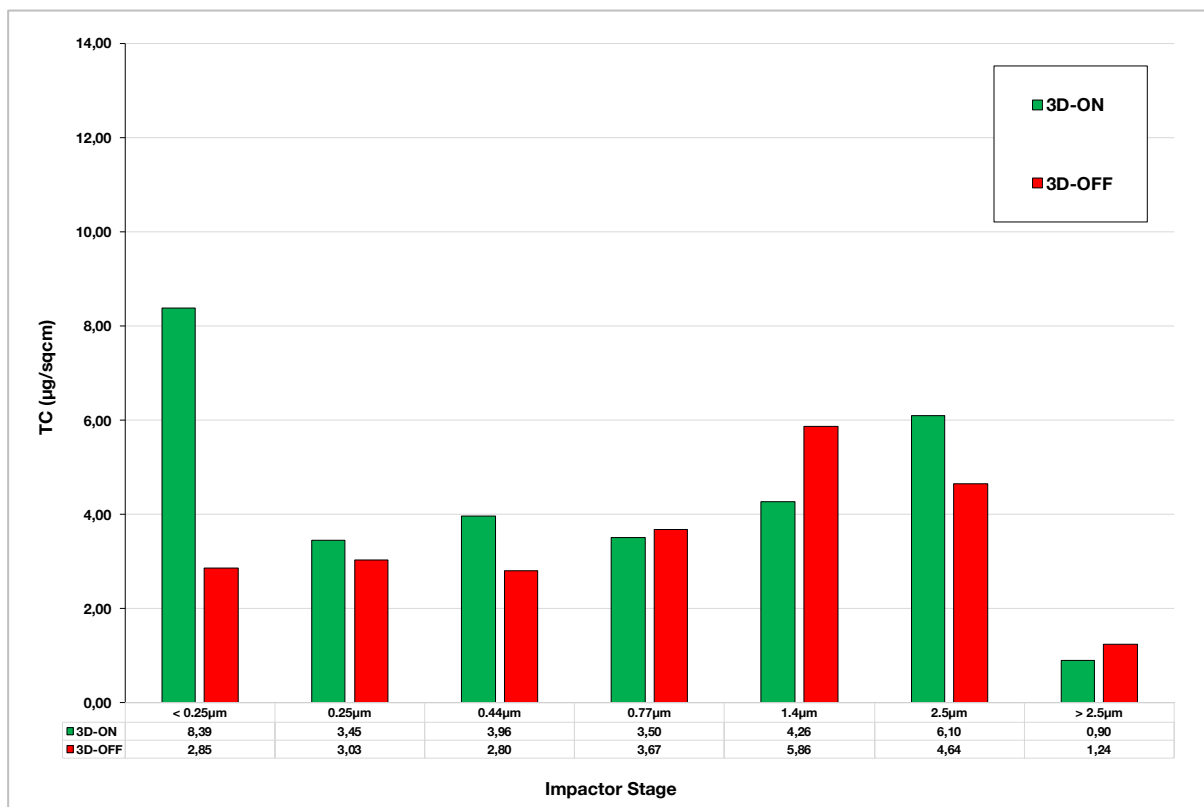


Figure 16: The measured TC concentrations in the samples from both experiments as measured with the SUNSET OC/EC analyser. Data from the ON-situation in shown green and the OFF-situation in red.

5. DISCUSSION AND CONCLUSION

5.1 Limitations of experiments

The results of the experiments clearly showed one clear difference. On the back-up filter ($< 0.25 \mu\text{m}$) we found almost three times higher TC concentrations when the 3D-printer was turned on compared to when it was turned off ($8.39 \mu\text{g}/\text{cm}^2$ compared to $2.85 \mu\text{g}/\text{cm}^2$). This translated to TC concentrations of $5.88 \mu\text{g}/\text{m}^3$ and $2.00 \mu\text{g}/\text{m}^3$. This result indicates that 3D-printers indeed release a significant number of nanoparticles, which was also shown and explained in section 4.1 of the previous chapter. This also means that a 3D-printer is likely a good source for nanoparticles in further testing with the cascade impactor. However, as mentioned before, we only sampled once for each situation (ON and OFF) and thus the sample size is quite small to get to any meaningful conclusions. Since the sample size was so small, statistical tests were also not performed. Therefore, more tests should be performed to prove that a cascade impactor can consistently sample nanoparticles in a 3D-printer room.

