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MASTER THESIS IN ENVIRONMENTAL GEOLOGY AND EARTH DYNAMICS

MICROPLASTIC DISTRIBUTION IN SEDIMENTS ALONG THE COURSE OF ARNO RIVER (ITALY)

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DEDICATION

To the unexpected adventures

and the family and friends made along the way.

“The one thing that doesn't abide by majority rule is a person's conscience.”

Harper Lee

Abstract

Microplastics are defined as plastic pieces that are less than five millimetres long. They originate from the breakdown of larger plastic wastes, forming secondary microplastics, or can be from primary sources, such as industries that expel microplastic pellets. They pose a huge threat to several ecosystems; however, the majority of the research so far has mostly been done on marine environments. Some studies are emerging on the terrestrial side of things, especially rivers, but much is yet to be understood.

To understand more about the behaviour of microplastics in rivers, we collected 27 sediment samples across the 241 km-long Arno River, in central Italy. The sediments were deposited along the river during a flooding event in mid-February 2024 which caused a rise in the water level of about 2.5 meters in the central part of the river reach (i.e. 150 km from the mouth). The idea was to understand the variation of microplastic content in sediments deposited in the same sedimentary facies throughout the river and understand the influence of definite features like the occurrence of dams, major towns and cities and lateral tributary rivers.

Microplastics were found in all 27 samples along the river, with an average microplastic concentration of 1963.4 MPs per kg. We notice that the upstream reach of the river is more polluted than the downstream if we consider its extremely reduced size. Our study shows that the effect of dams on the microplastic abundances upstream and downstream is not so obvious. One dam shows an increase in microplastics downstream while the other reduces the microplastic concentration. The major cities of Florence and Pisa inject a large amount of microplastics into the Arno River, whereas the occurrence of other important towns seems to have a minimum or null impact on microplastic content. A similar complex trend has been detected also for tributaries. The entrance of tributaries like the Elsa and Bisenzio create significant spikes, whereas Sieve and Ombrone create dips in the microplastic concentration, although all these rivers drain similar populated and anthropized areas. Their results are quite contrary to what the general assumption that microplastic contamination is correlated to population and human activities and that their concentration should increase moving downstream along a river that crosses populated anthropized areas. Our study suggests that other very local factors, such as localized

hydrodynamics of water flows, could be at play and we cannot make a general model for microplastic behaviour in rivers without investigating the role of local variables.

Rissaunto

Le microplastiche sono definite come frammenti di plastica di dimensioni inferiori ai cinque millimetri. Derivano dalla degradazione di rifiuti plastici più grandi, formando microplastiche secondarie, oppure possono provenire da fonti primarie, come le industrie che emettono pellet di microplastica. Rappresentano una grande minaccia per diversi ecosistemi; tuttavia, la maggior parte delle ricerche finora si è concentrata principalmente sugli ambienti marini. Alcuni studi stanno emergendo sul versante terrestre, in particolare sui fiumi, ma molto deve ancora essere compreso.

Per comprendere meglio il comportamento delle microplastiche nei fiumi, abbiamo raccolto 27 campioni di sedimenti lungo i 241 km del fiume Arno, nell'Italia centrale. I sedimenti sono stati depositati lungo il fiume durante un evento di piena a metà febbraio 2024, che ha causato un innalzamento del livello dell'acqua di circa 2,5 metri nella parte centrale del tratto fluviale (cioè a 150 km dalla foce). L'idea era di comprendere la variazione del contenuto di microplastiche nei sedimenti depositati nelle stesse facies sedimentarie lungo tutto il fiume e di analizzare l'influenza di elementi specifici, come la presenza di dighe, grandi città e affluenti laterali.

Le microplastiche sono state trovate in tutti i 27 campioni lungo il fiume, con una concentrazione media di 1963,4 MP per kg. Notiamo che il tratto a monte del fiume è più inquinato di quello a valle, considerando la sua dimensione estremamente ridotta. Il nostro studio mostra che l'effetto delle dighe sulla quantità di microplastiche a monte e a valle non è così ovvio. Una diga mostra un aumento delle microplastiche a valle, mentre un'altra riduce la concentrazione di microplastiche. Le grandi città di Firenze e Pisa immettono una grande quantità di microplastiche nel fiume Arno, mentre la presenza di altre città importanti sembra avere un impatto minimo o nullo sul contenuto di microplastiche. Un andamento complesso simile è stato rilevato anche per gli affluenti. L'ingresso di affluenti come l'Elsa e il Bisenzio crea picchi significativi, mentre il Sieve e l'Ombrone causano una diminuzione nella concentrazione di microplastiche, nonostante tutti questi fiumi drenino aree popolate e antropizzate in modo simile. I loro risultati sono piuttosto contrari all'assunto generale secondo cui la contaminazione da microplastiche è correlata alla popolazione e alle attività umane e che la loro concentrazione dovrebbe aumentare procedendo verso valle lungo un fiume che attraversa aree popolate e

antropizzate. Il nostro studio suggerisce che altri fattori molto locali, come l'idrodinamica localizzata dei flussi d'acqua, potrebbero essere in gioco e non possiamo formulare un modello generale per il comportamento delle microplastiche nei fiumi senza indagare il ruolo delle variabili locali.

Content

1 Introduction

Plastics have gained traction in human society since the early 20th century. These are synthetic polymers that can be used as a substitute for natural materials such as silk, rubber, and other natural materials that are becoming hard to produce in high quantities due to increased demand from the exponentially growing world population. Plastics have several unique properties. They are light, non-conductive and corrosion resistant. These unique properties of plastics helped make several technical and medical advancements.

The industrial production of plastics began right after the Second World War and since the 1950s, global plastic production has continued to grow tremendously from 1.5 million tonnes in the 1950s to 368 million tonnes in the year 2019 (Plastic Europe, 2020). They became a part of almost every household due to their cheap production cost and ease of usability. In Italy, plastic production was 1.9 Mt in the year 2020 and saw a consumption of about 5.9 Mt of plastic consumption. This averages to about 98.6 Kgs per person (*Plastics in Italy*, 2022).

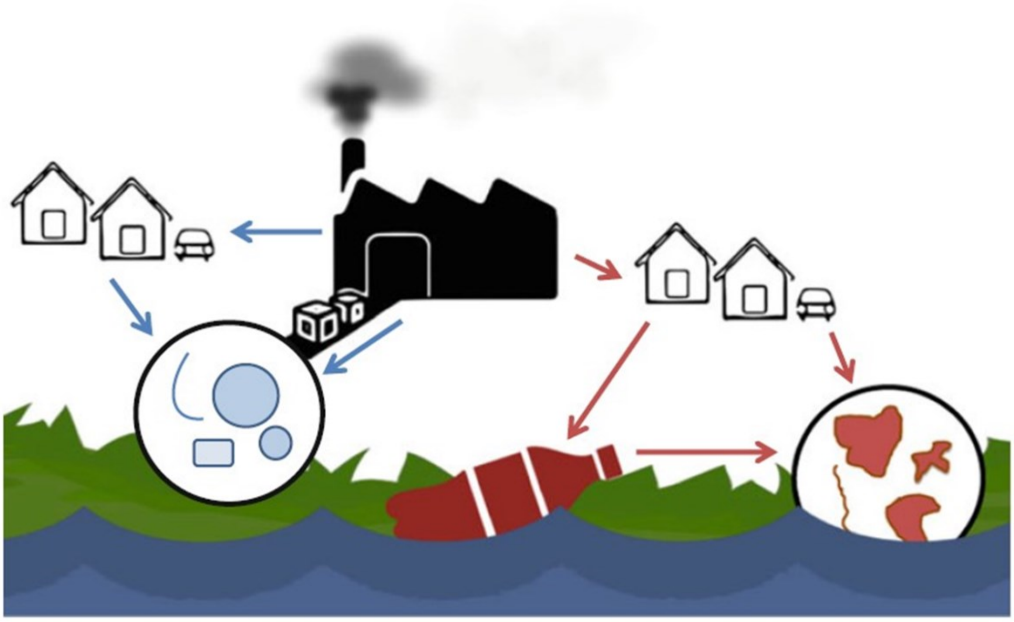


Figure 1:Microplastics can enter the environment from several pathways directly (blue arrows) or indirectly due to breakdown of larger plastic particles). (Wagner & Lambert, 2018)

Although it has been a boon to several industries and has helped transform human lives, plastics have also several downsides. Due to their non-degradable nature, it is exceedingly difficult to dispose of the plastic waste produced. Thus, plastics started to cause widespread pollution in many environments. Plastics can undergo mechanical breakdown and form smaller particles (<5mm) that we refer to as microplastics. They can stay persistent in almost any environment and continue to damage the biota for an exceptionally long time. Aside from the physical threats they pose to marine life, such as entanglement, drowning, inability to feed, or causing physical injury, the microplastics produced due to the degradation of these plastic waste materials can have more adverse effects on them. These microplastics, being similarly sized to planktons, can be ingested by planktivores, or ingested by other filter feeders, and become bioavailable. These can then cause a plethora of adverse effects in several organisms. For instance, they can accumulate in the digestive tracts of certain organisms and cause false satiation or gut blocking.

The first report on microplastics in marine systems was as early as 1972 (Dris et al., 2020). Since then, as the production and consumption of plastics have increased, so have the concerns about this form of pollution. However, the issue lacked interest from the scientific community for a long time until the next article to mention the term microplastic was published in 2004. Since then, there has been an increase in media attention to this issue, especially concerning the marine environment. (Qin, et al., 2020) showed that articles concerning microplastic research have also grown exponentially since 2004.

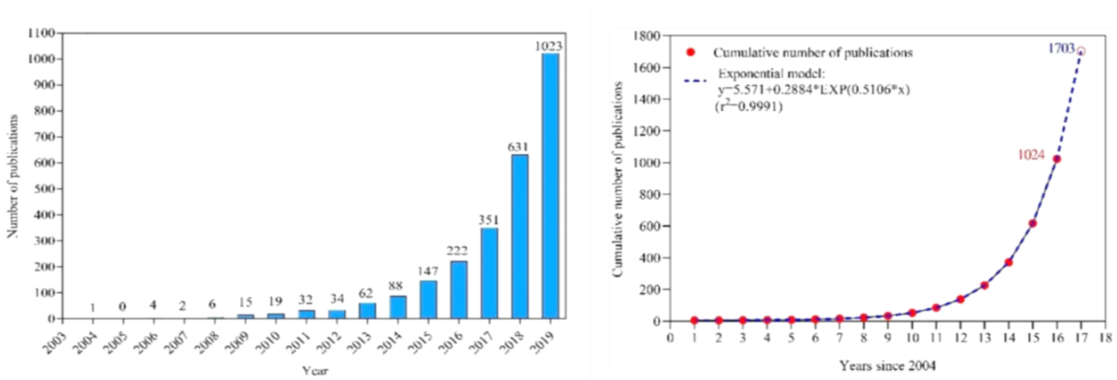


Figure 2: Histogram showing the number of publications about microplastics since 2004 (left), and an exponential fit to the number of publications each year (right). (Qin et al., 2020)

Microplastic pollution is present in marine, terrestrial as well as freshwater habitats globally. Marine plastic pollution is the most studied out of these and has given us a good insight into the matter. It is estimated that 4.8 to 12.7 million tonnes of plastic waste end up in the ocean annually (Jambeck et al., 2015). A large amount of plastic has already accumulated in the ocean and forms floating islands in the ocean gyres. The Great Pacific Garbage Patch in the North Pacific is among the most famous. It is known to cover an area of about 1.6 million km^2 and contains over 79 thousand tonnes of plastic waste. A recent study by (Kane & Clare, 2019) showed that these garbage patches eventually degrade into smaller pieces, forming microplastics, which get deposited into the abyssal plane. The transportation from the surface to the seafloor has been attributed to underwater currents carrying the suspended microplastic particles, or linked to ingestion by organisms, and their death and decomposition.

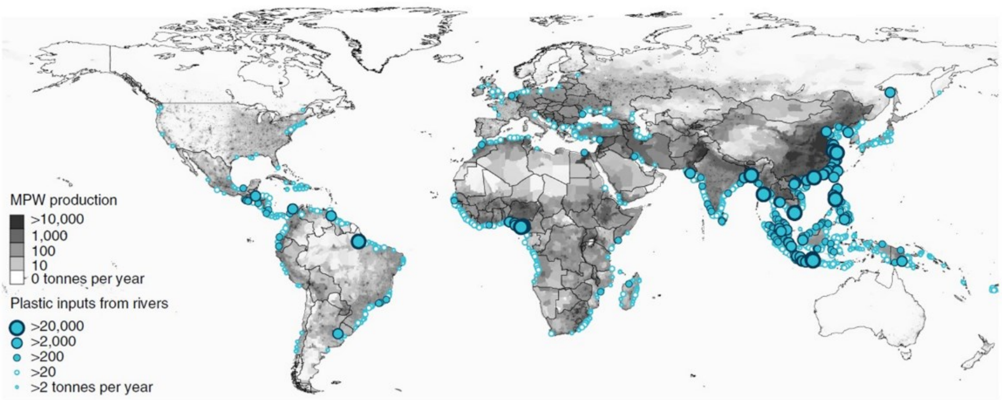


Figure 3: Mass of river microplastics flowing into the oceans in tonnes per year, and the mismanaged plastic waste production per country. (Lebreton et al., 2017)

On the terrestrial side of things, rivers are the major transporters of microplastics. They transport about 1.15 to 2.41 million tonnes of plastic waste into the ocean each year (Lebreton et al., 2017). They not only transport microplastics from the catchment to the seas but can also store them in the sediments they carry and deposit along the river. Microplastics in freshwater sources also pose a much higher threat to the local ecosystems as well as humans. Recently, several studies showed human consumption and the presence of microplastics in several body parts (Barrows et al., 2018; Corcoran et al., 2020; Dikareva & Simon, 2019; Du & Wang, 2021; Kunz et al., 2023).

Most of the past microplastic studies had mainly focused on marine environments while the freshwater environments, however, received little to no attention despite their severe implications. Recently, the studies related to microplastics in rivers have increased. The sources of microplastics in rivers include surface runoff from agricultural areas, aerial emissions, industries, and even wastewater treatment plants. Despite filtering out over 90% of the microplastics, wastewater treatment plants still contribute significantly to the microplastics in the fluvial systems (Horton et al., 2017; Laermanns et al., 2021). Studies show a correlation between the microplastic abundance in rivers with anthropogenic factors, such as land use and population. This was observed in several studies across Europe, Asia, and North America. A recent study on microplastics in rivers also showed the seasonality of river outputs of plastics into the ocean (Lebreton et al., 2017). The study suggests that there is a positive correlation between the monthly rainfall and the plastic output from the rivers in any region.

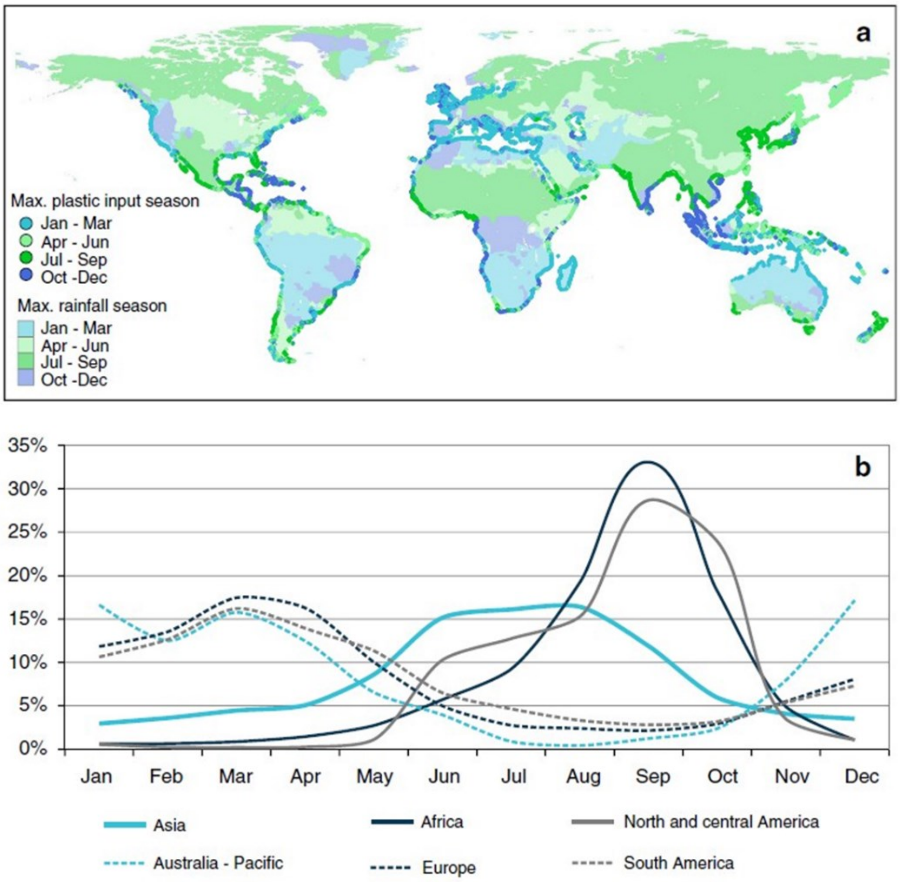


Figure 4: (a) Seasonality of regional inputs of river plastics to oceans and max rainfall season, suggesting a positive correlation between the two parameters. (b) A Plot of monthly plastic input from rivers into the sea, (Lebreton et al., 2017)

Although some broad patterns are emerging about the microplastics in terrestrial environments, much is yet to be known. There are several ambiguities related to land use patterns and microplastic abundance (Barrows et al., 2018; Corcoran et al., 2020; Kunz et al., 2023). Meanwhile, factors such as urbanization and industrialization in the river catchment have not been understood properly. It is widely accepted that the endpoint for microplastics is benthic sediments as they lose buoyancy and settle at the benthos over time. Yet very few studies have been done in this regard, especially for freshwater systems, particularly rivers.

Moreover, flooding events in rivers, when the rivers remobilize these low-density microplastics in the sediments are vastly ignored. To contribute to the understanding of these aspects of microplastic transport in rivers, we collected sediment samples from the Arno River. We then studied the presence of microplastics in these sediments which will help us map the distribution of microplastics along the river. We can further use these pieces of information to understand how different tributaries and dams, along with other anthropogenic factors, such as cities and factories contribute to the microplastic problem in the river. The study will also help us understand the distribution of microplastics in riverine systems as a function of sediment flux along the river course due to influx from its tributaries and the effects of manmade dams.

2 Study Area

The focus of this study is the Arno River, the 8th largest river in Italy and the principal stream of the Tuscany region in central Italy. The source of the river is close to Monte Falterona, in the Tuscan Apennines, at an elevation of 1385 m above mean sea level. The river passes through the Arezzo province, and some major historical cities like Florence and Pisa, travelling a total distance of about 241 km before entering the Tyrrhenian Sea at Marina di Pisa.

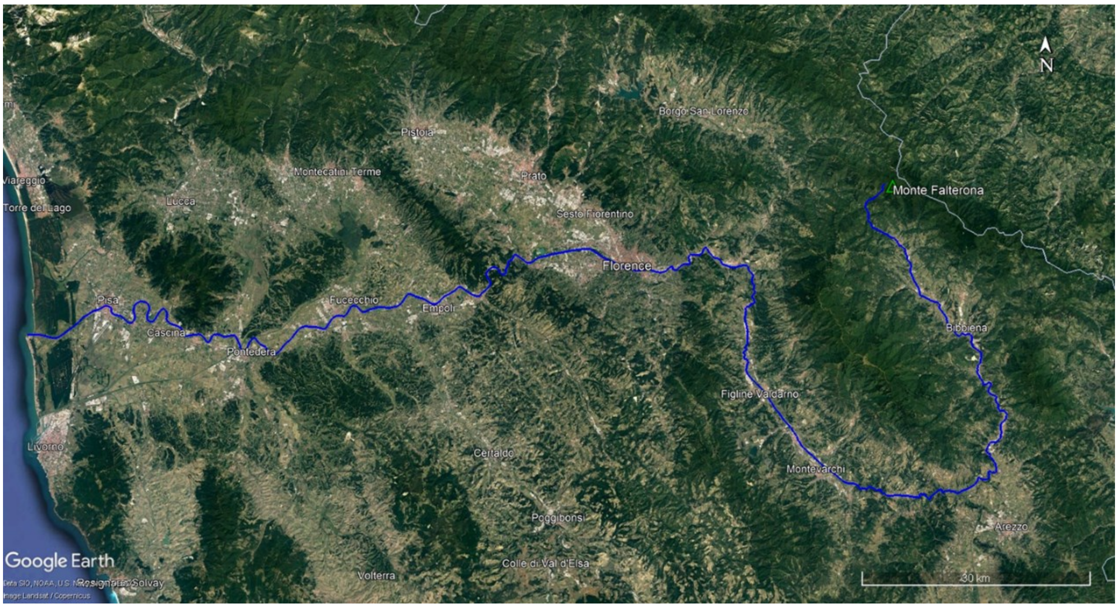


Figure 5: Satellite Imagery of Central Italy, showing the Arno River (marked in blue) and the major cities along its course. (source: Google Earth)

The river basin is rich in cultural and historical heritage. Florence, the capital of Tuscany, is renowned for its Renaissance art and architecture. Pisa, located at the mouth of the river, is famous for its leaning tower and medieval maritime history. The Arno River has been vital to the development of these cities and has played a crucial role in their historical narrative. The river has also been crucial for the region's agriculture, providing water for the cultivation of crops such as olives, grapes, and various vegetables. The Valdarno area, 40 km upstream of Florence, in the basin has been an important agricultural hub for centuries. Moreover, the river has historically supported industry and trade, particularly for Florence and Pisa, where it facilitated the transportation of goods.

The region experiences a Mediterranean climate, characterized by hot and dry summers, and mild and wet winters. During the summer, the average temperature is about 25 °C to 30 °C with low-lying areas around Florence and Pisa occasionally exceeding 35 degrees. The winter experiences an average temperature of about 5 °C to 10 °C in the plains with lower temperatures in the higher elevations. In some parts of the Apennines, the temperature drops below the freezing point, leading to occasional snowfall. The climate of the basin significantly affects the river's flow patterns. The summers are quite dry, this can lead to a much lower water level. This reduces the availability of water for agriculture and other uses. The winters, on the contrary, are wet. The region experiences very high rainfall, increasing the flow rate of the river significantly. Combined with the run-off from the Apennines, the water levels can rise rapidly, leading to severe floods. The river also carries a substantial amount of sediments, particularly during periods of high flow.