Regarding the experiments themselves, there are quite a few limitations. First of all, during both the ON and OFF experiments, the top impaction plate in the cascade impactor was covered by a protective, aluminium cover. Thus, the top impaction plate, and therefore the quartz fibre filter on it, was not exposed to any particles during both experiments. It is quite obvious that the results were influenced by this mistake, since there was almost no carbon present on the top impaction plates (**Figure 16**). However, since the top impactor plate is only used to get rid of the very largest particles, we think this did not influence the results of the experiment. Upon further inspection, the protective cover did not restrict the airflow in any way; particles were still able to pass through to the lower stages. However, since the protective cover is not aerodynamically shaped it could have disturbed the airflow, causing a turbulent airflow instead of the usual laminar airflow which may have influenced the results. Lastly, particles that should have impacted on the top impaction plate likely bounced off the protective cover, again, influencing the results in the lower stages. Ideally, both experiments should be repeated for more accurate results.

As explained before, the TC concentrations resulting from the SUNSET analysis do not reflect the number of micro- and nanoplastics particles sampled with the cascade impactor. We rather used the data as a preliminary analysis to confirm particle release by the 3D-printer for further experiments and further analysis with the TD-PTR-MS and IR-PiFM. By comparing the TC concentrations from the ON and OFF experiments, we could determine whether it was worth to use the 3D-printer for further experiments with the cascade impactor. In the OFF-experiment, we measured the background contamination in the 3D-printer room, whereas in the ON-experiment, we measured the particles released by the 3D-printer plus the background contamination. However, both experiments were performed on different days. Thus, there are many variables that could have influenced the results of the experiments.

First of all, the 3D-printer was situated in a computer room with unrestricted access of students and other staff members of the faculty (**Figure 15**). Depending on their movements in the room or around the cascade impactor, more or fewer particles could have been sampled in the cascade impactor. Thus, it could be that the TC concentrations were influenced, even though they were asked to keep their distance from the experimental setup. In a similar way, the air filtration system could have had an impact on the results. In this particular building and computer room, the air filtration system is poor and not constant at all. Thus, it could be that on one day it was working better than the other day, thereby influencing the results. Temperature and humidity differences on both days could also have impacted particle formation in and around the 3D-printer. In the future, the experiment should be done in a closed, restricted room or box to make sure the impactor only captures the particles from the 3D-printer.

Finally, for future sampling near a 3D-printer, another type of filament should be used. In our experiments we used the filament PLA, which is a biobased plastic made from either sugar beets or corn. We did not consider which type of filament to use before we performed the experiments with the cascade impactor. Since our department does not own the 3D-printer, we did not have an influence on the filament used for the print job. In hindsight, this turned out to be quite a limitation. Upon heating of PLA, there is a noticeable smell which indicates particle release to the air. However, in literature it is described that the heating of PLA by a 3D-printer does not release a significant number of nanosized particles compared to other types of filaments (Kim *et al.*, 2015), since the main constituent of PLA is the naturally occurring lactic acid. Other types of filaments, like the most commonly used ABS, were shown to release significantly more nanosized particles, which include acrylonitrile and styrene (Kim *et al.*, 2015). Thus, repeating the experiment with another type of filament could have resulted in more clear results.