Arno is also very prone to floods and has a long history of significant flooding. The flood of 1966 was catastrophic and submerged Florence underwater. It caused the death of several people and caused extensive damage to buildings, along with several other cities along its path, including Pisa. It also damaged several priceless cultural heritage sites, artworks, and manuscripts.

The Arno River basin covers an area of about 8,830 km^2 and has an average altitude of 353 m above sea level. The hydrographic basin exhibits varied morphology, defined by a series of structural alignments forming the northern Apennines. The exposed rocks here are mostly sedimentary, primarily comprising calcareous and arenaceous flysches from the Oligocene and Miocene periods (Cencetti & Tacconi, 2005). Large intermontane basins are present between these ridges:

- Casentino
  The Casentino encompasses the upper basin of the Arno River, extending from its source to the confluence with the Chiana Canal. Covering an area of about 883 km^2, it is bordered by the spurs of the Apennines and the Pratomagno and is fed by numerous tributaries, all characterized by their torrential nature.

- Val di Chiana

The Val di Chiana covers an extensive 1,368 km^2 area that is predominantly flat. Formerly a marshland, it has been reclaimed in recent times and is now divided between the Arno and Tiber basins.

- Upper Valdarno

  The Upper Valdarno is a broad plain extending over 984 km^2. It is bordered on the right by the Pratomagno and the left by the modest reliefs of the Siena province. The Ambra torrent, which originates in this area, is the only major tributary in the entire sub-basin.

- Mugello

  It is also known as the Sieve sub-basin. Spanning 843 km^2, it is situated at the toe of the Apennine ridge. It is drained by the Sieve River.

- Middle Valdarno

  The Middle Valdarno (1383 km^2) begins downstream of Pontassieve. It consists of the sub-basins of the Bisenzio and Ombrone in the North and the Greve-Ema on the South of the river. The Arno-Ombrone confluence determines the closure of the basin.

- Lower Valdarno

  The Lower Valdarno is characterized on the right by a large, reclaimed plain (2776 km^2) which consists of the the Valdinievole – Padule di Fucecchio sub-basin and on the left by long valleys in which important tributaries such as the Pesa, the Elsa and the Era flow. It also constitutes large outcrops of marine clastic sediments, mainly sandy and clayey, and forms a hilly landscape with a lot of erosive forms.

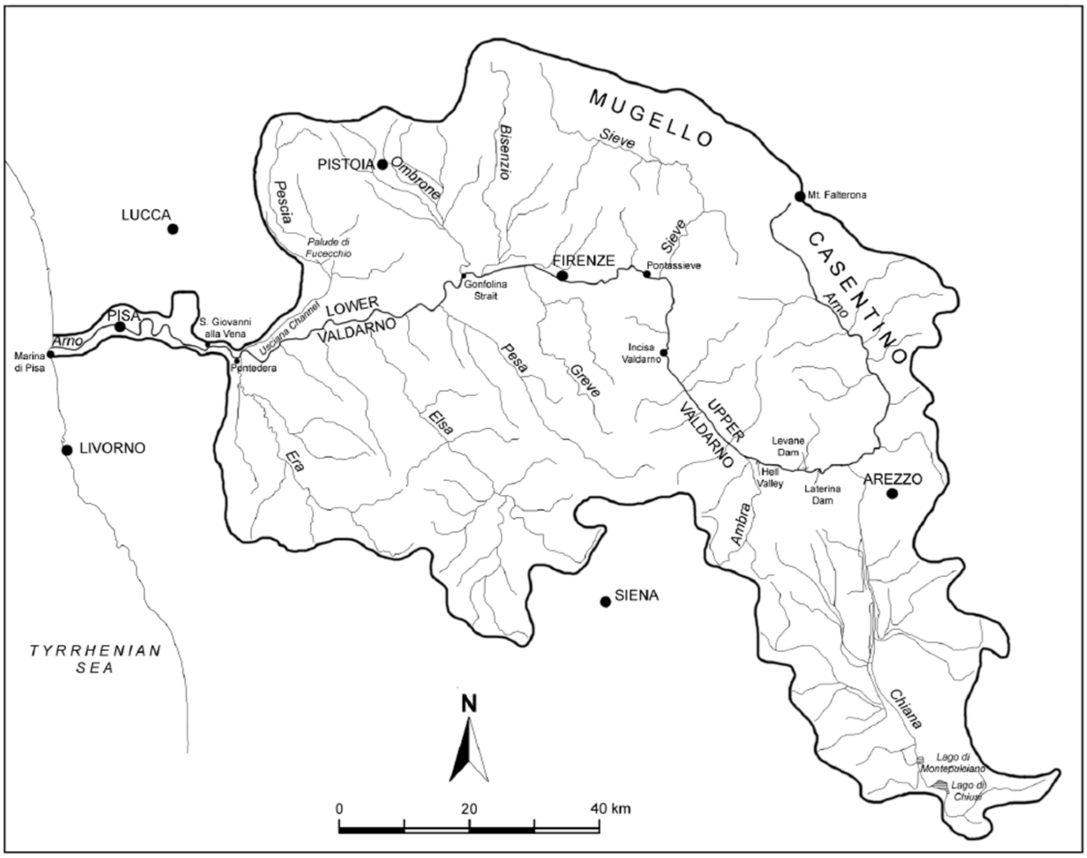


Figure 6: Hydrographic map of the Arno River basin, showing important features and major cities. (Cencetti & Tacconi, 2005)

These basins were occupied by swamps and poorly drained areas during the Pliocene and Pleistocene and have a stratigraphic series that consists of clastic sediments (conglomerate, sands, and clays) (Cencetti & Tacconi, 2005). They are separated by thresholds and narrow incisions such as Valle dell'Inferno (Hell's Valley), the threshold of Incisa Valdarno, and the Strait of Gonfolina.

The Arno River has several tributaries that contribute to its flow. The Sieve River is the main tributary of the Arno River. It drains the Mugello sub-basin and has many tributaries. It empties into the Arno just upstream of Florence. The Bisenzio River, which flows through the city of Prato has historical importance as it has supported the textile mills in Prato for centuries. Then we have the Ombrone that originates in the Pistoia Apennines and flows into Arno near Empoli, followed by Elsa, which runs through the provinces of Siena and Florence before merging into Arno near Castelfiorentino. Other tributaries like Era, Pesa, and Greve are also of historical or economic importance.

The Arno River's drainage basin has changed over geological timescales; however, the dynamics of the riverbed are much more short-lived due to the river's natural mobility and the impacts of human activities that have affected it since prehistoric times. (Cencetti & Tacconi, 2005).

A Historical Analysis of the Arno River (Cencetti & Tacconi, 2005) shows that in the past, the river was a mixture of braided and pseudo-meandering in the Casentino and Upper Valdarno regions. Moving downstream, it is suggested that the braiding index of the river kept increasing till the Florentine plain where the index was the highest. Passing the Gonfolina Strait, it assumed a form that can be associated with a lower ratio between bedload and total load. Following this, the river transitioned to a meandering form in the end, naturally being favored due to a weak gradient as well as fine sediments being injected by the Elsa and Era rivers, which primarily drain sandy-clayey terrains.

In the present times, however, the river has undergone significant changes due to its 'conditioning' by humans, altering it from its natural state. Considerable hydraulic works were carried out in the 18th and 19th centuries, that changed the form and hydro-morphological characteristics of the river significantly.

Several parts of the river have been subjected to regulatory projects aimed to facilitate navigation and prevent floods since the Middle Ages and the RenaissanceClick or tap here to enter text.. This included the construction of levees, embankments, and artificial channels. Due to this, several parts of the river are now confined to single straight channels in various stretches of the river, especially when it passes through cities like Florence, San Giovanni Valdarno, Pisa, and several other smaller towns. The Val di Chiana and Valdarno regions have also been reclaimed from being marshlands into arable land by the construction of the Maestro canal, a project that spanned centuries, and finally altered the natural hydrology of the basin (Alexander, 1984). Two dams, Levane and Laterina were constructed in the province of Arezzo, a few kilometers upstream of Montevarchi in the 1950s. The purpose of these dams was to generate hydroelectric power and to manage the Arno River's flow to reduce the risk of flooding in the region. The disastrous aftermath of the flood of 1966 also prompted the development of extensive flood control measures. The river embankments along several parts of the river were reinforced to contain the flood waters and early flood warning systems were installed.

The river has also experienced extensive instream mining for sand and gravel, which along with the sediment entrapment by the two dams, has created a sediment deficit in the river. This sediment deficit has triggered erosive processes along the bank of the river and its tributaries. (Cencetti & Tacconi, 2005; Rinaldi & Simon, 1998).

3 Methodology

3.1 Sampling

We collected 27 samples throughout the river. The samples were evenly spaced out to about 10 km apart from each other along the river; however, we adjusted the location of the individual samples methodically to understand the effects of important points along the river, such as dams, major cities, and the confluence of tributaries.

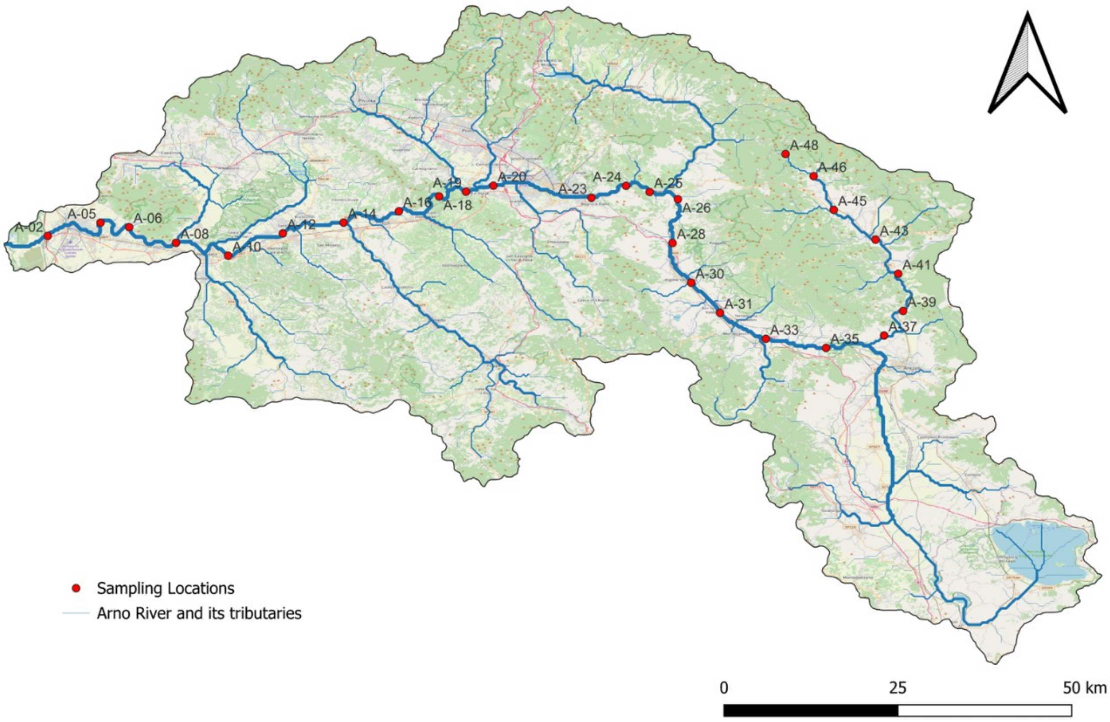


Figure 7: Map of Arno basin showing sampling locations along the river.

The samples were collected right after a flood event that took place at the end of the winter, around the end of February and the beginning of March. Due to heavy rainfall in the river basin, the Levane dam had to discharge a substantial amount of water into the river, resulting in the flood. The rise in the water level above the hydrometric zero was measured by a flood monitoring station a few kilometres downstream of the dam at Montevarchi. Figure 8 shows the flood level and the discharge rate from the dam during the flood. The flood had two peaks, one on the 27th of February and the other on the 2nd of March: both coinciding with the two major discharges from the dam.

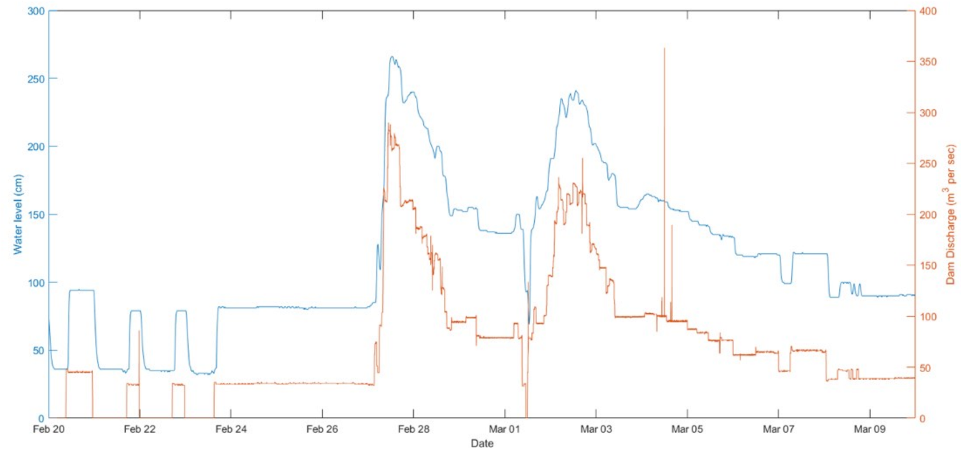


Figure 8: The water discharge from the Levane Dam and the flood level at the Montevarchi flood monitoring station, showing the flood that occurred at the end of winter that deposited the sediments collected for this study.

To be consistent with our sampling approach throughout the river and with the sedimentary facies from which we collected the samples, all the samples were picked up from the sand deposited at the riverbanks during the waning stage of the flood. Since sediments were freshly deposited, we were able to avoid any effects caused due to the reworking of the sediments (e.g. bioturbation).

Figure 9: Sampling Site A23(Left) and A25(Right): the blue marking shows the upper reach of the flood in this area, marked by the dead branches and dry grass that were carried by the flood; and the spot from where the sample was picked is shown by the red arrow.

Although the flood levels were different in various parts of the river, the peak level at each sampling site was marked by the floating plant debris that was carried by the flood, such as branches and dry grass, deposited along the river before the flood started to recede. These markers clearly indicated the upper level of the flood, below which the

Figure 10: Sampling site (A-25), The red line shows the lower boundary of the fresh sediments deposited during the most recent flood. The material below has roots, meaning it was deposited much earlier, allowing biological activity to take place.

samples were picked. The freshly deposited sands were easily distinguishable from the older sediments below due to the presence of roots in the lower sediments. The samples were picked using a metal shovel and packed with aluminium foil to prevent any contamination from other plastic sources. About 2 kg of sand was collected from each location.

Figure 11: The samples were collected using a metal shovel and packed in aluminium foil to avoid contamination.

The following table shows the location of each sampling site.

Sample No	Latitude	Longitude
A-48	43°50'23.33"N	11°39'18.67"E
A-46	43°48'3.19"N	11°42'16.68"E
A-45	43°44'28.75"N	11°44'24.05"E
A-43	43°41'20.23"N	11°48'49.18"E
A-41	43°37'44.22"N	11°51'12.88"E
A-39	43°33'47.92"N	11°51'44.11"E
A-37	43°31'12.69"N	11°49'43.65"E
A-35	43°29'53.85"N	11°43'35.35"E
A-33	43°30'51.42"N	11°37'13.23"E
A-31	43°33'36.28"N	11°32'23.25"E
A-30	43°36'47.29"N	11°29'20.39"E
A-28	43°40'59.14"N	11°27'21.94"E
A-26	43°45'37.28"N	11°27'56.09"E
A-25	43°46'22.69"N	11°24'56.97"E

A-24	43°47'1.91"N	11°22'27.16"E
A-23	43°45'45.72"N	11°18'47.74"E
A-20	43°47'2.75"N	11° 8'26.07"E
A-19	43°46'24.90"N	11° 5'32.70"E
A-18	43°45'54.30"N	11° 2'42.02"E
A-16	43°44'20.48"N	10°58'26.81"E
A-14	43°43'8.41"N	10°52'36.20"E
A-12	43°42'0.12"N	10°46'11.16"E
A-10	43°39'38.62"N	10°40'24.09"E
A-8	43°41'0.14"N	10°34'53.67"E
A-6	43°42'40.04"N	10°29'56.58"E
A-5	43°43'7.61"N	10°26'55.07"E
A-2	43°41'44.18"N	10°21'20.15"E

Table 1: List of all the sampling locations along with their GPS coordinates

3.2 Grain Size Analysis

The grain size of the samples was measured using a laser particle analyser, the *Malvern Mastersizer 3000*. The Instrument has two units, the optical unit, and the wet dispersion unit. The representative refractive index of the sediment sample is fed into the system as a preliminary step. Other preliminary steps involve keeping the sediment submerged in deionised water along with a small amount of sodium hexametaphosphate to help break down lumps of clay particles that could be sticking together.

Figure 12: Image of the Mastersizer 3000, used for grain size analysis. The wet dispersion unit in the front and the Optical unit at the back.

For the measurement, the sediment sample is added to a dispersant, (H_2O in our case) so that the obscurity for the laser is between 5% to 15%, ideally close to 10%. The sediment particles are mixed thoroughly in the dispersion unit and fed into the measurement cell, which is an interface between the dispersion unit and the optical unit. Here, the laser passes through the particles into the detector in the optical unit and generates a light scattering pattern caused by the particles in the sample. This scattering pattern is interpreted by the software to provide accurate particle size information.

Each sample was analysed five times by 2 different operators each (for a total of 10 runs per sample). This was done so that any bias while pipetting the sample to the dispersion unit is neutralised as different operators tend to have an inherent bias where they preferentially pick up heavier or lighter sediments more than the other, resulting in an inaccurate reading that is not representative of the actual sample.

3.3 Microplastic separation

Prior to the microplastic separation, the samples were treated with hydrogen peroxide to remove excess organic matter. 30% H_2O_2 solution was added to the sample and the samples were left to dissolve the organic matter for a week, after which the microplastic separation was performed.

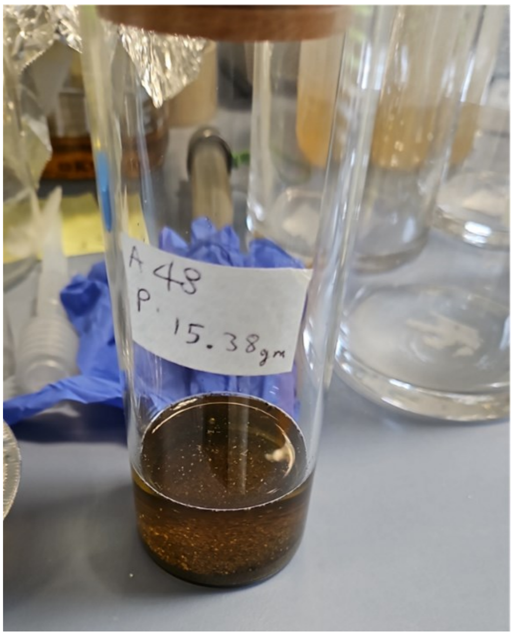


Figure 13: Sodium Polytungstate solution added to the sediment solution in a glass beaker. The lighter plastic particles and some debris float on top while the rest sink to the bottom.

The microplastics were separated using the density-based separation method. Around 15-20 g of each sample was used in this procedure. Sodium polytungstate, which has a density of 3 g per cm^3 was diluted with distilled water to a density of 1.6 g per cm^3. The samples were mixed well into this solution and let to rest in glass beakers. This was done as most of the plastic particles are lighter than the said density and float at the top of the column, whereas most minerals are heavier than this density and tend to sink at the bottom. (Bonotto, 2020) showed that this density for microplastic extraction has shown a 97% yield for microplastic extraction.

Once sufficient time had passed (at least a day) and all the heavier particles had settled at the bottom of the beaker, the supernatant liquid, which contains the plastic particles, was pipetted out and transferred to a filter paper, which collected all the microplastics along with some other lighter particles for further analysis.

3.4 Microplastic Detection

Figure 14: An example of a high-resolution photo of the filter paper containing the microplastic particles along with some debris.

A stereoscopic microscope was used to observe the filters that contained the microplastic. The microscope was equipped with a camera and Deltapix software to enable taking pictures. Firstly, a high-resolution image of the filter was taken for each sample, which was then used to mark the location of the microplastics in each sample. Each microplastic particle was labelled based on its shape (fibre, fragment, film, or foam), and colour. In several samples, the detection of microplastics was inhibited as the particles were hard to distinguish from small roots or were covered by other organic debris.

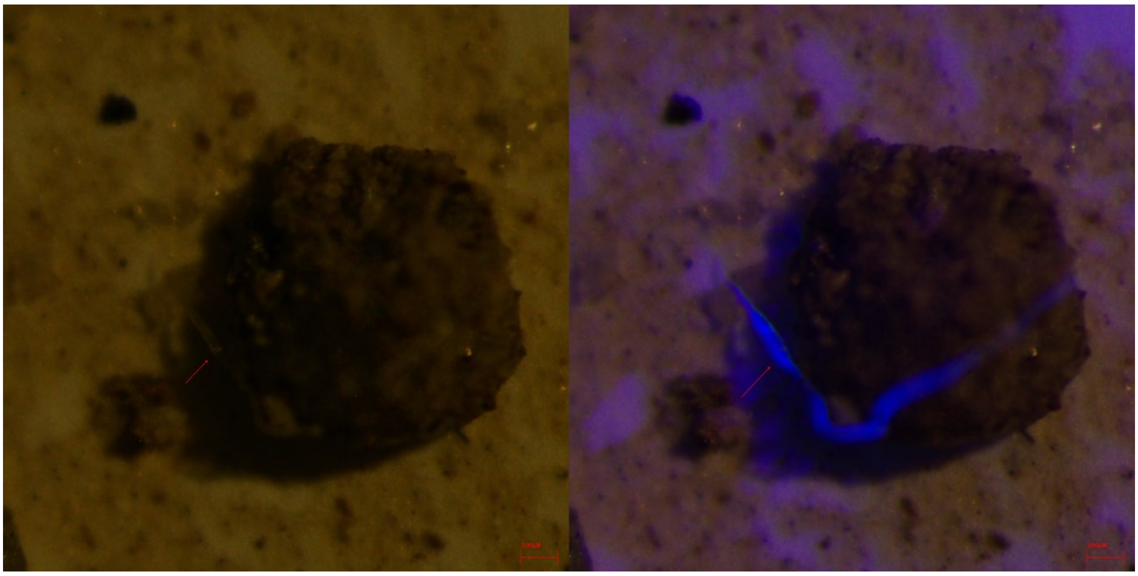


Figure 15: Image of a plastic fibre wrapped around organic debris in visible light (left) and under ultraviolet light (right). The plastic fibre glows bright blue under UV light, making it possible to detect smaller particles and otherwise hard-to-detect particle

To facilitate the detection of microplastics, a UV lamp was used. Many common plastics tend to be illuminated in the presence of ultraviolet light, thus making their detection much easier, especially in cases of transparent smaller particles. In certain cases, a hot needle was deployed to confirm a particle to be plastic. Plastic tends to react when it comes in contact with the hot needle whereas other organic matters do not.

4 Results

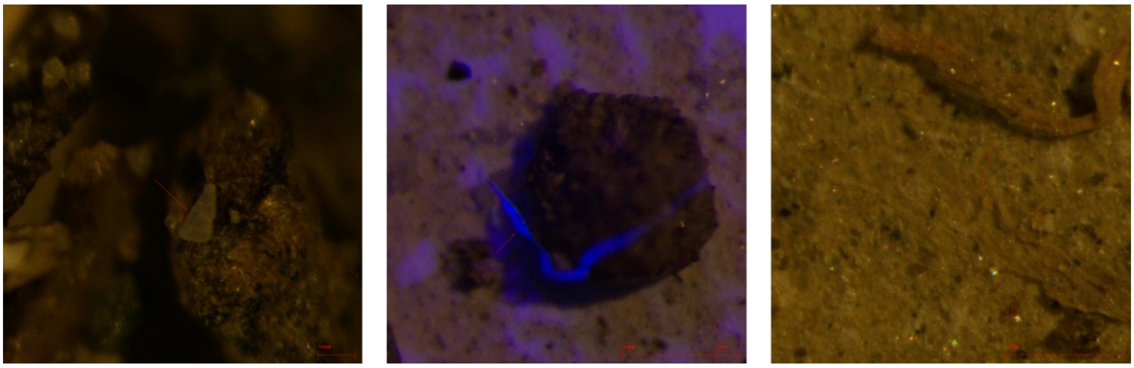


Figure 16: Different shapes of Microplastic particles detected in the samples. Fragments (left), fibres (middle) and film (right), were the three shapes recognised.

The observations made at the sampling locations, the outcome of the grain size analysis, and the microplastic analysis are described in this section. The microplastics are classified based on their shape (fibres, fragments and films), and colour wherever possible. In case the colour was not recognised because they were too small, and/or covered in mud and UV light was used to identify them, they were put in the unrecognised category. However, most of the fibres in the unrecognised category are transparent as most of them are practically invisible under visible light due to being too small. However, they glowed with a bright blue colour under UV light, making their detection fairly possible.

4.1 A-48

Figure 17: Image of sampling site A-48, red arrow marks the spot from where the sample was picked.

This is the most upstream sampling location, 4.5 km downstream of the spring. The Arno River cascades with an extremely high flow rate in this part and is very narrow (width approximately 8.5 metres), almost like a creek. The riverbanks are intensely vegetated, and some plastic wastes are trapped in the vegetation. No anthropogenic change to the river's course is observed in this area.

Figure 18: Many plastic waste materials were found entangled with the vegetation in the surroundings.

Figure 19: Close-up image of the sampling location, showing the recently deposited sediments over the older sediments, that have roots(bioturbation).

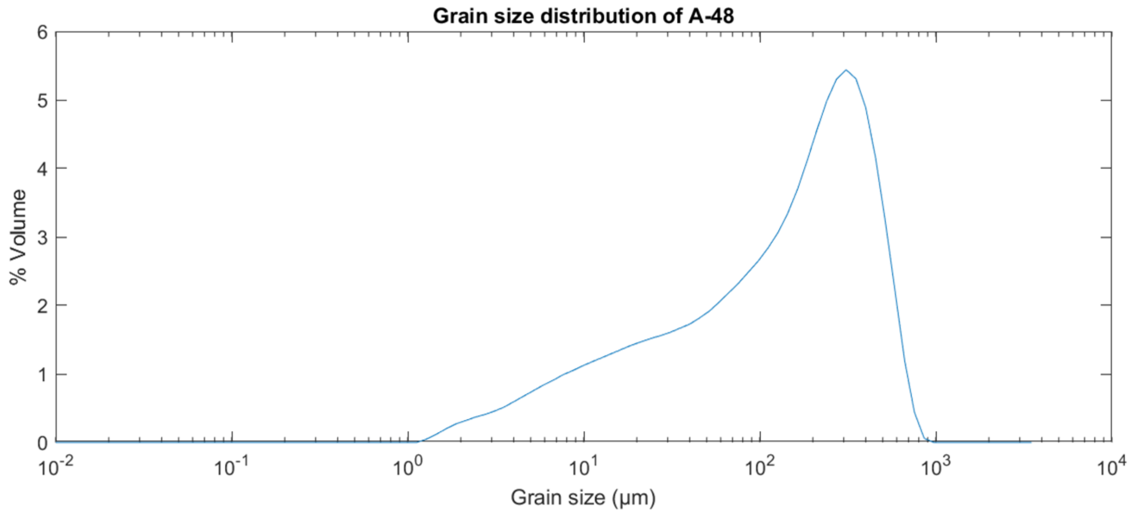


Figure 20: Grain size distribution of A-48

The sediments are very fine-grained sand. The sample is strongly fine-skewed and very poorly sorted. The following are the important Dv values:

Dv (10): 11,637 µm

Dv (50): 161,016 µm

Dv (90): 472,644 µm

Figure 21: Microplastic distribution for sample A-48. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

The microplastics consisted mostly of fibres (38) and a small number of films (2), totalling to 36 microplastic particles. Most of the plastics were either transparent or too small for their colours to be recognised.

4.2 A-46

Figure 22: Image of sampling site A-46, red arrow marks the spot from where the sample was picked.

Situated in the town of Stia. The river is still cascading down. The Sampling location is located right after a small meander. Drainage from the town is entering the river close to the sampling location. (shown in Figure 22). The left bank of the river, from where the sample was picked shows vegetation, whereas the other side is rocky. The width of the river channel is ca 5 metres. The parts of the riverbanks in the vicinity show artificial embankments to stabilise the river course.

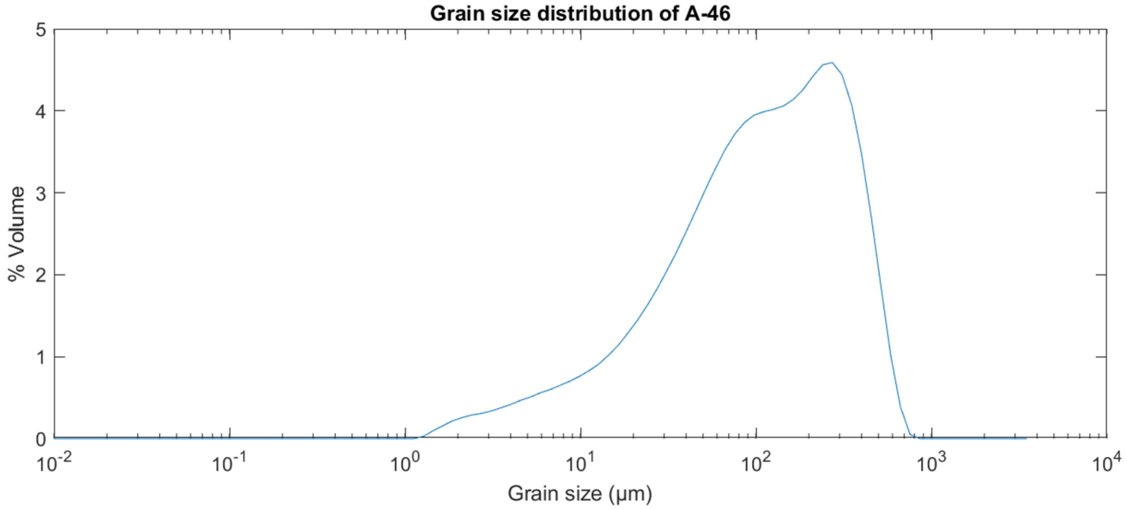


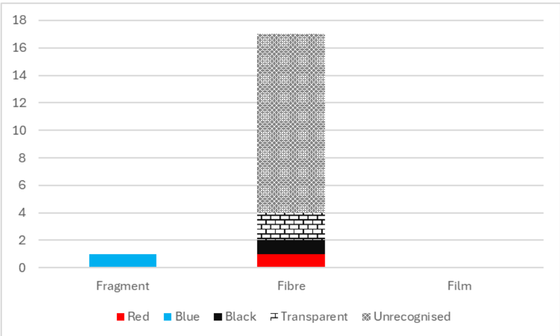
Figure 23: Grain size distribution of A-46

The sediments are very fine-grained sand. The sample is fine-skewed and poorly sorted. The following are the important Dv values:

Dv (10): 17,359 µm

Dv (50): 119,075 µm

Dv (90): 393,447 µm



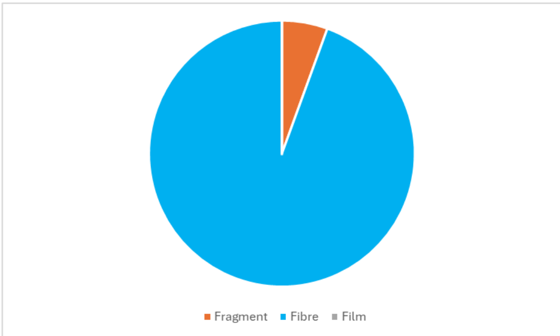


Figure 24: Microplastic distribution for sample A-46. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

The microplastic particles are mostly fibre counting up to 17, and one blue fragment was found. This totals the number of microplastics in this sample to be 18.

4.3 A-45

Figure 25: Image of sampling site A-45, red arrow marks the spot from where the sample was picked. The orange arrow shows plastic waste found in the location

Downstream of Ponte d’Arno, around 500 metres upstream of Fiume Solano. The riverbanks have a lot of vegetation and some plastic waste is entangled in it. The river has increased in width to 12 metres. Sidebars are present in this section of the river. The river at the sampling site does not show any signs of modification by humans.

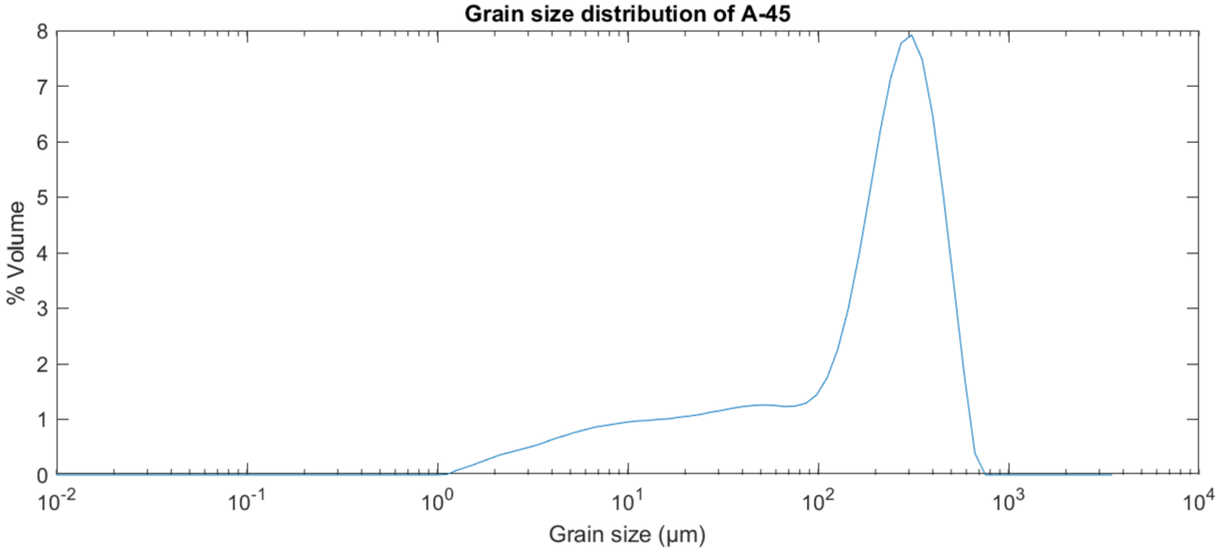


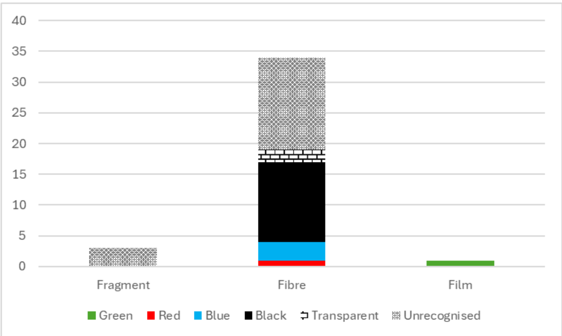
Figure 26: Grain size distribution of A-45

The sediments are fine-grained sand. The sample is strongly fine-skewed and poorly sorted. The following are the important Dv values:

Dv (10): 11,781 µm

Dv (50): 227,219 µm

Dv (90): 461,361 µm



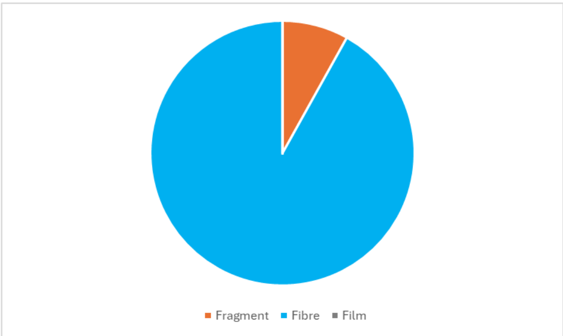


Figure 27: Microplastic distribution for sample A-45. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

The sample is again mostly fibres with 35 of them. Some are black, and a few are too small to recognise the colour, while a few seem to be transparent. A couple of fragments (3) and films (1) were also found. The final count for all the microplastics in this sample is 37.

4.4 A-43

Figure 28: Image of sampling site A-43, red arrow marks the spot from where the sample was picked.

Just downstream of the city of Bibbiena. The river width has further increased to 16 metres. The sampling site is situated at a gravelly sidebar. The left bank, where the sample was collected has some vegetation present, whereas the right side is artificially embanked to prevent erosion.

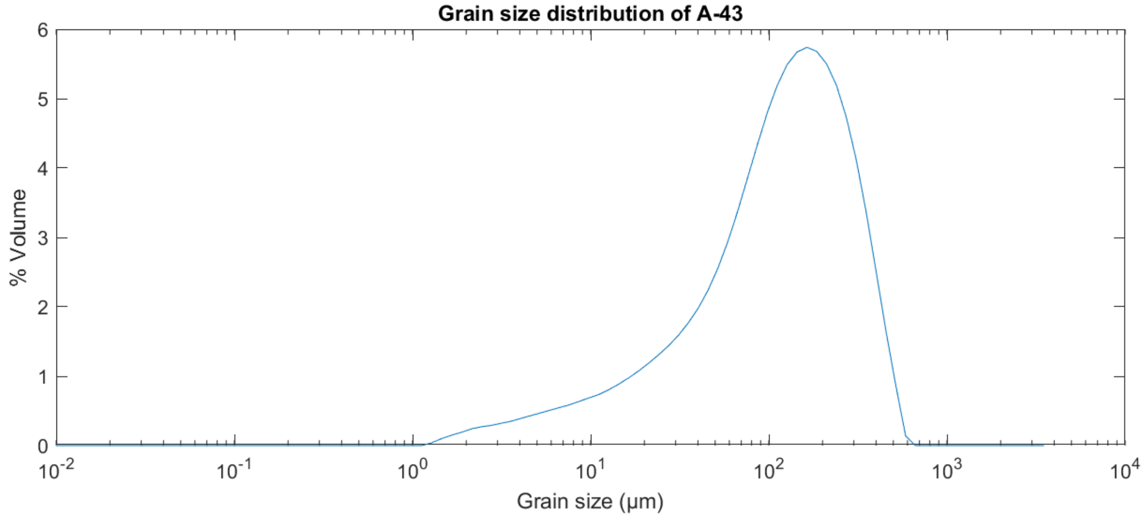


Figure 29: Grain size distribution of A-43

The sediments are very fine-grained sand. The sample is strongly fine-skewed and poorly sorted. The following are the important Dv values:

Dv (10): 19,466 µm

Dv (50): 128,630 µm

Dv (90): 336,205 µm

Figure 30: Microplastic distribution for sample A-43. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

The proportion of plastic fragments in this sample has increased, with 13 of them being fragments, while 18 are fibres. Most of the particles were again too small to detect their colour, and UV light was used to detect them.

4.5 A-41

Figure 31: Image of sampling site A-41, red arrow marks the spot from where the sample was picked.

The sampling site is situated close to the small town of Santa Mama. The channel width of the river has increased to 18 metres. The riverbanks have a decent amount of vegetation, with dead plant debris entangled to them. No significant anthropogenic alteration of the channel geometry at this site was observed.

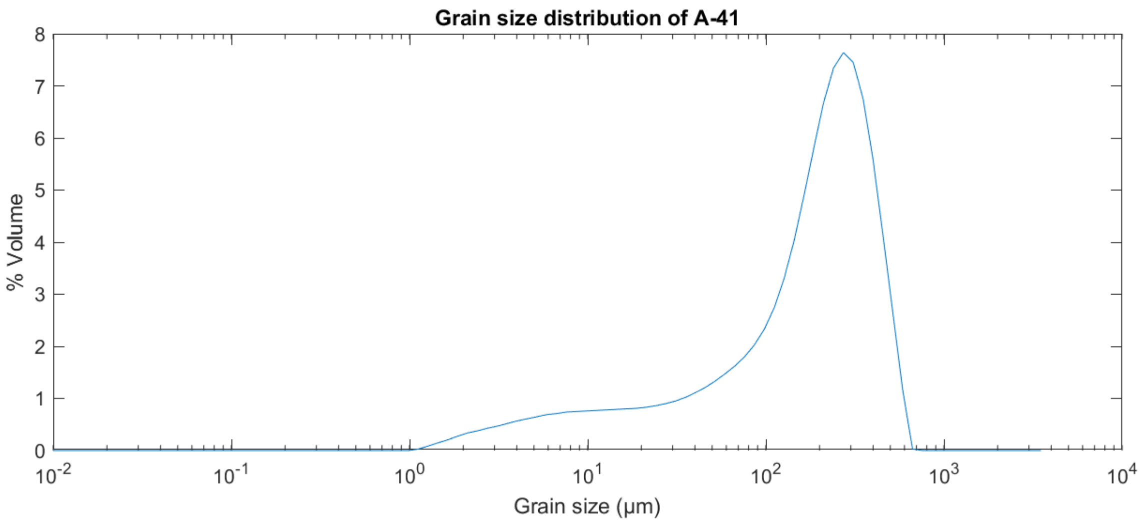


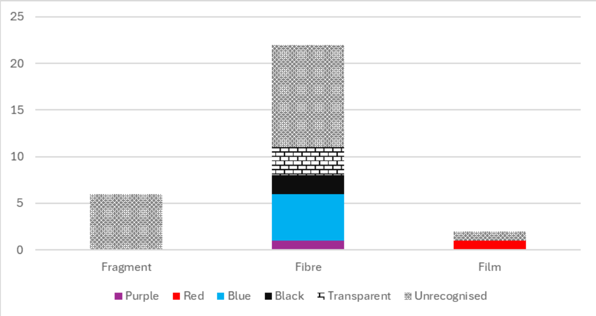
Figure 32: Grain size distribution of A-41

The sediments are fine-grained sand. The sample is strongly fine-skewed and poorly sorted. The following are the important Dv values:

Dv (10): 14,610 µm

Dv (50): 208,557 µm

Dv (90): 433,831 µm



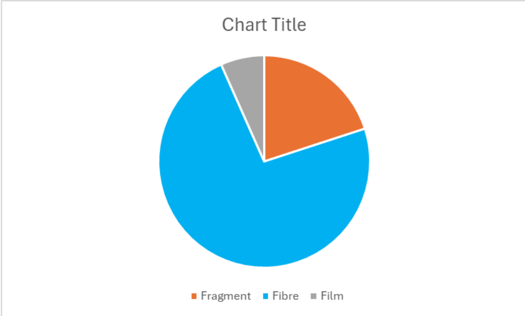


Figure 33: Microplastic distribution for sample A-41. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

The sample has mostly fibres (22), 6 fragments, and two pieces of film. A couple of films were also found. A few were large enough for their colour to be recognisable, they were mostly blue, while the rest were too small to assign any colour.

4.6 A-39

Figure 34: Image of sampling site A-39, red arrow marks the spot from where the sample was picked.

Situated in the Capolona village. The river width is significantly higher here, at 39 metres. A barrier on the river is situated about 70 metres downstream of the collection site, for hydroelectric power generation. There is a decent amount of vegetation present on the riverbanks. There are some signs of human alteration, such as artificial embankments along the river is observed in this area.

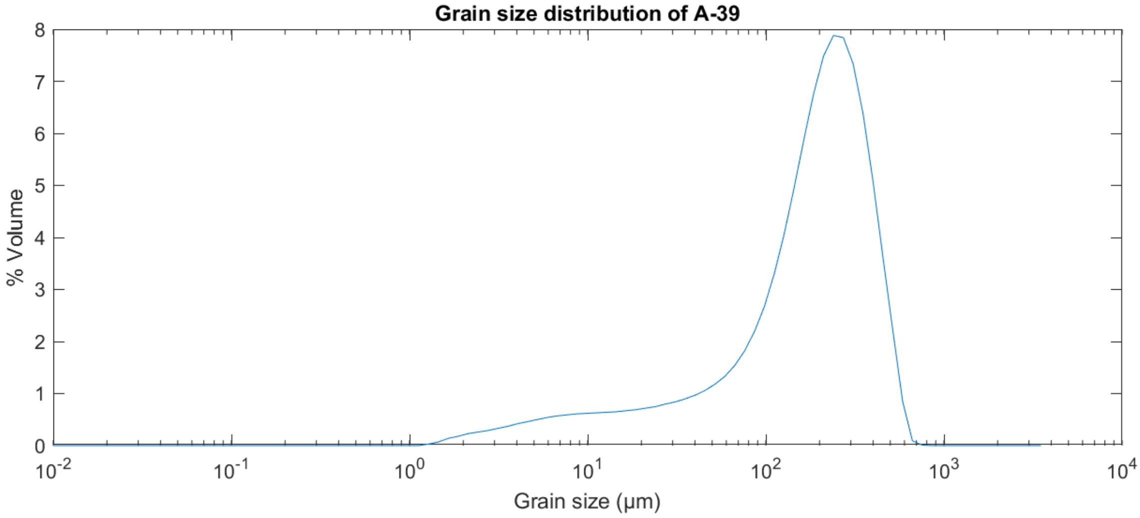


Figure 35: Grain size distribution of A-39

The sediments are fine-grained sand. The sample is strongly fine-skewed and poorly sorted. The following are the important Dv values:

Dv (10): 23,191 µm

Dv (50): 206,262 µm

Dv (90): 418,842 µm

Figure 36: Microplastic distribution for sample A-39. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

The majority of the microplastics were again fibres (16), albeit a bigger proportion of fragments were also present totalling up to 8. Some were blue in colour, a couple were black, and the majority were again too small to be detected under visible light, so a UV lamp was used to detect them. No films were present.