5.2 Uncertainties

This thesis highlights the use of a cascade impactor to simultaneously sample atmospheric micro- and nanoplastics in a single experiment. It was pointed out that the separation of particles based on their diameter is the main advantage over previous sampling methods and devices. By separating particles during sampling stage, analysis will be more efficient due to the reduced contamination of other particles in the sample. Particle separation during sampling has been done previously (as shown before by Abbassi *et al.*, 2017), but researchers have not been able to accurately sample nanosized particles yet. Almost all studies that were discussed in this paper highlighted that small microplastics and nanoplastics are likely present in all samples. This could however not be proven due to the absence of adequate analysis techniques and the contamination of samples with larger particles.

Using the cascade impactor for sampling atmospheric micro- and nanoplastics would therefore be a good alternative to existing methods. Besides sampling in a 3D-printer room we also wanted to sample in a laundry room, in which plastic fibres can be released to the air by washing and drying machines. In aerosol research the cascade impactor is mostly used to sample compact particles. However, many of the discussed studies focused on atmospheric synthetic fibres, which are the most predominant type in air samples when compared with plastic particles. Thus, to assess whether the cascade impactor is suitable for micro- and nanoplastics research, the sampling of synthetic fibres should also be tested. In the study by Abbassi *et al.* (2017), the design of their air sampler prevented the accurate sampling of fibres. This sampling depended heavily on the orientation of the fibres with respect to the inlet of the air sampler. This could also be the case with the cascade impactor. However, the airflow in the cascade impactor is laminar and this theoretically increases the chance of correct alignment of the fibres with respect to the jets in the impactor. Still, this remains quite uncertain since we were not able to test this.

Another uncertainty concerns the analysis of micro- and nanoplastics with the IR-PiFM method. For an accurate IR-PiFM analysis, the particles should be sampled on a surface as flat as possible (Holzinger, *Personal communication*, May 2020). In our first experiments, we used the quartz fibre filters to sample particles. These samples can easily be cut and analysed with the TD-PTR-MS. However, the surface of quartz fibre filters does not meet the requirements for analysis with IR-PiFM. During the experiments, we worked together with a team at Utrecht University that sent us silicon wafers for the analysis of particles with IR-PiFM. While testing, we found out that the silicon wafers (Siegert Wafer, J12007) are suitable for impaction sampling in a cascade impactor. However, due to the smooth and flat surface of the silicon wafers, micro- and nanoplastics are likely to bounce off, which is usually a limitation of impaction sampling (Hinds, 1999). Therefore, separation of particles could become inaccurate, which also reduces the accuracy of the final results. Particle bounce on the silicon wafers has not been tested yet, but we imagine it could be a limitation while sampling micro- and nanoplastics. In addition, these silicon wafers can also not be used in the final back-up filter of the cascade impactor.

Regular quartz fibre filters allow air to pass through, allowing the vacuum pump to pump air through the cascade impactor. Placing a silicon wafer in this final stage of the impactor would restrict air from being pumped through, thus preventing a correct operation of the cascade impactor. Particles < 0.25 µm can therefore not be sampled, which is the opposite of what we want to achieve with the cascade impactor in this field of research. In conclusion, for analysis with IR-PiFM the sampling with the cascade impactor should be carried out with filters that have a smooth and flat surface and that allow air to pass through. The possibilities for such a filter have not been researched at the time of writing.

5.3 Conclusion and future research

In the current society, pollution of the environment is a serious problem that is becoming more and more evident. The pile of plastic waste on landfills around the world is growing by the day, and policymakers have still found no adequate solutions to deal with the problem. Plastics are easily transported into the environment, which has caused phenomena like the Great Pacific garbage patch for example. It was shown that micro- and nanoplastics are formed from larger plastics through fragmentation and degradation under the influence of sunlight (UV-light) or mechanical forces (waves or wind). In this thesis and through the references therein, it was pointed out that these micro- and nanoplastics are easily transported through the environment due to their small size, which also means they remain undetected in most cases. There is increasing evidence that exposure to micro- and nanoplastics through ingestion, inhalation and dermal contact can be harmful to humans and animals alike, potentially giving rise to lung diseases or even cancer related symptoms. Thus, there is increasing concern about micro- and nanoplastics ending up in the environment, which resulted in a new field of research.

It has become increasingly important to study the sources, pathways and receptors of micro- and nanoplastics. Previous research efforts have done exactly that. However, the research efforts have not been divided equally amongst the different environmental compartments. Till date, micro- and nanoplastics in the aerial environment have been studied the least. In addition, we pointed out that research methods, including sampling and analysis, are not adequate in the context of atmospheric micro- and nanoplastics. Furthermore, it is difficult to compare studies since there are not standardized research protocols in the field. Thus, there is a need for improved sampling and analysis techniques. This literature review gave an overview of the current research in the field of atmospheric micro- and nanoplastics, while also trying to answer the main question **“How can we improve research of atmospheric micro- and nanoplastics?”**. Four different sub-questions were answered, each in their respective chapter:

- 1) What is the *status quo* of the research into atmospheric micro- and nanoplastics?
- 2) Which sampling and analytical procedures are currently used and available, and what are their advantages and disadvantages in the context of micro- and nanoplastics?
- 3) How can we improve on existing sampling and analytical procedures and what would be the best alternative with current technologies?
- 4) Can we sample atmospheric micro- and nanoplastics using a novel sampling protocol?

We answered the first question by providing a chronological overview of the previous studies in the field of atmospheric micro- and nanoplastics. The pioneer in this field is the research group surrounding *R. Dris*, who at the time was working at the *Université Paris-Est*. In their first large scale experiment (*Dris et al., 2017*) they provided an excellent and thorough overview of indoor and outdoor microplastic concentrations. Other research groups soon followed their study, which increased the release of research papers every year since then. Until now, there are three ways to study atmospheric

micro- and nanoplastics: by sampling the air, the atmospheric fallout, or via dust collection. Large or small cities seem to be the main source of atmospheric plastics, after which the plastics are transported to surrounding environments. Long-range transport has not been proven yet, although some findings indicate that it is indeed possible for micro- and nanoplastics to be transported to remote areas. From this, it follows that micro- and nanoplastics are horizontally distributed, with higher concentrations in densely populated areas compared to rural areas. Vertical distribution could not be proven yet, although a dilution effect is expected to occur at larger altitudes. It was also shown that atmospheric plastics are largely fibrous. However, due to current detection size limits, there is still a possibility that nanoplastic particles are the most abundant in the atmosphere. There are a few factors that influence micro- and nanoplastics in the atmosphere, like precipitation events, wind speed, temperature, humidity, or human and industrial activity. Still, there are still some uncertainties regarding these factors; uncertainties that will disappear when more research is performed on the subject.

In the second chapter, we addressed the second sub-question by explaining the details of the currently used sampling and analysis methods. Sampling and analysis have not been adequate and has not been standardized yet. When it comes to sampling micro- and nanoplastics, there are three main methods, corresponding to the three ways to study atmospheric plastics. Air samples, both indoors and outdoors, are taken with a stand-alone vacuum pump. Such a device will pump air through a filter, thereby leaving the particles in the air on the filter. Atmospheric fallout can be collected through dry and wet deposition, by passively collecting particles in a funnel attached to a bottle or beaker. Dust samples are simply collected with the help of an anti-static brush. We briefly reviewed the treatment procedure of samples, in which the samples are usually pre-treated (filtration), separated for density (flotation method), and rinsed. In addition, some studies also treated their samples with a Nile Red dye to aid analysis.