4.7 A-37

Figure 37: Image of sampling site A-37, red arrow marks the spot from where the sample was picked.

Situated on a meander bend, just downstream of Castelluccio village. This site is a few kilometres upstream of the La Penna (Laterina) Dam. The river channel has a width of 19 metres here. The point bar associated with the river bend is quite gravelly, and there is a decent amount of vegetation present along the river. The outer bank of the meander shows signs of artificial reinforcement.

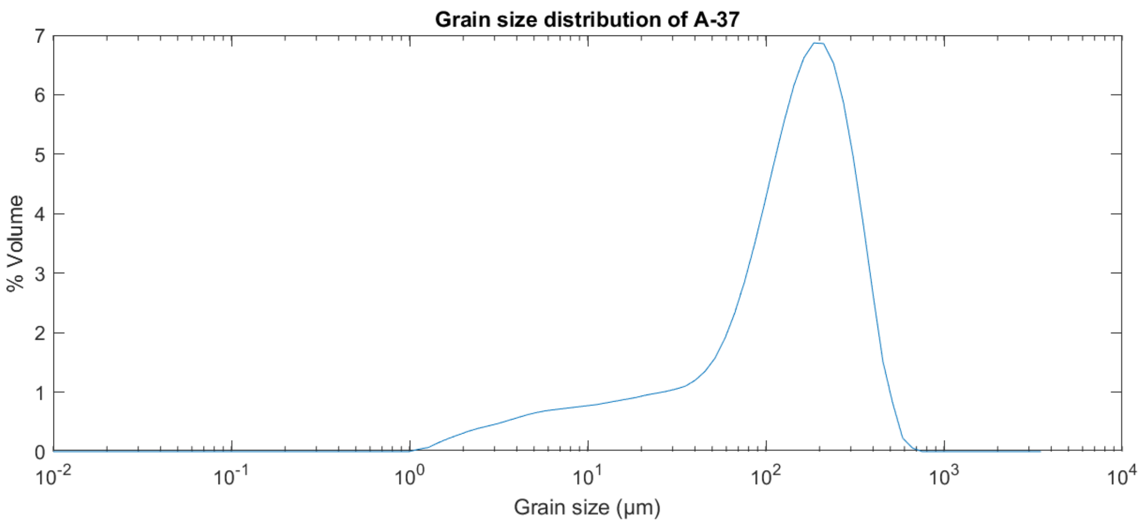


Figure 38: Grain size distribution of A-37

The sediments are very fine-grained sand. The sample is strongly fine-skewed and poorly sorted. The following are the important Dv values:

Dv (10): 14,385 µm

Dv (50): 153,097 µm

Dv (90): 343,745 µm

Figure 39: Microplastic distribution for sample A-37. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

The sample was again full of fibres with 23 of them, while only a small proportion of fragments, with only 2 of them. Less than half were identifiable under visible light to assign a colour.

4.8 A-35

Figure 40: Image of sampling site A-35, red arrow marks the spot from where the sample was picked, (behind the bag). The orange arrow shows a plastic bag entangled to the branches.

Situated between the La Penna (Laterina) dam(upstream) and the Levane dam (downstream). The site is located at the back of a residential house. The channel width has increased to 47 metres. The riverbank was quite sandy with some vegetation present. The vegetation had some plastic waste entangled to it. No signs of human alteration to the river is observed here.

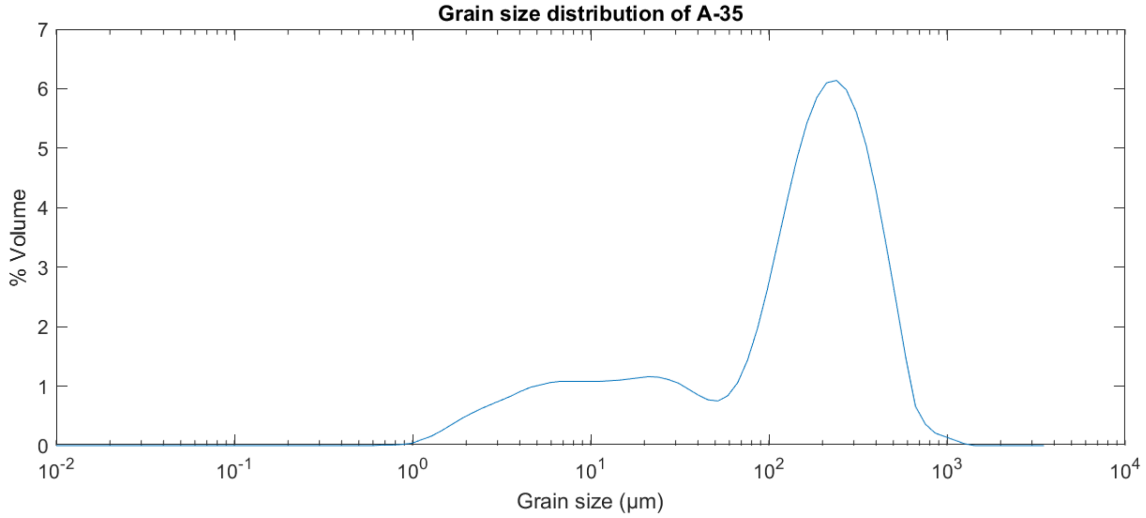


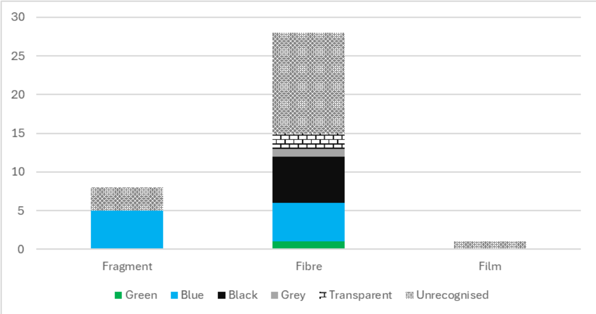
Figure 41: Grain size distribution of A-35

The sediments are very fine-grained sand. The sample is strongly fine-skewed and poorly sorted. The following are the important Dv values:

Dv (10): 7,739 µm

Dv (50): 176,629 µm

Dv (90): 438,507 µm



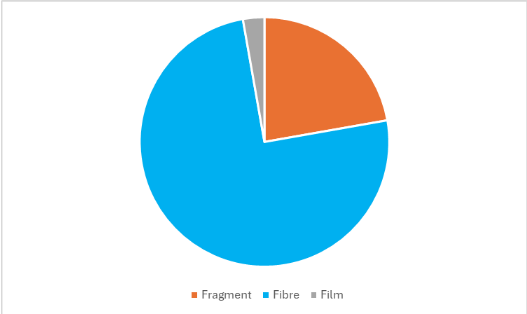


Figure 42: Microplastic distribution for sample A-35. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

This sample again had higher numbers of fibres than the other shapes. There were 27 fibres, 8 fragments, and 1 film. Only some blue and black pieces were recognisable under visible light, while the rest were very small or transparent.

4.9 A-33

Figure 43: Image of sampling site A-33, red arrow marks the spot from where the sample was picked.

Located about 1.2 km downstream of the Levane dam, and a few kms upstream of Montevarchi. With a channel width of 19 metres, the riverbanks were full of vegetation, and some plastic wastes were trapped in the plants. The sediments had a significant amount of plant debris. No sign of alteration by humans was observed here.

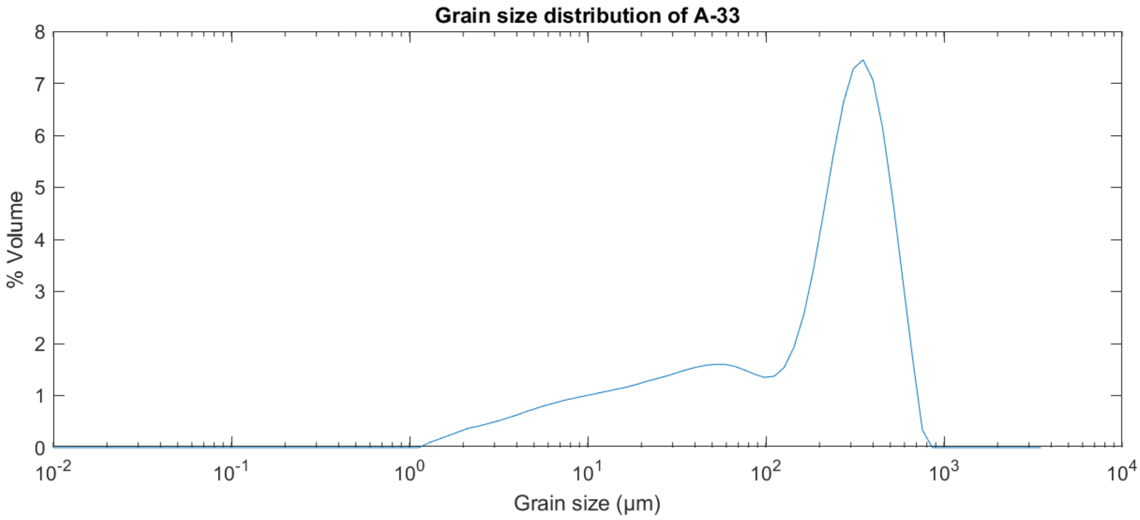


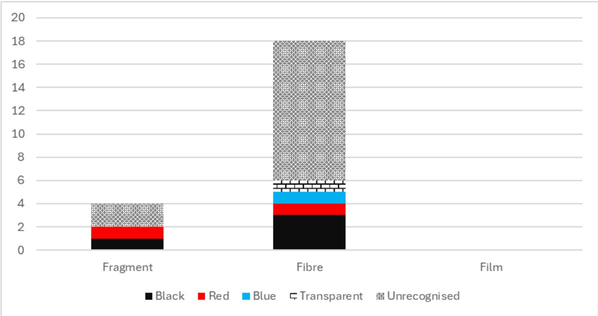
Figure 44: Grain size distribution of A-33

The sediments are fine-grained sand. The sample is strongly fine-skewed and very poorly sorted. The following are the important Dv values:

Dv (10): 11,539 µm

Dv (50): 241,186 µm

Dv (90): 517,082 µm



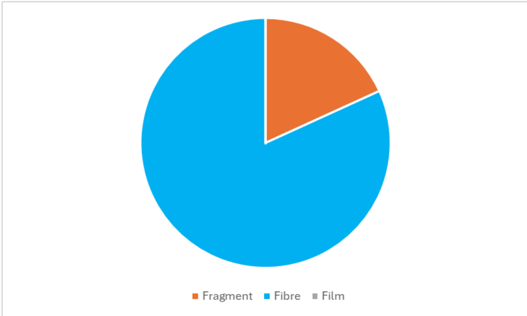


Figure 45: Microplastic distribution for sample A-33. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

The sample continues to be dominated by fibres over other shapes, with 18 being fibres, 4 pieces of fragments, and no films. Some black and red fibres and fragments were recognised, whereas most of them were detected under UV light.

4.10 A-31

Figure 46: Image of sampling site A-31, red arrow marks the spot from where the sample was picked.

The sampling site is situated just upstream of San Giovanni Valdarno. The channel width is about 25 metres. The Battagli Canal enters the river close to the sampling site, which is situated on a sidebar. The sidebar is quite gravelly and has a good amount of vegetation (mostly grass) present. Artificial levees are constructed on both sides of the river.

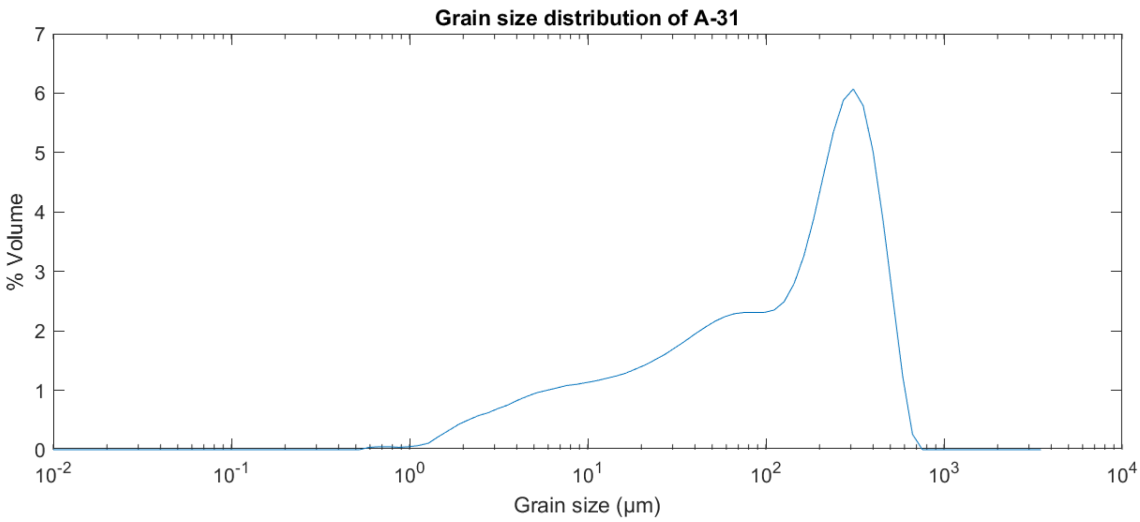


Figure 47: Grain size distribution of A-31

The sediments are very fine-grained sand. The sample is strongly fine-skewed and poorly sorted. The following are the important Dv values:

Dv (10): 8,356 µm

Dv (50): 148,005 µm

Dv (90): 430,806 µm

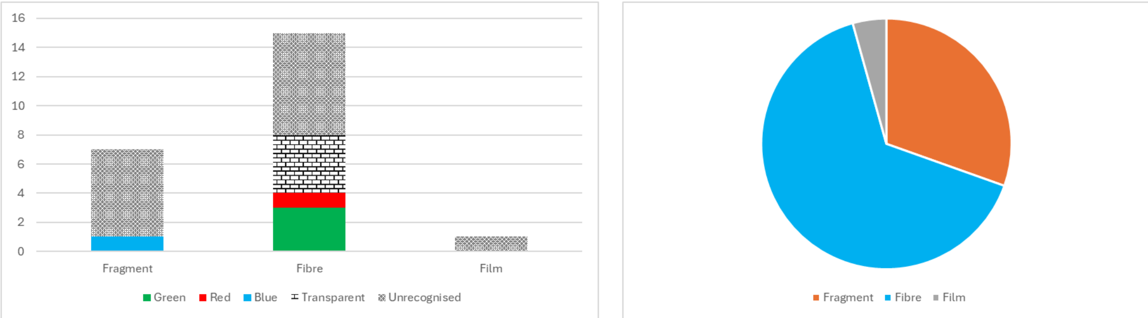


Figure 48: Microplastic distribution for sample A-31. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

The sample has 15 fibres and 7 fragments, and one film was also found. Most of them were not assigned a colour due to being transparent or being detected under UV light.

4.11 A-30

Figure 49: Image of sampling site A-30, red arrow marks the spot from where the sample was picked.

Situated just upstream of Figline Valdarno, on a sidebar, just upstream of a small creek that enters the river. The river width has increased again to 45 metres here. The sidebar is gravelly, with some grass growing on the top. The river has taken a very straight course, but no obvious sign of human intervention is visible here.

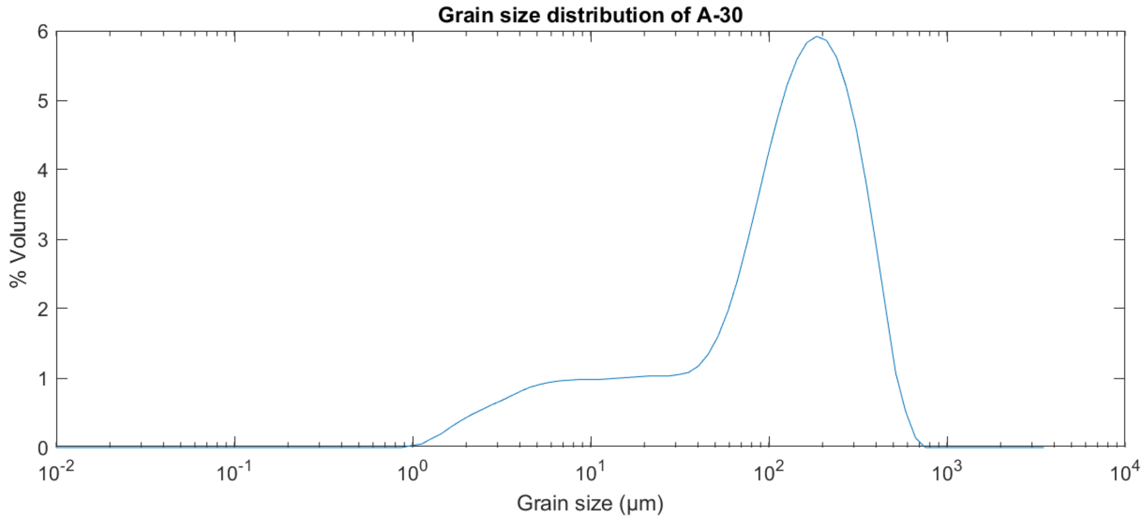


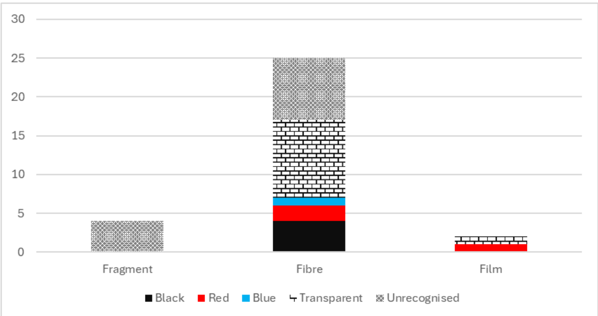
Figure 50: Grain size distribution of A-30

The sediments are very fine-grained sand. The sample is strongly fine-skewed and poorly sorted. The following are the important Dv values:

Dv (10): 9,134 µm

Dv (50): 140,628 µm

Dv (90): 357,115 µm



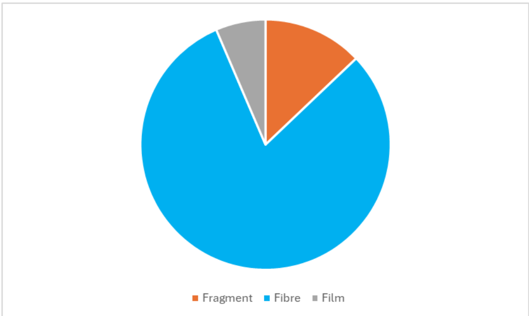


Figure 51: Microplastic distribution for sample A-30. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

The Sample is full of fibres, with 25 of them, whereas only 4 fibres and 2 films were found. 4 fibres were black in colour, whereas 2 fibres and one fragment were red. Most were again too small or transparent so no colours were assigned to them.

4.12 A-28

Figure 52: Image of sampling site A-28, red arrow marks the spot from where the sample was picked.

Further downstream, the river crosses through the farmlands, slightly upstream of the small village of Santa Maria Maddalena. A small quarry is present close to the collection site, and a small creek enters the river just downstream of the sampling location. The river width is 42 metres here. Both riverbanks are rich in vegetation, and some plastic wastes are trapped by this vegetation. The river has started to meander in regions close to this location but seems to have artificial levees here.

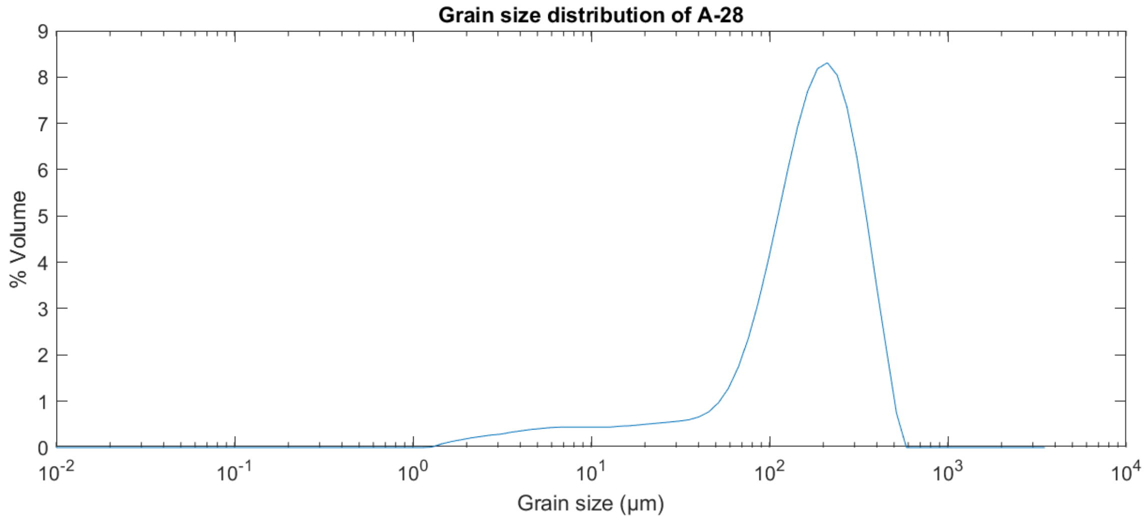


Figure 53: Grain size distribution of A-28

The sediments are fine-grained sand. The sample is strongly fine-skewed and poorly sorted. The following are the important Dv values:

Dv (10): 39,015 μm

Dv (50): 183,721 μm

Dv (90): 362,866 μm

Figure 54: Microplastic distribution for sample A-28. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

The proportions of different shapes of microplastics have changed in this sample, with 13 being fibres, 10 fragments and 2 films. Except for one green fibre, all were detected under UV light.

4.13 A-26

Figure 55: Image of sampling site A-26, red arrow marks the spot from where the sample was picked.