In the analysis step we broadly defined two stages, which are the identification and quantification of particles and the chemical characterisation. It is important to distinguish plastic particles from other (in)organic particles to make the quantification more accurate. Furthermore, visual identification is also used to determine characteristics like colour or shape of the particles. Quantification is important, because the number of particles per unit volume of air, water, or dust will provide information on the concentration of micro- and nanoplastics. Chemical characterisation is used to examine the polymer composition of a plastic particle. By determining the polymer type, researchers can roughly determine from where the micro- or nanoplastic particles originate from and potentially from which product type they are.

At the moment, the visual identification is mostly done with different types of microscopy, among which regular or binocular microscopy is by far the most used type. Fluorescence microscopy in combination with Nile Red staining has also been used several times. However, these techniques all fall short. Even with a high-quality microscope, visual identification of small microplastics is difficult and inaccurate. For accurate visual identification the detection limit is around 500 μm , thus nanoplastics are not even considered here. There is a high potential of false positives, even when analysis is aided by a Nile Red staining. The use of SEM would be better suited to analyse micro- and nanoplastics. However, the laborious and time-consuming process makes it not suitable for standardized methods. Still, visual identification with microscopy is a useful pre-analysis step, before a more thorough analysis of particles with other techniques. In addition, it is also the only method thus far that has been used to quantify microplastics. Mass spectrometry techniques could be a promising alternative for quantifying micro- and nanoplastics. When it comes to chemical characterisation of micro- and nanoplastics, spectroscopy techniques are the most commonly used. With atmospheric plastics FTIR and Raman spectroscopy stand out, of which the former is used the most, likely due to its widespread use in aquatic microplastic research. However, while these techniques are excellent to characterise microplastics, the detection size limit prevents the analysis of nanoplastics. Thus, other techniques are needed for a more thorough analysis of atmospheric plastics.

The issues with current sampling methods could be solved by using a cascade impactor, which samples high volumes of air and can separate particles into size classes during sampling. In addition, nanoplastics could potentially be sampled in the lowest stages of the cascade impactor. Whilst this results in more samples that should be analysed, the separation of particles makes it easier to distinguish them. Furthermore, size distributions are automatically created by the design of the impactor. Using the cascade impactor with quartz fibre filters makes it compatible for analysis with the mass spectrometry method TD-PTR-MS. It was shown that this technique has a higher sensitivity than other mass spectrometry techniques, making it suitable for accurate characterisation and quantification of micro- and nanoplastics. However, the analysis provides no information about sizes and shapes of particles. Therefore, we propose a combination of TD-PTR-MS with IR-PiFM, an infrared microscopy technique that is able to image the topography and the chemical composition of particles in the nanosized range. This tandem should provide researchers with the atmospheric micro- and nanoplastic concentrations that are important to assess human exposure and environmental burden, as well as the particle characteristics and chemical composition of micro- and nanoplastics to assess degradation, weathering, and possible sources.

In the final chapter, we went ahead and tested the cascade impactor in a small-scale experiment. A 3D-printer was used as a source for micro- and nanoplastic particles, which we sampled on quartz fibre filters. Since the TD-PTR-MS and IR-PiFM were not accessible to us due to COVID-19 restrictions, we did a preliminary analysis of the samples by measuring the TC concentrations. While indirectly, the results indicated that a cascade impactor is indeed suitable for sampling of micro- and nanoplastics. However, the experiments had a few limitations, and the sample size was too small. Therefore, more experiments have to be done to prove the suitability of the cascade impactor in a standardized protocol for atmospheric micro- and nanoplastics. In addition, the TD-PTR-MS and IR-PiFM have to be tested as well. This review has tried to put forward the current issues in the field of atmospheric micro- and nanoplastic research by providing an overview of the previous research, the advantages and disadvantages of currently used sampling and analysis methods. In addition, a new sampling method and analysis tandem of atmospheric plastics has been proposed, which should help researchers find out more about micro- and nanoplastics in general. By writing this review I hope that the accuracy and comparability of future research of atmospheric plastics improves, which ultimately helps to once and for all eradicate the problem of micro- and nanoplastics in the environment.

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