Located just upstream of Massolina a couple of kilometres upstream of the Sieve confluence, on the outer bank of a meander bend. The river width has increased to 59 metres. The riverbank has a considerable amount of vegetation present, including trees. An artificial levee is likely present on the outer bank, although it is not obvious.

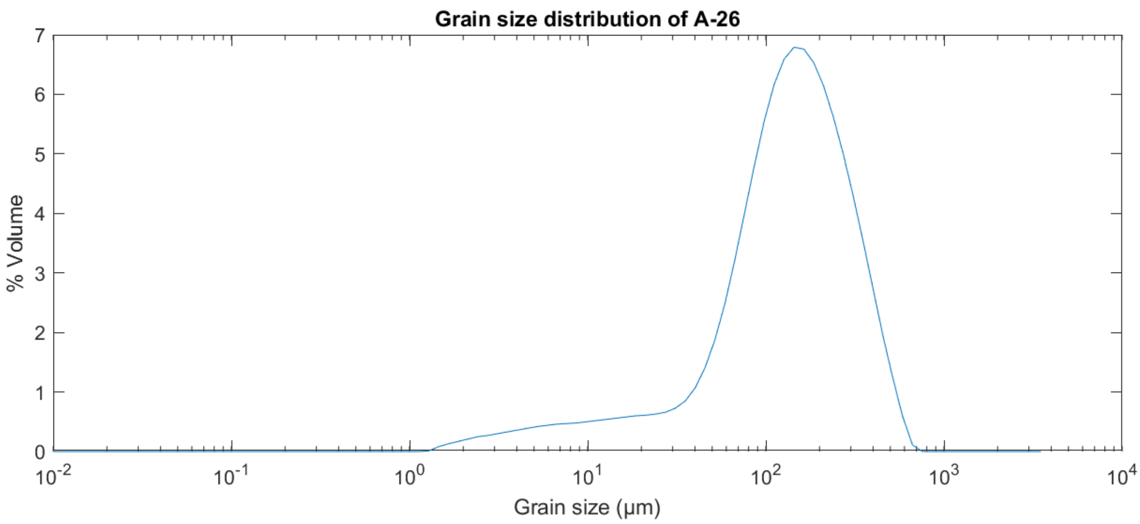


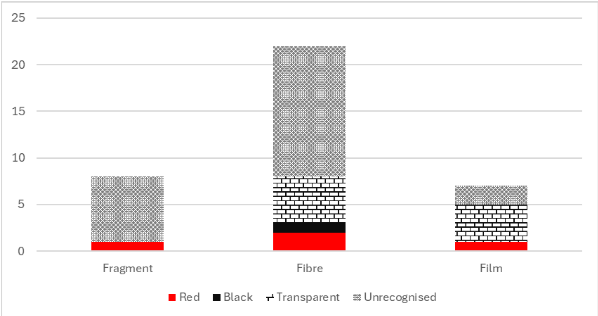
Figure 56: Grain size distribution of A-26

The sediments are fine-grained sand. The sample is fine-skewed and poorly sorted. The following are the important Dv values:

Dv (10): 31,247 µm

Dv (50): 147,376 µm

Dv (90): 353,743 µm



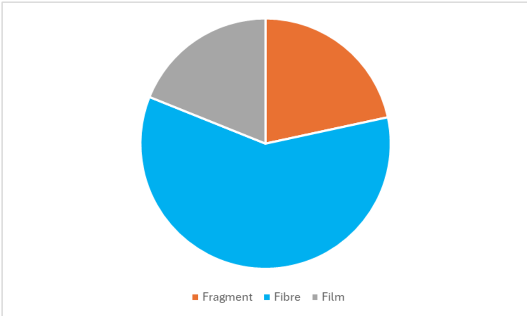


Figure 57: Microplastic distribution for sample A-26. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

The sample is mostly fibres, with 22 of them, and we have 8 fragments and 7 films found here. Most pieces were either transparent or too detected under UV light, so no colour was assigned, however, some pieces were recognised as red in colour.

4.14 A-25

Figure 58: Image of sampling site A-25, red arrow marks the spot from where the sample was picked. The Person at the back is standing at the marker made by plant debris for the upper reach of the flood in this area.

Located over a sidebar, just downstream of Pontasieve, a town situated at the confluence of the Sieve River with the Arno River. The channel width is low near the sampling location due to the sidebar, at 20 metres. A significant amount of vegetation is present on top of the sidebar, and the dead vegetation carried by the river clearly marks the upper reach of the flood. No obvious signs of human alteration are present.

Figure 59: Close-up shot of the sampling location, showing fresh sediments over older ones.

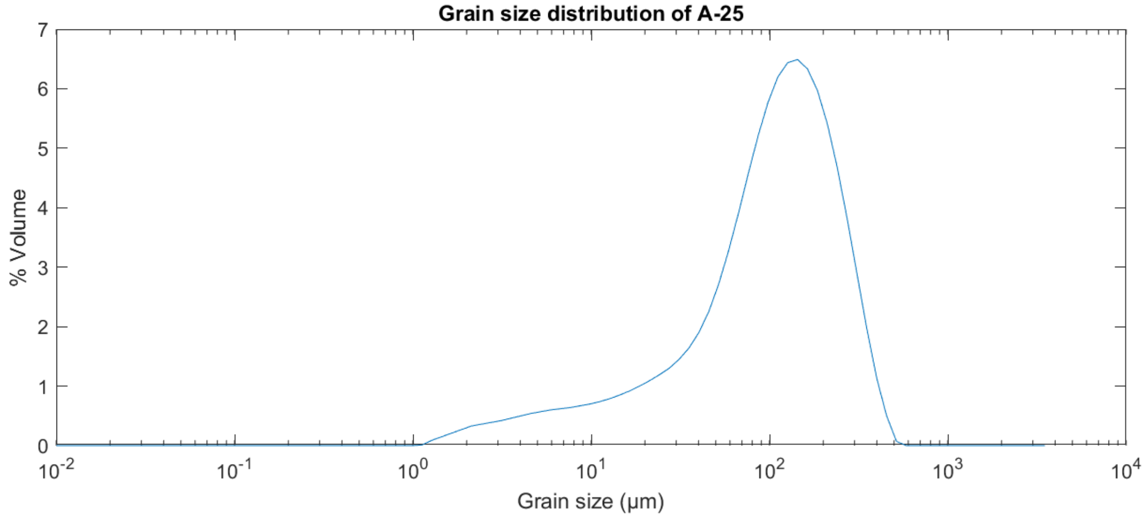


Figure 60: Grain size distribution of A-25

The sediments are very fine-grained sand. The sample is strongly fine-skewed and poorly sorted. The following are the important Dv values:

Dv (10): 16,605 μm

Dv (50): 115,940 μm

Dv (90): 275,871 μm

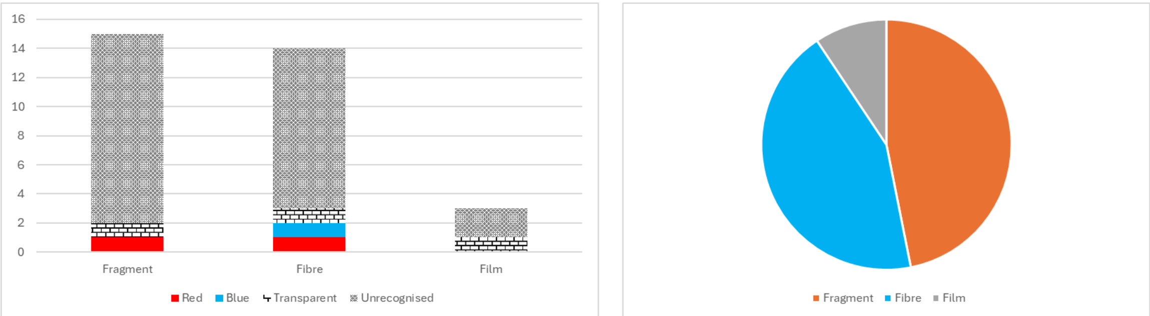


Figure 61: Microplastic distribution for sample A-25. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

The sample has a more even distribution between fibre and fragments, with 15 fragments and 14 fibres. 3 films were also detected. Most were detected under UV light, hence colours were not recognised.

4.15 A-24

Figure 62: Image of sampling site A-24, red arrow marks the spot from where the sample was picked.

Situated at the small settlement of Ellera, just upstream of a barrier across the river. The channel width increases here significantly, to 97 metres. There is a small amount of vegetation present along the river, and some concrete reinforcements are present.

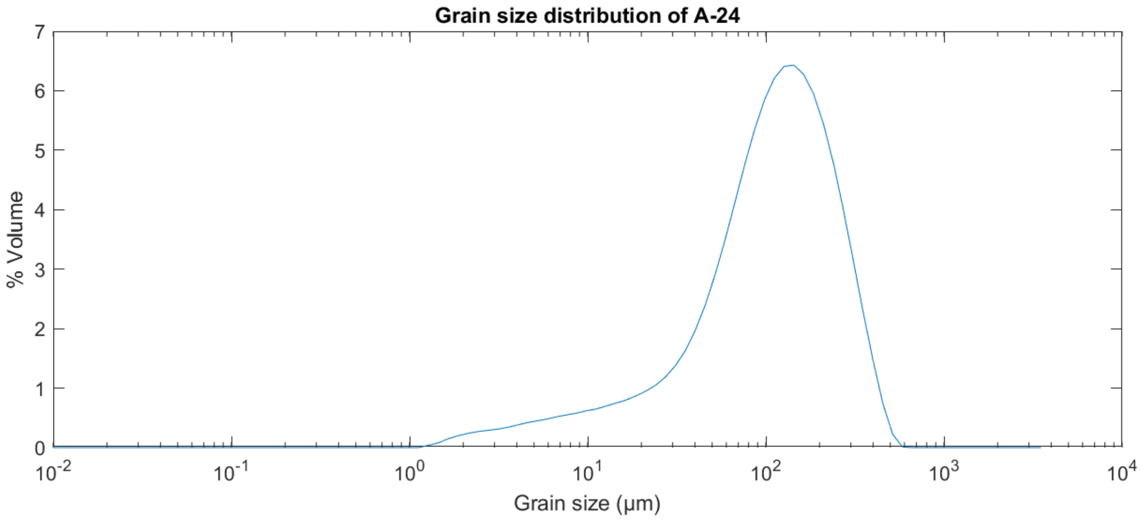


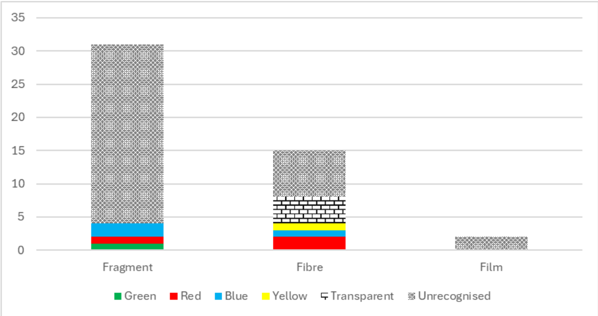
Figure 63: Grain size distribution of A-24

The sediments are very fine-grained sand. The sample is strongly fine-skewed and poorly sorted. The following are the important Dv values:

Dv (10): 22,110 µm

Dv (50): 119,371 µm

Dv (90): 289,094 µm



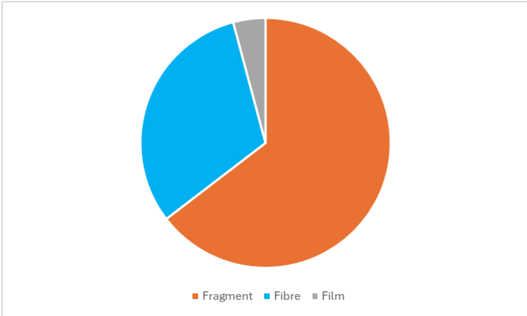


Figure 64: Microplastic distribution for sample A-24. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

The sample is dominated by fragments, with 31 of them, whereas we have less proportion of fibres here, with 15 of them, and 2 films. Some red, blue, green and yellow pieces were identified, while the majority were not assigned any colour.

4.16 A-23

Figure 65: Image of sampling site A-23, red arrow marks the spot from where the sample was picked.

Located just upstream of the historical city of Florence, the channel width here is 58 metres. The riverbank is covered with vegetation, and there are artificial levees on both sides. There is a barrier present just upstream of this sampling site.

Figure 66: View from another angle, showing the flood markers(dead plant debris) and the sampling spot.

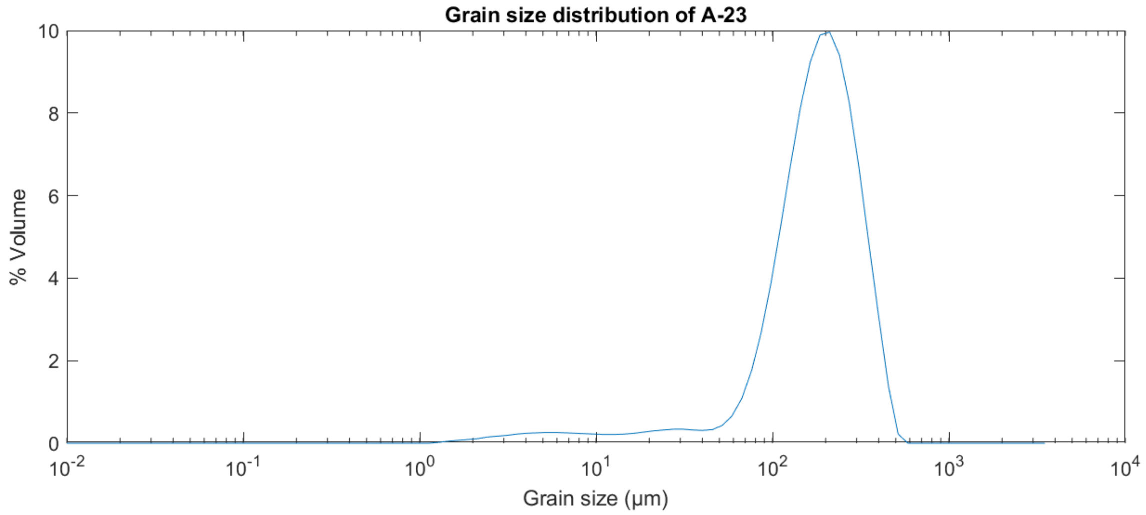


Figure 67: Grain size distribution of A-23

The sediments are fine-grained sand. The sample is fine-skewed and moderately sorted. The following are the important Dv values:

Dv (10): 84,203 μm

Dv (50): 194,810 μm

Dv (90): 348,540 μm

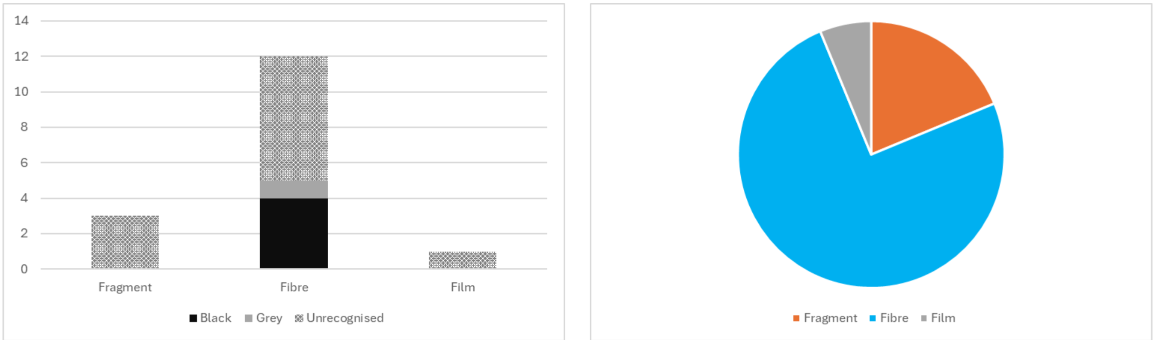


Figure 68: Microplastic distribution for sample A-23. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

The microplastics were mostly fibres, with 12 of them, and 3 fragments and 1 film were also found. Besides a few black and 1 grey fibres the rest were not assigned any colour.

4.17 A-20

Figure 69: Image of sampling site A-20, red arrow marks the spot from where the sample was picked.

Situated downstream of Florence. The channel width is 59 metres here. There is a good amount of vegetation around, but not close to the water level. Both riverbanks have artificial levees, and there is a footbridge just upstream of the collection site. The river channel is very straight around this part, suggesting human intervention to stabilise the river course.

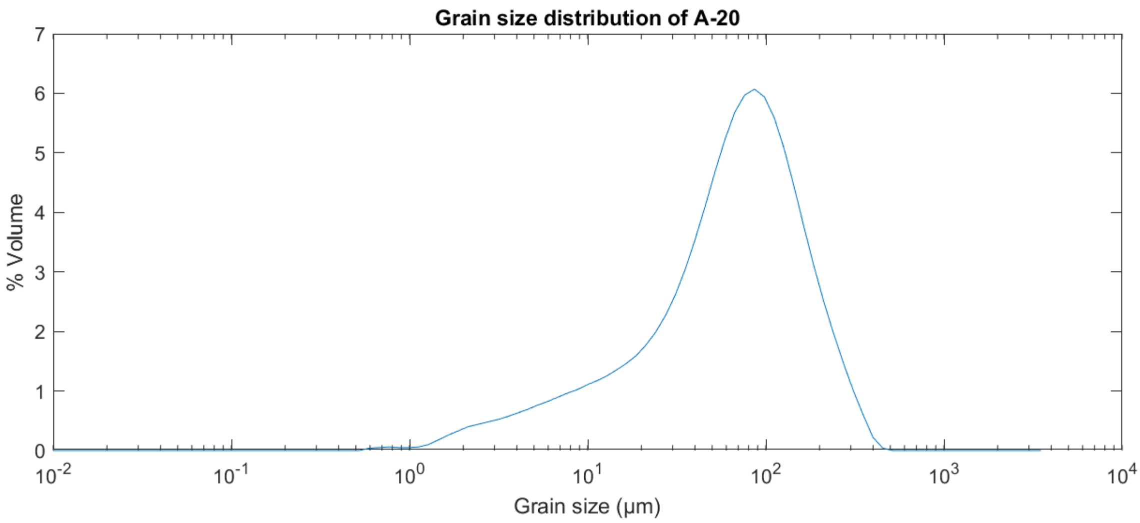


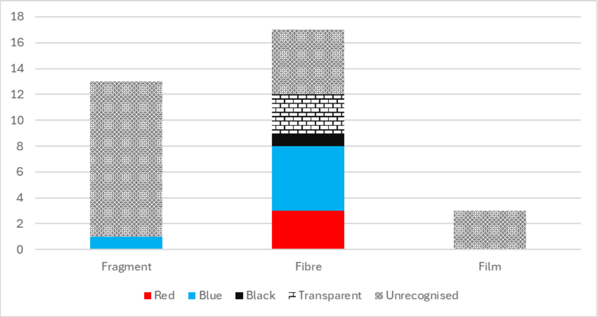
Figure 70: Grain size distribution of A-20

The sediment is coarse silt. The sample is strongly fine-skewed and poorly sorted. The following are the important Dv values:

Dv (10): 10,595 µm

Dv (50): 72,314 µm

Dv (90): 192,966 µm



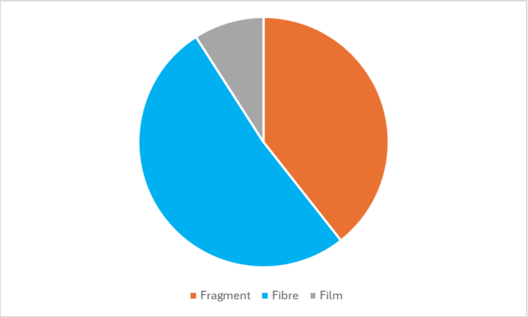


Figure 71: Microplastic distribution for sample A-20. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

The sample has 17 fibres, 13 fragments and 3 films. Some blue and red pieces were identified, however colours were not recognisable in the other pieces.

4.18 A-19

Figure 72: Image of sampling site A-19, red arrow marks the spot from where the sample was picked.

Located just 500 m downstream of the confluence of the Bisenzio River, which drains the city of Prato. The river width is 67 metres here. The sampling site did not have vegetation, but the surroundings in general did. The riverbanks are enforced with concrete on both sides. There are drainage outlets flowing into the river.

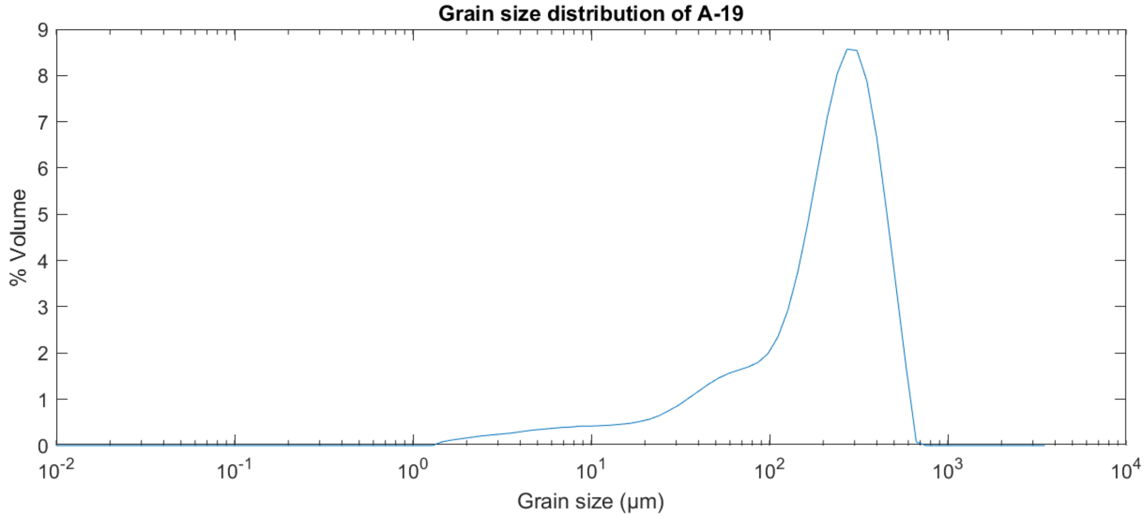


Figure 73: Grain size distribution of A-19

The sediments are fine-grained sand. The sample is strongly fine-skewed and poorly sorted. The following are the important Dv values:

Dv (10): 36,870 µm

Dv (50): 239,017 µm

Dv (90): 455,543 µm

Figure 74: Microplastic distribution for sample A-19. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

The sample is dominated by fibres with 11 of them, and there are 3 fragments along with it. Besides a few green and blue pieces, most were not assigned any colour.

4.19 A-18

Figure 75: Image of sampling site A-18, red arrow marks the spot from where the sample was picked. The orange arrow shows a plastic bag entangled between the vegetation.

Positioned about 3.3 km downstream of the Ombrone River, the channel width is 73 metres. Vegetation was sparsely present on the riverbank. No significant anthropogenic changes to the river were observed here.

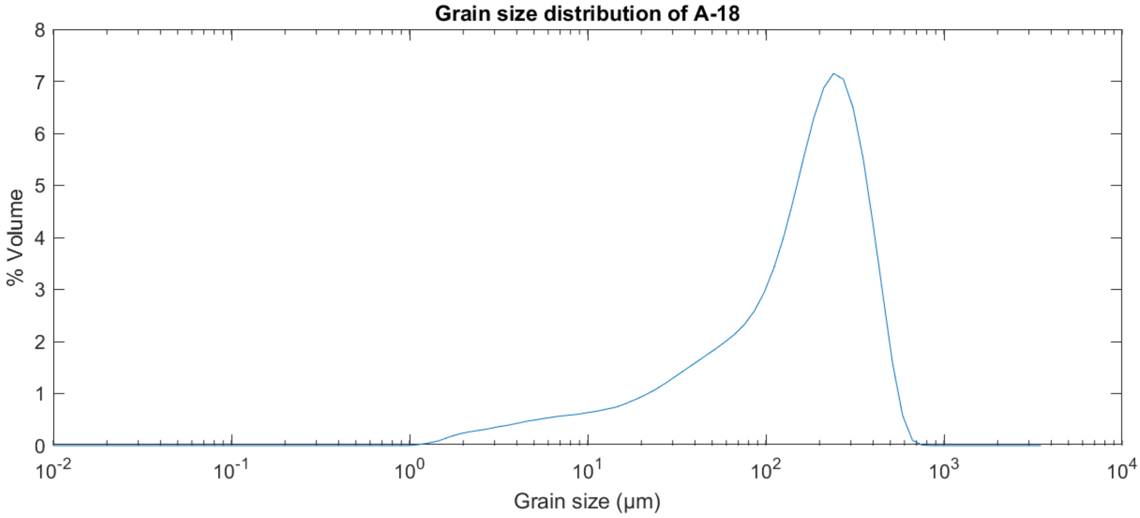


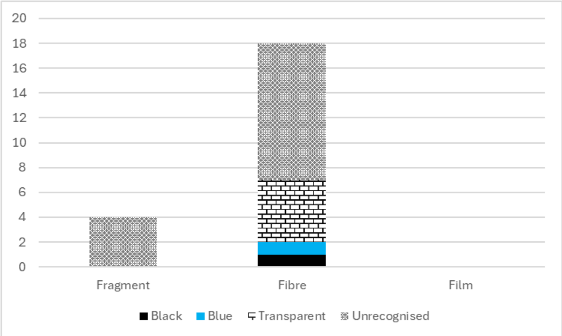
Figure 76: Grain size distribution of A-18

The sediments are fine-grained sand. The sample is strongly fine-skewed and poorly sorted. The following are the important Dv values:

Dv (10): 20,458 μm

Dv (50): 180,479 μm

Dv (90): 394,095 μm



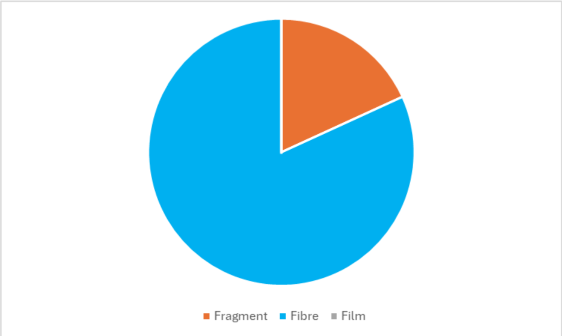


Figure 77: Microplastic distribution for sample A-18. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

The sample is full of fibres, with 18 of them, followed by fragments, that were 4 in number. Most pieces in this sample were hard to detect so a UV light was used for assistance.

4.20 A-16

Figure 78: Image of sampling site A-16, red arrow marks the spot from where the sample was picked. The orange arrow shows a plastic bag entangled between the vegetation.

This site is located just downstream of the comune of Limite. The river has reduced in width to 44 metres. There is a substantial amount of vegetation present at the sampling location. Some plastic wastes were found trapped between the plants. There are artificial levees on both sides of the river, and a barrier is present 1km downstream of this site.

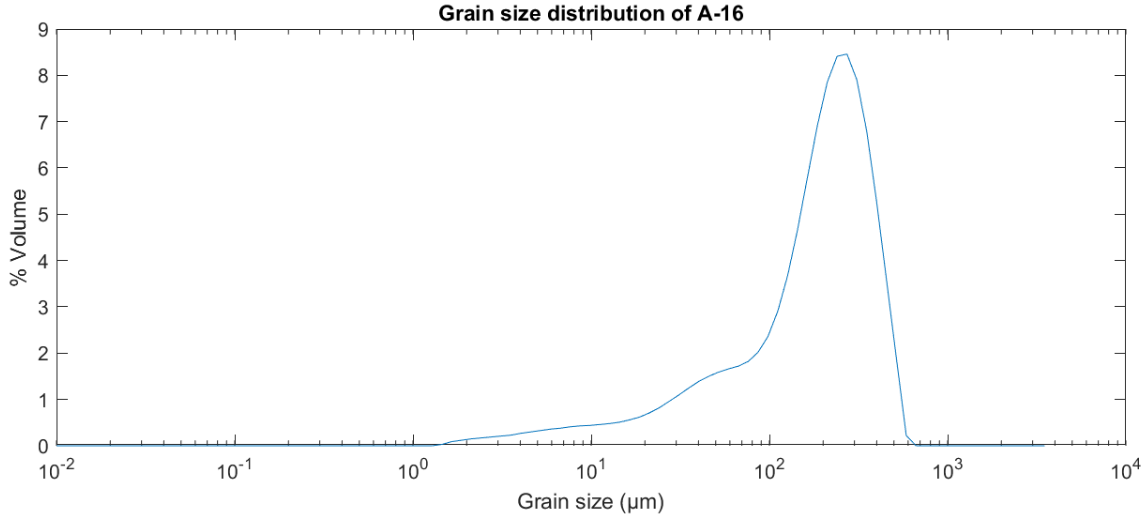


Figure 79: Grain size distribution of A-16

The sediments are fine-grained sand. The sample is strongly fine-skewed and poorly sorted. The following are the important Dv values:

Dv (10): 34,023 μm

Dv (50): 212,373 μm

Dv (90): 409,069 μm

Figure 80: Microplastic distribution for sample A-16. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

The sample is again full of fibres (19) and fragments (15). Some colours were recognised for some pieces but most were not assigned any colour.

4.21 A-14

Figure 81: Image of sampling site A-14, red arrow marks the spot from where the sample was picked.

Situated almost exactly at the confluence between Arno and Elsa, barely a few metres downstream in the Arno River. The channel width is 72 metres here. A significant amount of vegetation and dead plant debris is present, and the riverbank is extremely muddy. No obvious signs of artificial works on the Arno River were observed in this location.

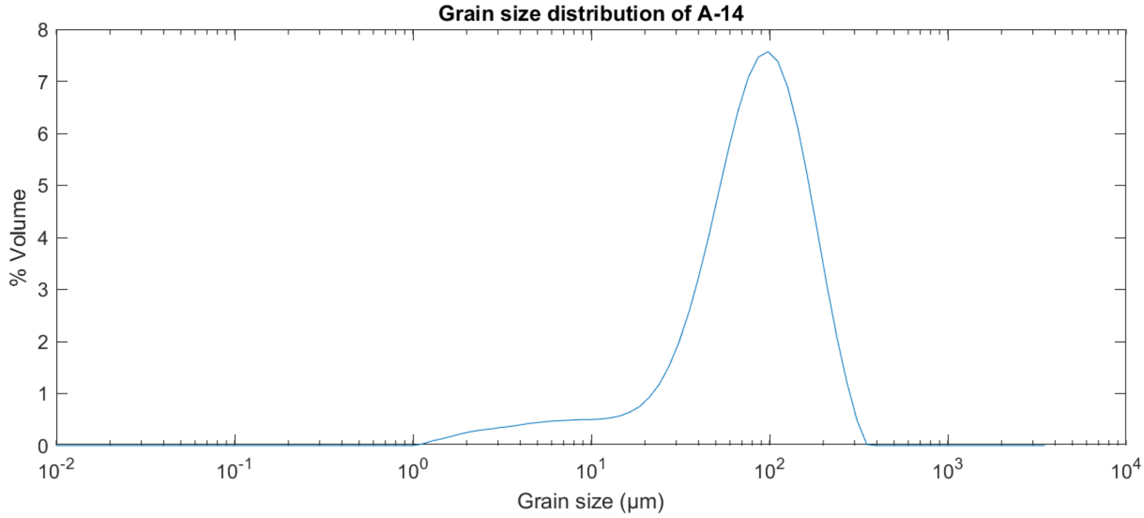


Figure 82: Grain size distribution of A-14

The sediments are very fine-grained sand. The sample is fine-skewed and poorly sorted. The following are the important Dv values:

Dv (10): 24,263 µm

Dv (50): 88,566 µm

Dv (90): 191,091 µm

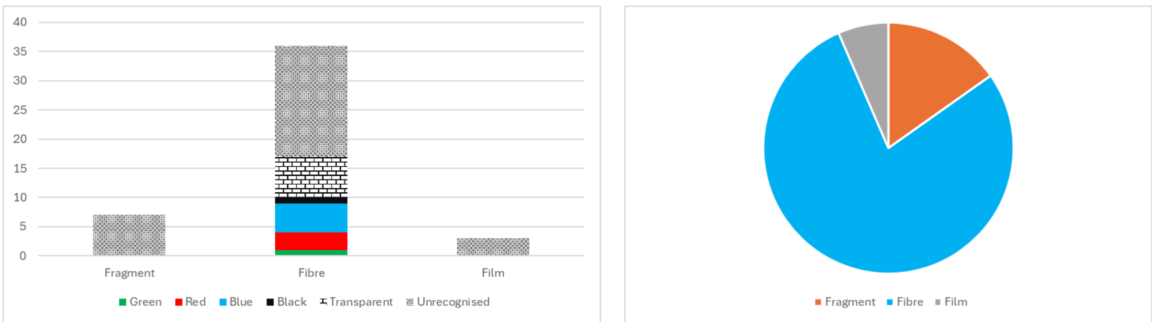


Figure 83: Microplastic distribution for sample A-14. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

Dominated by fibres, we have a total of 36 fibres in this sample, 7 fragments and 3 films. Some red, blue and green pieces were identified, however, most remained in the unrecognised category.

4.22 A-12

Figure 84: Image of sampling site A-12, red arrow marks the spot from where the sample was picked.

Located just downstream of the town of Santa Croce sull'Arno, the site is at an inflexion point between two meander bends. The river's width here is 64 metres. Vegetation is present on the riverbanks; however, the sample was picked from a spot that did not have much vegetation. No obvious signs of anthropogenic changes were observed here.

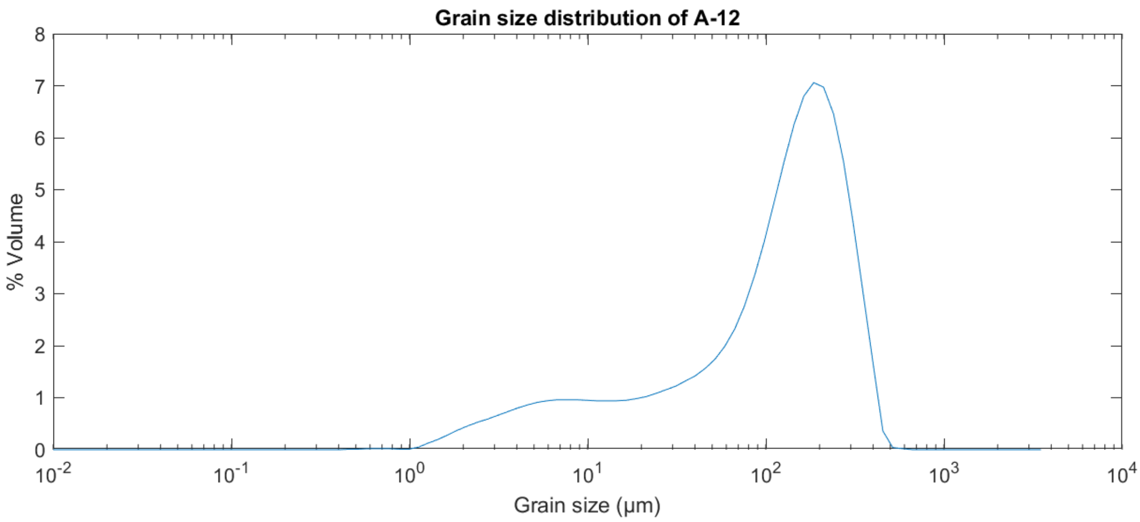


Figure 85: Grain size distribution of A-12

The sediments are very fine-grained sand. The sample is strongly fine-skewed and poorly sorted. The following are the important Dv values:

Dv (10): 9,228 µm

Dv (50): 139,192 µm

Dv (90): 305,693 µm

Figure 86: Microplastic distribution for sample A-12. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

The sample had 22 fibres, 7 fragments, and no film. Besides a few black, 1 pink and 1 blue fibres, colours were not recognised for the rest of them.

4.23 A-10

Figure 87: Image of sampling site A-10, red arrow marks the spot from where the sample was picked.

Situated downstream of the town of La Rotta on one side, and open farmland on the other side of the river, the river has a width of 65 metres here. There is a significant amount of vegetation present here. No obvious signs of manmade changes were observed in this part of the river.

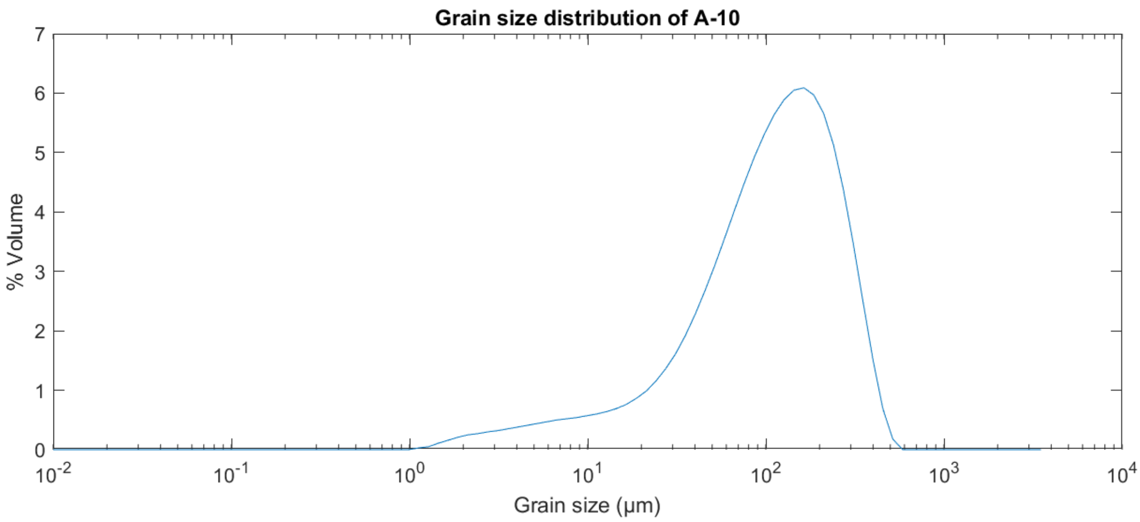


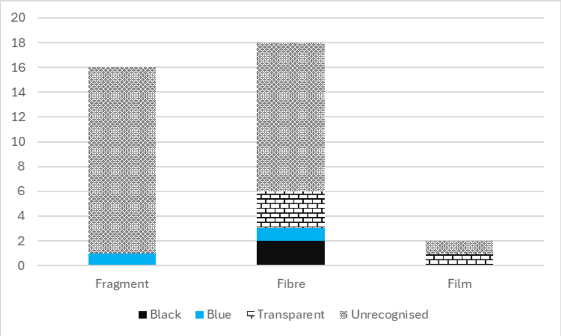
Figure 88: Grain size distribution of A-10

The sediments are very fine grained. The sample is strongly fine skewed and poorly sorted. The following are the important Dv values:

Dv (10): 22,835 µm

Dv (50): 119,656 µm

Dv (90): 294,833 µm



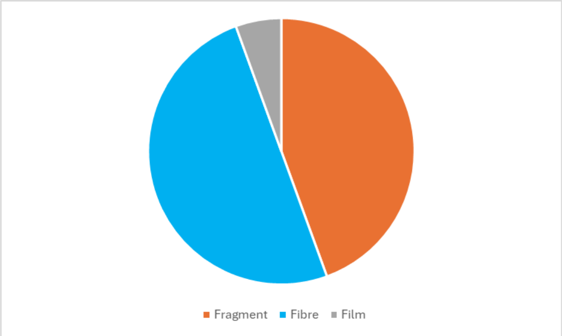


Figure 89: Microplastic distribution for sample A-10. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

The sample had a slightly even distribution between fibres and fragments, with 18 fibres, 16 fragments, and 2 films. We were unable to recognise their colour properly.

4.24 A-8

Figure 90: Image of sampling site A-8, red arrow marks the spot from where the sample was picked.

This sample collection site is located about 4 km downstream of Pontedera. The width of the river here is about 106 metres The sampling area is quite sandy. There is vegetation present in the surroundings, with a lot of plastic waste entangled in the plants. Just upstream of the place, there is a bridge, with a barrier-like structure under it, which creates a cascading flow in the river.

Figure 91: Closeup image of the sampling location, the layers are visible for new and older sediments (left). Plastic wastes entangled with the vegetation in this site (right).

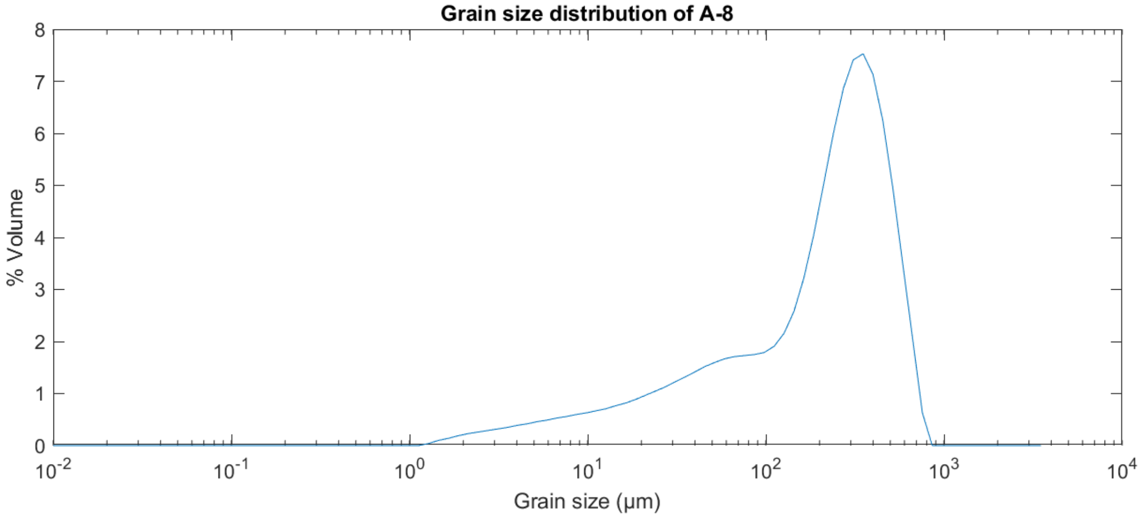


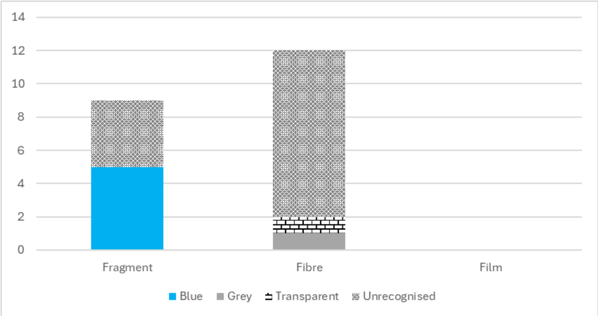
Figure 92: Grain size distribution of A-8

The sample is fine-grained sand. It shows strong fine skewness and is poorly sorted. The following are the important Dv values:

Dv (10): 21,634 µm

Dv (50): 251,969 µm

Dv (90): 531,478 µm



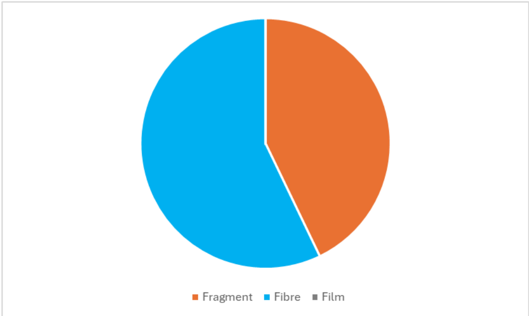


Figure 93: Microplastic distribution for sample A-8. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

The sample has 12 fibres and 9 fragments, some fragments were blue, whereas the rest were not assigned any colour.

4.25 A-6

Figure 94: Image of sampling site A-6, red arrow marks the spot from where the sample was picked.

This place is situated downstream of a place named Caprona. The channel width here is about 50 metres. Much vegetation is present in this region. There is a canal called Zambra di Calci, that flows along with the river and merges with it just downstream of the collection site.

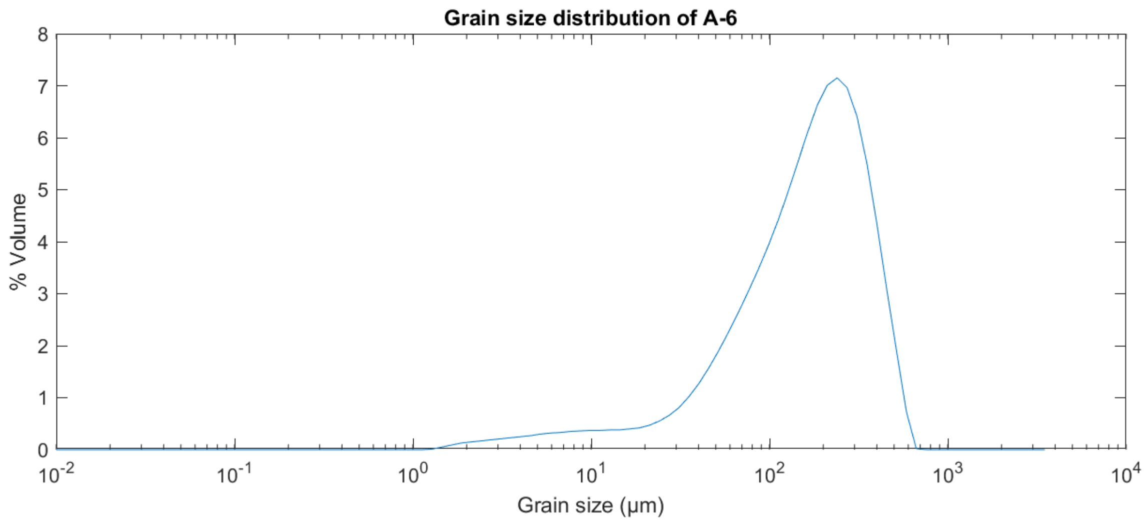


Figure 95: Grain size distribution of A-6

The sediments are fine-grained sand. The sample is strongly fine-skewed and poorly sorted. The following are the important Dv values:

Dv (10): 43,387 µm

Dv (50): 184,894 µm

Dv (90): 400,892 µm

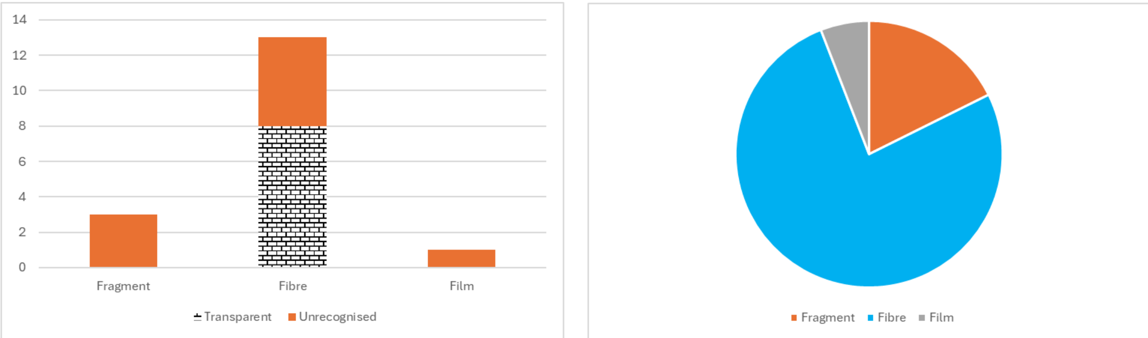


Figure 96: Microplastic distribution for sample A-6.

Full of mostly fibres over other shapes, we found 13 fibres, 3 fragments and 1 film in this sample. All the pieces in this sample were either transparent or too difficult to assign any colour, so they all belong in the unrecognised category.

4.26 A-5

Figure 97: Image of sampling site A-5, red arrow marks the spot from where the sample was picked.

This sampling site is located upstream of Pisa, between farmlands and small villages. The channel width has changed to 94 metres here. The sample was picked up from the inner bank of a meander bend. The riverbank had a lot of shrubs, along with dead plant debris. No signs of anthropogenic changes were observed here.

Figure 98: Closeup of the sampling location, the freshly deposited sand is distinguishable from the bud below.

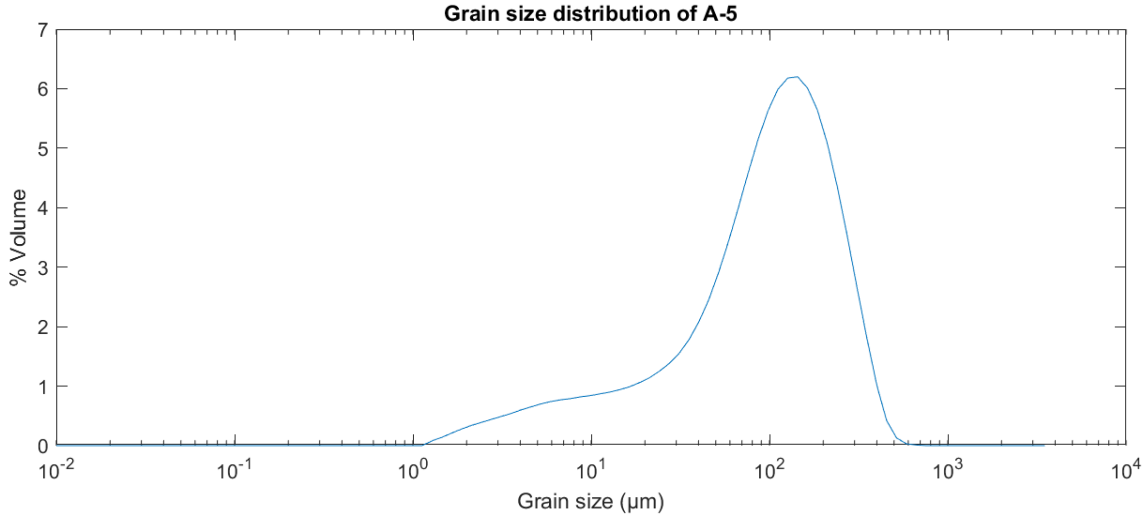


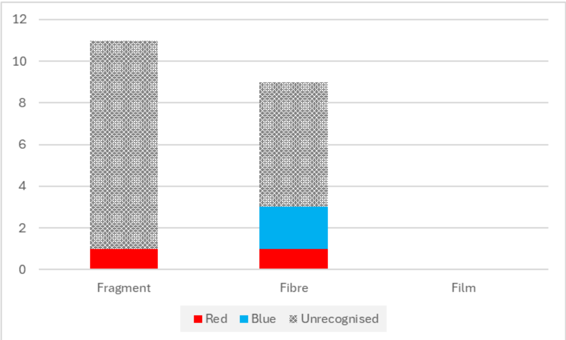
Figure 99: Grain size distribution of A-5

The sediments are very fine-grained sand. The sample is strongly fine-skewed and poorly sorted. The following are the important Dv values:

Dv (10): 13,277 µm

Dv (50): 109,145 µm

Dv (90): 269,369 µm



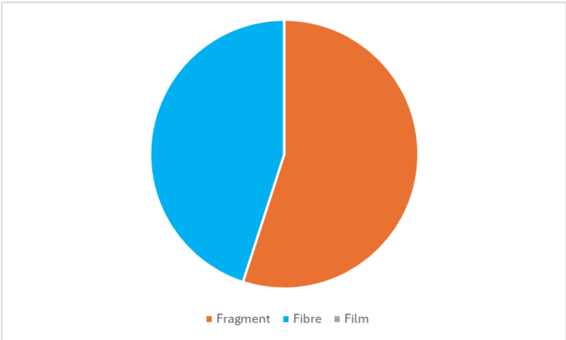


Figure 100: Microplastic distribution for sample A-5. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

Dominated by fragments, we have 9 fibres and 11 fragments in this sample. Most of the pieces remain to be assigned any valid colour, but a couple of red and blue pieces were recognised.

4.27 A-2

Figure 101: Image of sampling site A-2, red arrow marks the spot from where the sample was picked.

Located about 3.5 km downstream of Pisa, this was the last sample collected before reaching the mouth of the river where sand deposited during the flood could be found. The river has a width of 118 metres here. The sampling site was deeply vegetated (reeds), and the riverbank seemed to be stabilised on one side anthropogenically.

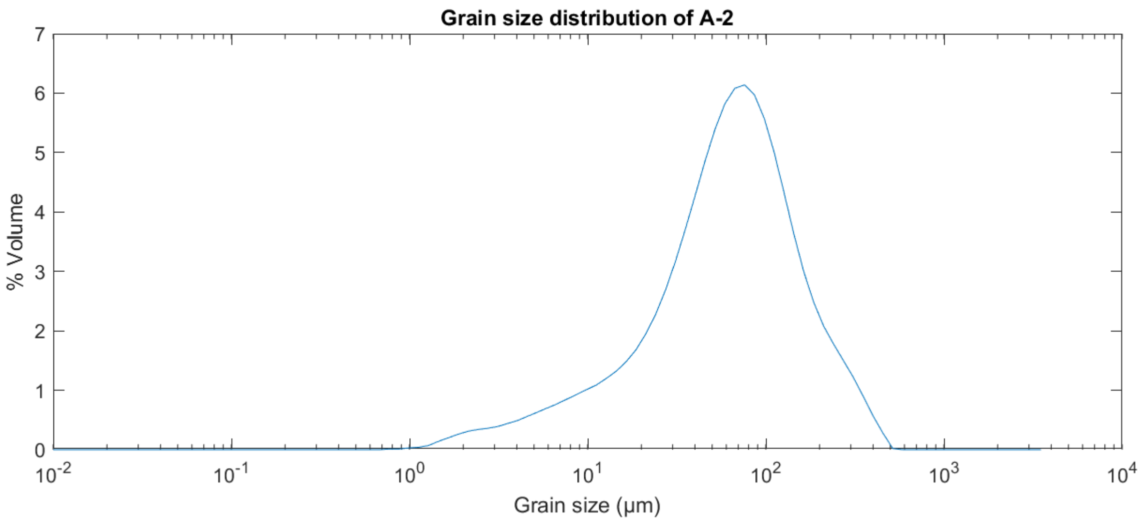


Figure 102: Grain size distribution of A-2

The sediment is coarse silt. The sample is strongly fine-skewed and poorly sorted. The following are the important Dv values:

Dv (10): 13,218 µm

Dv (50): 67,649 µm

Dv (90): 193,974 µm

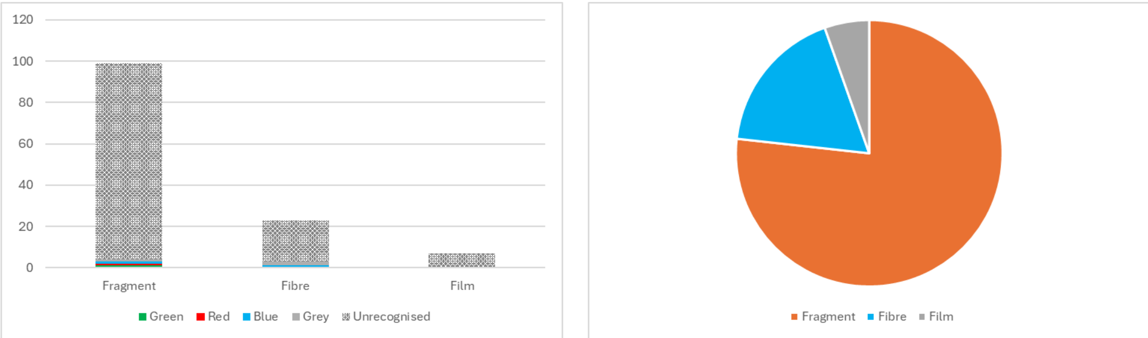


Figure 103: Microplastic distribution for sample A-2. The colour distribution of different shapes (left) and the proportions of different shapes in the sample(right)

With an outrageously high number of fragments, most of them being extremely small, this sample has 99 of them, followed by 23 fibres and 7 films. Totalling up, the microplastic count to 129 in this sample. Most pieces, due to their extremely small size, were detected under UV, and no colour was assigned.

4.28 Overview

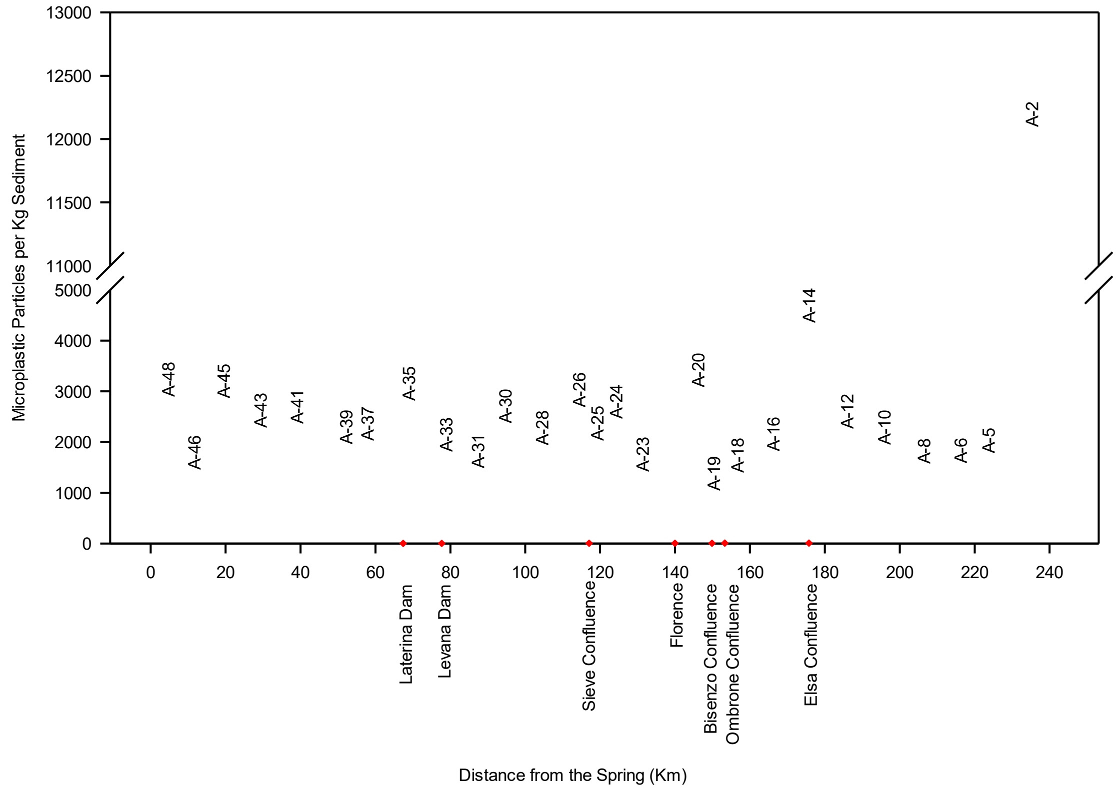


Figure 104: Plot of microplastics in each sample along the Arno River, and their distance from the spring, along with important points along the river.

The analysis of the collected samples shows that there is no absolute trend in the microplastic distribution along the river. Most samples seem to have a concentration of around 2000 MPs per Kg. There are a few spikes, one after Florence (A-20), another at the confluence of Elsa, and one downstream of Pisa. The microplastic concentration fluctuates throughout the course of the river.

The following table shows the overview of all 27 samples.

Sample No.	Fragments	Fibres	Films	Total	Sample weight (g)	MPs per Kg Sediment
A-48	0	33	3	36	15.38	2340.702211
A-46	1	17	0	18	16.52	1089.588378
A-45	3	34	0	37	15.22	2431.011827

A-43	13	18	0	31	15.62	1984.635083
A-41	6	22	2	30	15.01	1998.667555
A-39	8	16	0	24	15.05	1594.684385
A-37	2	23	0	25	15.05	1661.129568
A-35	8	27	1	36	15.1	2384.10596
A-33	4	18	0	22	15.22	1445.466491
A-31	7	15	1	23	20.54	1119.76631
A-30	4	25	2	31	15.46	2005.174644
A-28	10	13	2	25	15.88	1574.307305
A-26	8	22	7	37	15.04	2460.106383
A-25	15	14	3	32	19.22	1664.932362
A-24	31	15	2	48	17.63	2722.631877
A-23	3	12	1	16	15.13	1057.501652
A-20	13	17	3	33	12.15	2716.049383
A-19	3	11	0	14	20.65	677.9661017
A-18	4	18	0	22	21.18	1038.71577
A-16	15	19	0	34	24.02	1415.487094
A-14	7	36	3	46	11.02	4174.228675
A-12	7	22	0	29	15.24	1902.887139
A-10	16	18	2	36	22.65	1589.403974
A-8	9	12	0	21	18.77	1118.806606
A-6	3	13	1	17	15.05	1129.568106
A-5	11	9	0	20	15.11	1323.626737
A-2	99	23	7	129	11.22	11497.3262

Table 2: Overview of microplastics extracted from all the samples collected along the Arno River.

To sum things up, a total of 310 fragments, 522 fibres and 40 films were found in the samples, totalling the microplastics count found in the study to be 872. This averages the number of microplastics in the Arno River to be 1963.4 MPs per kg of sediment.

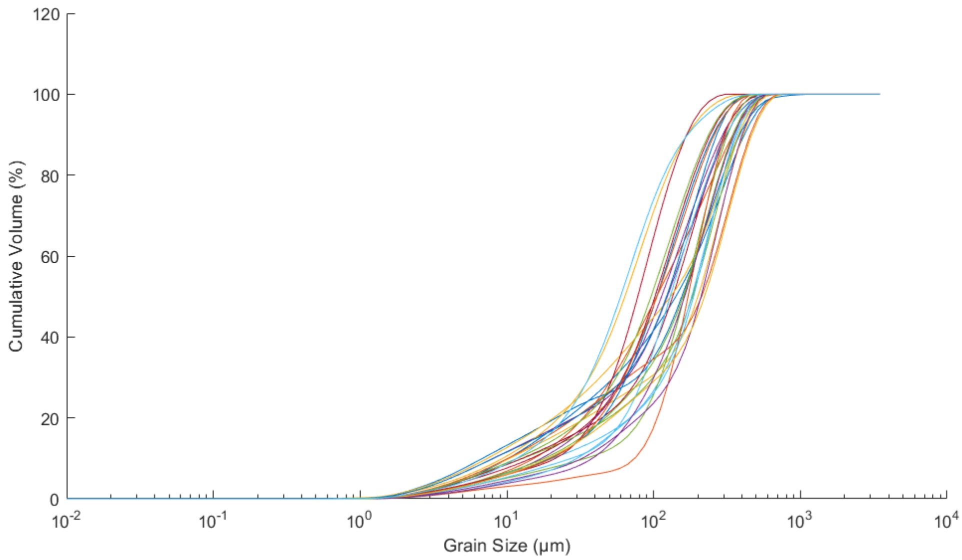


Figure 105: Cumulative plot of the grain size of all the samples. All the samples lie in a narrow range of grain sizes.

Looking at the cumulative plot of all the grain sizes for all the samples collected throughout the river (Figure 105), they all lie in a very narrow range between 50-200 μm. Most of them are fine to very fine-grained sand. They are all fine-skewed, and poorly sorted.

5 Discussion

5.1 Microplastic content in the Arno River: comparison with other rivers

Microplastics were present in all the samples at a significantly high amount. The sediments in the Arno River show significant variability in microplastic abundance throughout its course, with a minimum of 677.97 MPs per kg (A-19) to 11497.37 MPs per kg (A-2), and an average microplastic concentration of 1963.4 MPs per kg sediment. With the exception of a few spikes, it is noticed that the microplastic concentration has roughly decreased along the course of the river. However, a definite trend can hardly be detected. We compared this result with other studies done in the sediments of different rivers globally, and the values are quite comparable.

Microplastic Abundance	River	Location	Reference
2.05±0.75	Ebro River	Spain	(Simon-Sánchez et al., 2019)
0,13 - 0,74	Thame Tributaries	England	(Horton et al., 2017b)
0,16 - 0,43	River Kelvin	Scotland	(Blair et al., 2019)
0,53 - 8,07	Tisza River	Hungary	(Kiss et al., 2021)
0,065 - 7,56	St. Lawrence River	Canada	(Crew et al., 2020)
1.97(average)	Nakdong River	South Korea	(Eo et al., 2019)
0,23 - 3,76	Rhine River	Germany	(Klein et al., 2015)
0,19 - 0,58	Vistula River	Poland	(Sekudewicz et al., 2021)
0,36 - 1,32	Wei River	China	(Ding et al., 2019)
2,56 - 10,24	West River	China	(Huang et al., 2021)
0.082±0.06	Yangtze	China	(Di & Wang, 2018)
0,1 - 0,58	Yangtze River	China	(Fan et al., 2019)

0,42 - 8,18	Amazon Rivers	Brazil	(Gerolin et al., 2020)
0.018-0.629	Antuã River	Portugal	(Rodrigues et al., 2018)
58.04±52.64	Besòs	Spain	(Gonzalez-Saldias et al., 2024)
55.78±21.29	Tordera	Spain	(Gonzalez-Saldias et al., 2024)
1.96 (average)	Arno River	Italy	This Study

Table 3: List of microplastic concentrations found in rivers worldwide

Table 3: List of microplastic concentrations found in rivers worldwideTable 3 shows the abundance of microplastic in some major rivers worldwide. This table shows that the Arno River appears to be among the most polluted rivers in the world. The microplastic abundance in the sediments from the Arno River is much higher than that found in the sediments of several rivers in China (Ding et al., 2019; Fan et al., 2019; Huang et al., 2021) that are considered to be heavily polluted. This is quite concerning as the Arno River basin is not as large as some of the rivers such as the Yangtze River, or the Wei River. Looking at this figure at face value, however, have several issues. The dominance of fibres over the other shapes of microplastics is consistent with several other studies in riverine systems such as the Wei River in China (Ding et al., 2019b). It is also observed that the proximal parts of the Arno River, which is sparsely populated, show much higher microplastic concentrations than the rivers from densely populated countries.

The sampling methods for all these studies are not the same. Different studies sample sediments from different facies and cannot be compared directly. Sediments picked up from sidebars cannot be compared to the sediments from bedload. (Ghinassi et al., 2023) showed that the mechanism of microplastic entrapment in sediment under different sedimentary facies is different. Moreover, they showed slight enrichment in microplastic content in the surface samples compared to the bedload sediments. Several of the studies in Table 3 do not specify the sedimentary facies from where the sampling was done. This creates a major issue for comparison. Furthermore, the biggest ambiguity arises from the method of separation. Several studies use NaCl solution, due to its affordability and non-hazardous nature. However, NaCl solutions can have a maximum density of 1.2 g cm^{-3}, which is not heavy enough to recover some of the commonly used plastic types (up to 1.4

g cm^{-3}). This can make the values lower than the real microplastic concentration(Sbarberi et al., 2024). This makes the comparison between different studies quite problematic.

5.2 Effect of Dams on Microplastic Downstream Propagation

Dams tend to store microplastics within their sediments over time (Gao et al., 2023). (Watkins et al., 2019) showed that microplastics accumulate in the sediments behind dams. They showed that the sediments trapped by the dams consistently had significantly higher microplastic abundance when compared to the sediments upstream or downstream of the dams, with higher numbers upstream when compared to downstream. They attributed this to the availability of long settling times and relatively slow flow velocities within reservoirs. However, another study from dams in the Orange-Vaal River shows that there is no significant difference in microplastic abundance upstream and downstream of dams (Weideman et al., 2019).

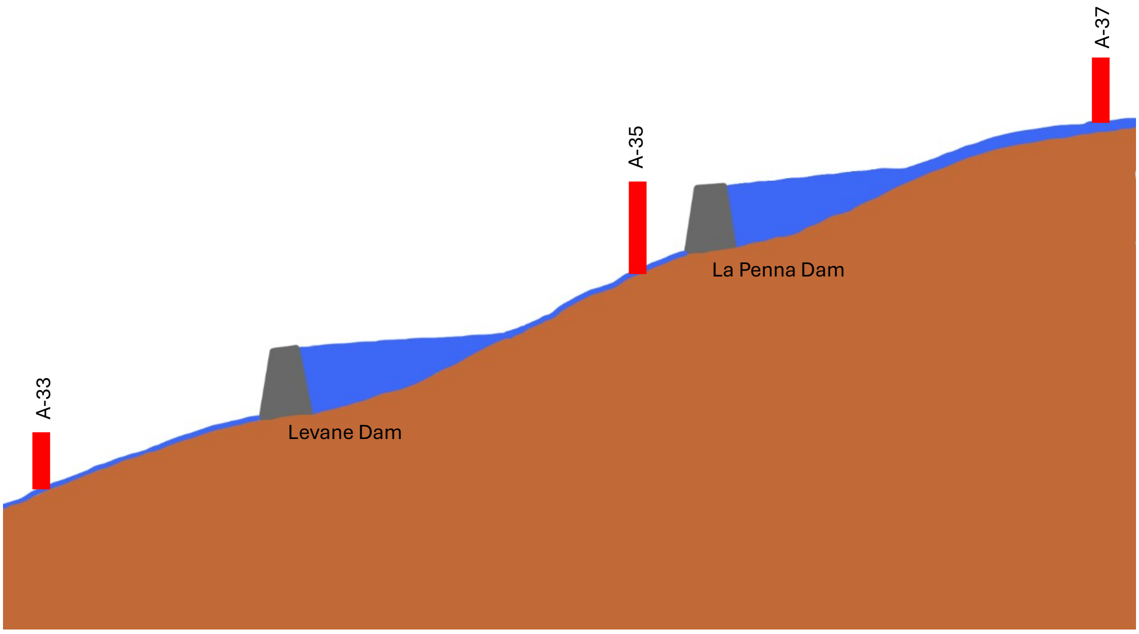


Figure 106: Schematic sketch describing the microplastic abundances across the two dams. The height of the bars are proportional to the microplastic abundance.

In our study, we have two dams, La Penna and Levane Dams, about 10 km apart. Looking at the microplastic abundances across the La Penna dam, the concentration measured downstream of the dam (A-35) is higher than the concentration upstream (A-37). This suggests that this dam is acting as a source, rather than a sink for microplastics. We also have the Maestro canal merging with the Arno River just above the dam, which could be carrying more microplastics, however, the high concentration downstream of the dam appears certainly anomalous compared to previous studies. The downstream dam (Levane) seems to be acting as a sink, as microplastic abundance has decreased in the sample downstream (A-33). The result is contradictory to what (Watkins et al., 2019) suggest, and we do not see a consistent trend in the behaviour of these two dams when looking at the concentration of microplastic in sediments upstream and downstream of them.

5.3 Effects of Major Cities and Tributaries

The role of major towns and cities in injecting microplastics into rivers is well-known (Jin et al., 2023; Kunz et al., 2023) Riverien tributaries, draining densely populated areas, can also inject a significant amount of microplastics into the river (Kukkola et al., 2023).

Looking at the influence of major cities, results from this study show that both Florence and Pisa are injecting a significant amount of microplastics into the river, giving rise to major spikes in the microplastic concentration in the sediments. The sample picked downstream of Pisa (A-2) was the most polluted throughout the river with a concentration of 11497.33 MPs per kg. As for the effect of major tributaries, The Elsa River is adding a significant amount of microplastics into the Arno River. The Ombrone River is also causing a small increase in the microplastic concentration along the Arno River. However, the Bisenzio River, which drains the city of Prato, is reducing the concentration of microplastics in Arno. Prato has been known to be a major industrial hub for centuries in the frame of textile (Bellandi & Santini, 2019), however, the Bisenzio River, surprisingly, is not carrying microplastics from that area into the Arno River, and sample A19 show a content lower than that documented in the spring areas. Looking at the Sieve River, the largest tributary of Arno, it seems to be reducing the microplastic concentration as well, despite it draining the large and densely populated area of the Mugello basin. The effect of different tributaries in the Arno River varies significantly. We can partly attribute this to the drainage basin of the individual tributaries, but, for situations like the Bisenzio River, where we know that it drains highly polluted areas, this logic does not work.

5.4 General Trend

Our results suggest that the general rule with regards to dams, cities and tributaries suggested by previous studies, although holds in some cases, cannot be applied to all cases. Significant variations in microplastic trends are observed between different cities and tributaries along the river. Both dams along the river tend to behave differently despite being relatively close to one another.

Looking at the overall distribution of microplastics throughout the river, the microplastic abundance is roughly decreasing along the course within an overall irregular distribution. Except for the spikes created by the major cities and the Elsa River, the upper reaches of the river in the Casentino and upper Valdarno sub-basins are more polluted than the lower reaches. The forest sites in the upper reaches of the river, although scarcely populated, were treated as illegal garbage dumping grounds a few decades ago, as highlighted by the presence of plastic waste at the riverbanks. The breakdown of these plastic waste particles could be contributing to the high concentrations of microplastics in these areas, especially if we consider the reduced size of the river at these sites. Several small towns and cities do not show a proper pattern concerning microplastic input into the river. In the case of San Giovanni Valdarno (A-30), an increase in microplastic abundance is observed, whereas, in some other cities such as Bibbiena (A-43) and Stia (A-46), the microplastic abundance decreases. Looking downstream, we do not see any trends concerning smaller towns/cities. The city of Pontedera does not seem to contribute to the microplastic pollution at all (A-8), whereas a small village of Limite (A-16), which is much smaller than Pontedera has a higher microplastic abundance.

We did not find any significant relationship between the microplastic abundance and sediment characteristics, this result is similar to what was observed in another study in the Po River (Sbarberi et al., 2024).

The sediments investigated here were deposited during the same flood event, consistently collected from the same sedimentary facies, characterized by a very similar grain size and processed in the same extraction method. This eliminates any possible variability in microplastic abundances due to different depositional environments, sampling methods, seasonal variability and extraction methods. The high degree of variability in microplastic throughout the river does not follow many trends with land use patterns and population density, as different cities show different levels of microplastic pollution with not much correlation to the size or population of these cities. This suggests that very local hydrodynamic processes probably played an important role in controlling localized accumulation. These processes dominantly rule the distribution of microplastics, preventing or accelerating the deposition of microplastics differently in different areas. The relationships between watershed land use, surface runoff generation, and the sources of microplastics are still not understood properly(Correa-Araneda et al., 2022). Our study shows there is a high degree of variability in these parameters within the river along the different reaches. The influence of river hydrodynamics on microplastic transport, settling and re-suspension presents complex questions about mechanisms and microplastic dynamics(Correa-Araneda et al., 2022), and an intuitive downstream increase of microplastic content within a riverine system cannot be assumed as a rule

The shape could influence the microplastic dynamics along the catchment (Correa-Araneda et al., 2022; Meng et al., 2020). In this study, we did not see any relevant role in the shape of the microplastic particles as most of the samples were dominated by fibres, with only a few exceptions in some places, but no pattern emerged.

The microplastic concentration along rivers is generally attributed to human presence or activities. However, these environmental variables can differ significantly in different areas and do not seem to follow any general rule. Microplastics likely enter rivers from a wide range of sources and through various pathways such as runoff from soils (e.g., landfills), other water bodies, wastewater treatment plant effluents, and human activities such as fishing, agriculture, and recreation (Meng et al., 2020; Rodrigues et al., 2018), influencing the microplastic concentration along rivers to different extents in different places.

6 Conclusion

Our study shows that microplastics were present in all 27 samples collected along the 241 km stretch of the Arno River. Our study shows an average microplastic concentration of 1963.4 MPs per kg, which places it amongst the most polluted rivers worldwide. However, this comparison is quite troublesome due to different methodologies and separation processes.

The results from the two dams suggest that there is no general "one size fits all" rule when it comes to the upstream and downstream concentrations of microplastics across dams. Similarly, the effects of major cities into the river are quite substantial and cause major spikes in the microplastic abundances both in Florence and Pisa. The concentrations across confluences with some important tributaries are quite variable, as some tend to inject more microplastics into the river (Elsa and Ombrone) whereas others unexpectedly tend to 'dilute' the microplastics in the river.

The overall trend along the river reveals some complex patterns as the microplastic abundance tends to fluctuate in a seemingly random fashion. Factors such as population size and land use patterns do not seem to play a major role in the distribution of microplastics along the river. Our study shows that there are significant variabilities in microplastic concentrations within the same river system in different areas due to the influence of very local factors. Thus, a better understanding of microplastic dynamics in freshwater systems is required to regulate the different factors that could be contributing to the microplastics in different areas.

References

Barrows, A. P. W., Cathey, S. E., & Petersen, C. W. (2018). Marine environment microfiber contamination: Global patterns and the diversity of microparticle origins. *Environmental Pollution*, *237*, 275–284. https://doi.org/10.1016/j.envpol.2018.02.062

Bellandi, M., & Santini, E. (2019). Territorial servitization and new local productive configurations: the case of the textile industrial district of Prato. *Regional Studies*, *53*(3), 356–365. https://doi.org/10.1080/00343404.2018.1474193

Blair, R. M., Waldron, S., Phoenix, V. R., & Gauchotte-Lindsay, C. (2019). Microscopy and elemental analysis characterisation of microplastics in sediment of a freshwater urban river in Scotland, UK. *Environmental Science and Pollution Research*, *26*(12), 12491–12504. https://doi.org/10.1007/s11356-019-04678-1

Bonotto, G. (2020). *Analisi di microplastiche in sedimenti fluviali* [Tesi di laurea magistrale in Scienze e Tecnologie per l'Ambiente e il Territorio].

Cencetti, C., & Tacconi, P. (2005). The Fluvial Dynamics of the Arno River. *Giornale Di Geologia Applicata*, *1*, 193–202. https://doi.org/10.1474/GGA.2005-01.0-19.0019

Corcoran, P. L., de Haan Ward, J., Arturo, I. A., Belontz, S. L., Moore, T., Hill-Svehla, C. M., Robertson, K., Wood, K., & Jazvac, K. (2020). A comprehensive investigation of industrial plastic pellets on beaches across the Laurentian Great Lakes and the factors governing their distribution. *Science of the Total Environment*, *747*. https://doi.org/10.1016/j.scitotenv.2020.141227

Correa-Araneda, F., Pérez, J., Tonin, A. M., Esse, C., Boyero, L., Díaz, M. E., Figueroa, R., Santander-Massa, R., Cornejo, A., Link, O., Jorquera, E., & Urbina, M. A. (2022). Microplastic concentration, distribution and dynamics along one of the largest Mediterranean-climate rivers: A whole watershed approach. *Environmental Research*, *209*. https://doi.org/10.1016/j.envres.2022.112808

Crew, A., Gregory-Eaves, I., & Ricciardi, A. (2020). Distribution, abundance, and diversity of microplastics in the upper St. Lawrence River. *Environmental Pollution*, *260*. https://doi.org/10.1016/j.envpol.2020.113994

Di, M., & Wang, J. (2018). Microplastics in surface waters and sediments of the Three Gorges Reservoir, China. *Science of the Total Environment*, *616–617*, 1620–1627. https://doi.org/10.1016/j.scitotenv.2017.10.150

Dikareva, N., & Simon, K. S. (2019). Microplastic pollution in streams spanning an urbanisation gradient. *Environmental Pollution*, *250*, 292–299. https://doi.org/10.1016/j.envpol.2019.03.105

Ding, L., Mao, R. fan, Guo, X., Yang, X., Zhang, Q., & Yang, C. (2019a). Microplastics in surface waters and sediments of the Wei River, in the northwest of China. *Science of the Total Environment*, *667*, 427–434. https://doi.org/10.1016/j.scitotenv.2019.02.332

Ding, L., Mao, R. fan, Guo, X., Yang, X., Zhang, Q., & Yang, C. (2019b). Microplastics in surface waters and sediments of the Wei River, in the northwest of China. *Science of the Total Environment*, *667*, 427–434. https://doi.org/10.1016/j.scitotenv.2019.02.332

Dris, R., Agarwal, S., & Laforsch, C. (2020). Plastics: From a Success Story to an Environmental Problem and a Global Challenge. In *Global Challenges* (Vol. 4, Issue 6). John Wiley and Sons Inc. https://doi.org/10.1002/gch2.202000026

Du, H., & Wang, J. (2021). Characterization and environmental impacts of microplastics. In *Gondwana Research* (Vol. 98, pp. 63–75). Elsevier Inc. https://doi.org/10.1016/j.gr.2021.05.023

Eo, S., Hong, S. H., Song, Y. K., Han, G. M., & Shim, W. J. (2019). Spatiotemporal distribution and annual load of microplastics in the Nakdong River, South Korea. *Water Research*, *160*, 228–237. https://doi.org/10.1016/j.watres.2019.05.053

Fan, Y., Zheng, K., Zhu, Z., Chen, G., & Peng, X. (2019a). Distribution, sedimentary record, and persistence of microplastics in the Pearl River catchment, China. *Environmental Pollution*, *251*, 862–870. https://doi.org/10.1016/j.envpol.2019.05.056

Fan, Y., Zheng, K., Zhu, Z., Chen, G., & Peng, X. (2019b). Distribution, sedimentary record, and persistence of microplastics in the Pearl River catchment, China. *Environmental Pollution*, *251*, 862–870. https://doi.org/10.1016/j.envpol.2019.05.056

Gao, B., Chen, Y., Xu, D., Sun, K., & Xing, B. (2023). Substantial burial of terrestrial microplastics in the Three Gorges Reservoir, China. *Communications Earth and Environment*, *4*(1). https://doi.org/10.1038/s43247-023-00701-z

Gerolin, C. R., Pupim, F. N., Sawakuchi, A. O., Grohmann, C. H., Labuto, G., & Semensatto, D. (2020). Microplastics in sediments from Amazon rivers, Brazil. *Science of the Total Environment*, *749*. https://doi.org/10.1016/j.scitotenv.2020.141604

Ghinassi, M., Michielotto, A., Uguagliati, F., & Zattin, M. (2023). Mechanisms of microplastics trapping in river sediments: Insights from the Arno river (Tuscany, Italy). *Science of the Total Environment*, *866*. https://doi.org/10.1016/j.scitotenv.2022.161273

Gonzalez-Saldias, F., Sabater, F., & Gomà, J. (2024a). Microplastic distribution and their abundance along rivers are determined by land uses and sediment granulometry. *Science of the Total Environment*, *933*. https://doi.org/10.1016/j.scitotenv.2024.173165

Gonzalez-Saldias, F., Sabater, F., & Gomà, J. (2024b). Microplastic distribution and their abundance along rivers are determined by land uses and sediment granulometry. *Science of the Total Environment*, *933*. https://doi.org/10.1016/j.scitotenv.2024.173165

Horton, A. A., Svendsen, C., Williams, R. J., Spurgeon, D. J., & Lahive, E. (2017a). Large microplastic particles in sediments of tributaries of the River Thames, UK – Abundance, sources and methods for effective quantification. *Marine Pollution Bulletin*, *114*(1), 218–226. https://doi.org/10.1016/j.marpolbul.2016.09.004

Horton, A. A., Svendsen, C., Williams, R. J., Spurgeon, D. J., & Lahive, E. (2017b). Large microplastic particles in sediments of tributaries of the River Thames, UK – Abundance, sources and methods for effective quantification. *Marine Pollution Bulletin*, *114*(1), 218–226. https://doi.org/10.1016/j.marpolbul.2016.09.004

Huang, D., Li, X., Ouyang, Z., Zhao, X., Wu, R., Zhang, C., Lin, C., Li, Y., & Guo, X. (2021a). The occurrence and abundance of microplastics in surface water and sediment of the West River downstream, in the south of China. *Science of the Total Environment*, *756*. https://doi.org/10.1016/j.scitotenv.2020.143857

Huang, D., Li, X., Ouyang, Z., Zhao, X., Wu, R., Zhang, C., Lin, C., Li, Y., & Guo, X. (2021b). The occurrence and abundance of microplastics in surface water and sediment of the West River downstream, in the south of China. *Science of the Total Environment*, *756*. https://doi.org/10.1016/j.scitotenv.2020.143857

Jambeck, J. R., Geyer, R., Wilcox, C., Siegler, T. R., Perryman, M., Andrady, A., Narayan, R., & Law, K. L. (2015). Plastic waste inputs from land into the ocean. *Science*, *347*(6223), 768–771. https://doi.org/10.1126/science.1260352

Jin, X., Fu, X., Lu, W., & Wang, H. (2023). The effects of riverside cities on microplastics in river water: A case study on the Southern Jiangsu Canal, China. *Science of The Total Environment*, *858*, 159783. https://doi.org/10.1016/J.SCITOTENV.2022.159783

Kane, I. A., & Clare, M. A. (2019). Dispersion, accumulation, and the ultimate fate of microplastics in deep-marine environments: A review and future directions. In *Frontiers in Earth Science* (Vol. 7). Frontiers Media S.A. https://doi.org/10.3389/feart.2019.00080

Kiss, T., Fórián, S., Szatmári, G., & Sipos, G. (2021). Spatial distribution of microplastics in the fluvial sediments of a transboundary river – A case study of the Tisza River in Central Europe. *Science of the Total Environment*, *785*. https://doi.org/10.1016/j.scitotenv.2021.147306

Klein, S., Worch, E., & Knepper, T. P. (2015). Occurrence and spatial distribution of microplastics in river shore sediments of the rhine-main area in Germany. *Environmental Science and Technology*, *49*(10), 6070–6076. https://doi.org/10.1021/acs.est.5b00492

Kukkola, A., Runkel, R. L., Schneidewind, U., Murphy, S. F., Kelleher, L., Sambrook Smith, G. H., Nel, H. A., Lynch, I., & Krause, S. (2023). Prevailing impacts of river management on microplastic transport in contrasting US streams: Rethinking global microplastic flux estimations. *Water Research*, *240*. https://doi.org/10.1016/j.watres.2023.120112

Kunz, A., Schneider, F., Anthony, N., & Lin, H. T. (2023). Microplastics in rivers along an urban-rural gradient in an urban agglomeration: Correlation with land use, potential sources and pathways. *Environmental Pollution*, *321*. https://doi.org/10.1016/j.envpol.2023.121096

Laermanns, H., Reifferscheid, G., Kruse, J., Földi, C., Dierkes, G., Schaefer, D., Scherer, C., Bogner, C., & Stock, F. (2021). Microplastic in Water and Sediments at the Confluence of the Elbe and Mulde Rivers in Germany. *Frontiers in Environmental Science*, *9*. https://doi.org/10.3389/fenvs.2021.794895

Lebreton, L. C. M., Van Der Zwet, J., Damsteeg, J. W., Slat, B., Andrady, A., & Reisser, J. (2017). River plastic emissions to the world's oceans. *Nature Communications*, *8*. https://doi.org/10.1038/ncomms15611

Meng, Y., Kelly, F. J., & Wright, S. L. (2020). Advances and challenges of microplastic pollution in freshwater ecosystems: A UK perspective. In *Environmental Pollution* (Vol. 256). Elsevier Ltd. https://doi.org/10.1016/j.envpol.2019.113445

Plastic Europe. (2020). *Position Paper A Circular Economy to End Plastic Pollution-Sustainable Production and Consumption*.

Plastics in Italy. (2022).

Qin, F., Du, J., Gao, J., Liu, G., Song, Y., Yang, A., Wang, H., Ding, Y., & Wang, Q. (2020). Bibliometric Profile of Global Microplastics Research from 2004 to 2019. *International Journal of Environmental Research and Public Health*, *17*, 5639. https://doi.org/10.3390/ijerph17165639

Rinaldi, M., & Simon, A. (1998). Bed-level adjustments in the Arno River, central Italy. In *Geomorphology* (Vol. 22). ELSEVIER.

Rodrigues, M. O., Abrantes, N., Gonçalves, F. J. M., Nogueira, H., Marques, J. C., & Gonçalves, A. M. M. (2018a). Spatial and temporal distribution of microplastics in water and sediments of a freshwater system (Antuã River, Portugal). *Science of the Total Environment*, *633*, 1549–1559. https://doi.org/10.1016/j.scitotenv.2018.03.233

Rodrigues, M. O., Abrantes, N., Gonçalves, F. J. M., Nogueira, H., Marques, J. C., & Gonçalves, A. M. M. (2018b). Spatial and temporal distribution of microplastics in water and sediments of a freshwater system (Antuã River, Portugal). *Science of the Total Environment*, *633*, 1549–1559. https://doi.org/10.1016/j.scitotenv.2018.03.233

Sbarberi, R., Magni, S., Boggero, A., Della Torre, C., Nigro, L., & Binelli, A. (2024). Comparison of plastic pollution between waters and sediments in four Po River tributaries (Northern Italy). *Science of the Total Environment*, *912*. https://doi.org/10.1016/j.scitotenv.2023.168884

Sekudewicz, I., Dąbrowska, A. M., & Syczewski, M. D. (2021). Microplastic pollution in surface water and sediments in the urban section of the Vistula River (Poland). *Science of the Total Environment*, *762*. https://doi.org/10.1016/j.scitotenv.2020.143111

Simon-Sánchez, L., Grelaud, M., Garcia-Orellana, J., & Ziveri, P. (2019). River Deltas as hotspots of microplastic accumulation: The case study of the Ebro River (NW Mediterranean). *Science of the Total Environment*, *687*, 1186–1196. https://doi.org/10.1016/j.scitotenv.2019.06.168

Wagner, M., & Lambert, S. (2018). *Freshwater Microplastics The Handbook of Environmental Chemistry 58 Series Editors: Damià Barceló · Andrey G. Kostianoy*. http://www.springer.com/series/698

Watkins, L., McGrattan, S., Sullivan, P. J., & Walter, M. T. (2019). The effect of dams on river transport of microplastic pollution. *Science of the Total Environment*, *664*, 834–840. https://doi.org/10.1016/j.scitotenv.2019.02.028

Weideman, E. A., Perold, V., & Ryan, P. G. (2019). Little evidence that dams in the Orange–Vaal River system trap floating microplastics or microfibres. *Marine Pollution Bulletin*, *149*. https://doi.org/10.1016/j.marpolbul.2019.110664

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