Microplastics in beach sediments of the Attica coastal area, Saronic Gulf and the island of Andros, Cyclades, Aegean Sea

Ioanna-Maria Trifona

Master's Thesis

MSc in Sustainability & Quality in Marine Industry

Department of Maritime Studies

University of Piraeus

March, 2022

Supervisor: Professor Fani Sakellariadou

Abstract

The present study is an assessment of microplastic pollution in beach sediments from the Attica coastal area, Saronic Gulf and the island of Andros, Cyclades. Sediment sampling was performed at the high tide line of selected stations during the summer of 2021. In total, twenty-five sediment samples from Attica and five samples from Andros Island were collected and examined. The presence of large microplastic particles (1-5 mm) was investigated. Their abundance varied, ranging from 0 to 8 items per 5 grams of dry sediment. Higher concentrations were noticed on Voula, Agios Kosmas and Faliro – Naftikos Omilos beaches in Attica, and on Gialia beach in the island of Andros. The possible relation between granulometry and microplastic distribution was also examined, with greater microplastic concentration found in coarser sediments. Moreover, the morphology of detected microplastics was recorded; fragments, fibers, foams and films consisted the observed microplastic shapes. The fragment type was dominant in samples from Attica, while fibers were more numerous in samples from Andros Island. Regarding the color, black/grey, blue, green, purple, red, white/yellow, transparent and colorful microplastics were noticed. Green and blue particles were more common. Additionally, the polymer composition of selected microplastics was investigated using FT-IR analysis, which revealed the probable presence of five polymers: Polystyrene, Polypropylene, Low-Density Polyethylene, Polyvinyl Chloride and Ethylene-Vinyl Acetate. The results of FT-IR analysis showed that Polystyrene is possibly the dominant identified polymer. The probable origin of microplastic presence in the studying areas was also discussed. Samples from the Saronic Gulf presented greater occurrence of microplastics, perhaps due to Attica’s high population and to the proximity to major urban sources.

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1. Introduction

Nowadays, the abundance and distribution of plastics into the world are so extensive that the scientific community uses them as key indicators of the recent and contemporary period, defining a new historical epoch; "The Plasticene" (Campanale *et al.*, 2020). Durability and longevity are the main distinct properties of plastic, leading to fragmentation to smaller pieces and finally in so-called microplastics instead of degrading (Streit-Bianchi *et al.*, 2020).

Plastic debris has been detected worldwide in all types of ecosystems and in sizes from picometers to many meters. According to size definition, plastic litter can be mainly classified as macroplastics (over 25 mm), mesoplastics (5-25 mm), large microplastics (1-5 mm), small microplastics (smaller than 1 mm) and also nanoplastics (1-1,000 nm) (Figure 1.1). The subgroup that has raised particular concern is microplastics, as they are becoming ubiquitous and persistent pollutants in the natural environment (De Ruijter *et al.*, 2019).

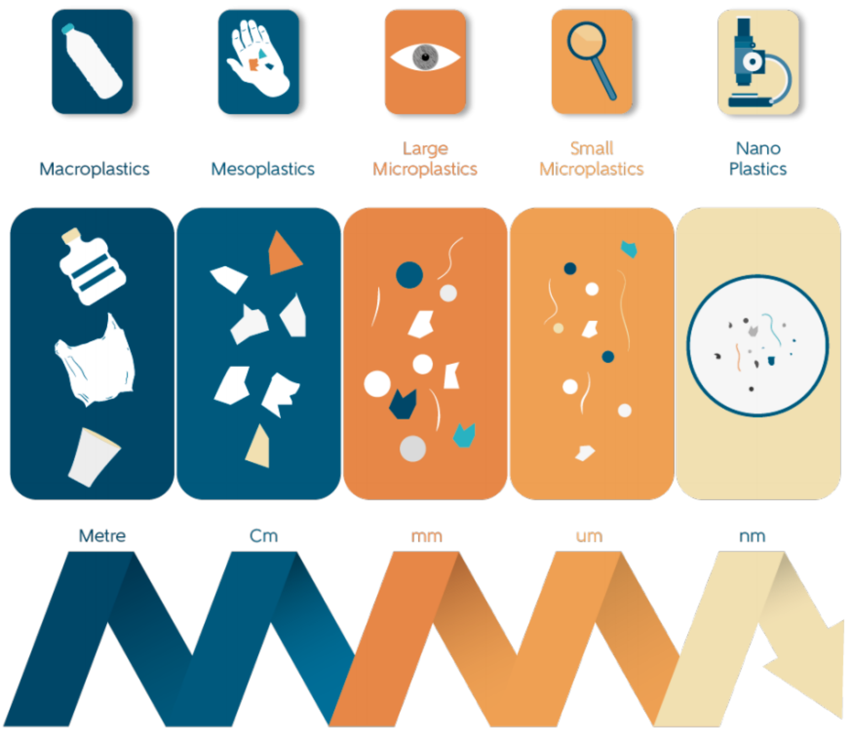

Figure 1.1: Size definition of plastics. Source: Stothra Bhashyam *et al.*, 2021.

Microplastics are defined as smaller plastic pieces or fragments that derive from physical and/or photochemical fragmentation of larger plastic debris such as bags, clothes, household items, building materials or fishing and aquaculture gear, as well as by accidental release of plastic resin pellets used as raw materials in the plastics industry (Cole *et al.*, 2011).

Microplastic pollution is among the global environmental concerns of the 21st century, making microplastics indicators of the Anthropocene (Frias *et al.*, 2021). Plastics do not always behave the same way, and that is why it is hard to know generically their origin and their final destination in the marine and coastal environment (de Haan *et al.*, 2019). Microplastic debris has been found in all potential reservoirs, such as coastlines, sea surface, seafloor, biota as well as the water column, sediments and sea ice (Figure 1.2) (Law, 2016).

Considering that the more abundant ecosystems are in coastal seas than in the open ocean, microplastics are more likely to enter the ecosystem in coastal seas (Sagawa *et al*., 2018). Coastal food webs are more susceptible to the trophic transfer of microplastics than those in other habitats (Browne *et al.*, 2010).

Beach sediments are suggested to be long-term sinks and have a high potential to accumulate microplastics (Martellini *et al.*, 2018). Being in immediate interaction with the sea, they function as permanent or transient reservoirs of plastic debris during its drift history (Karkanorachaki *et al.*, 2018).

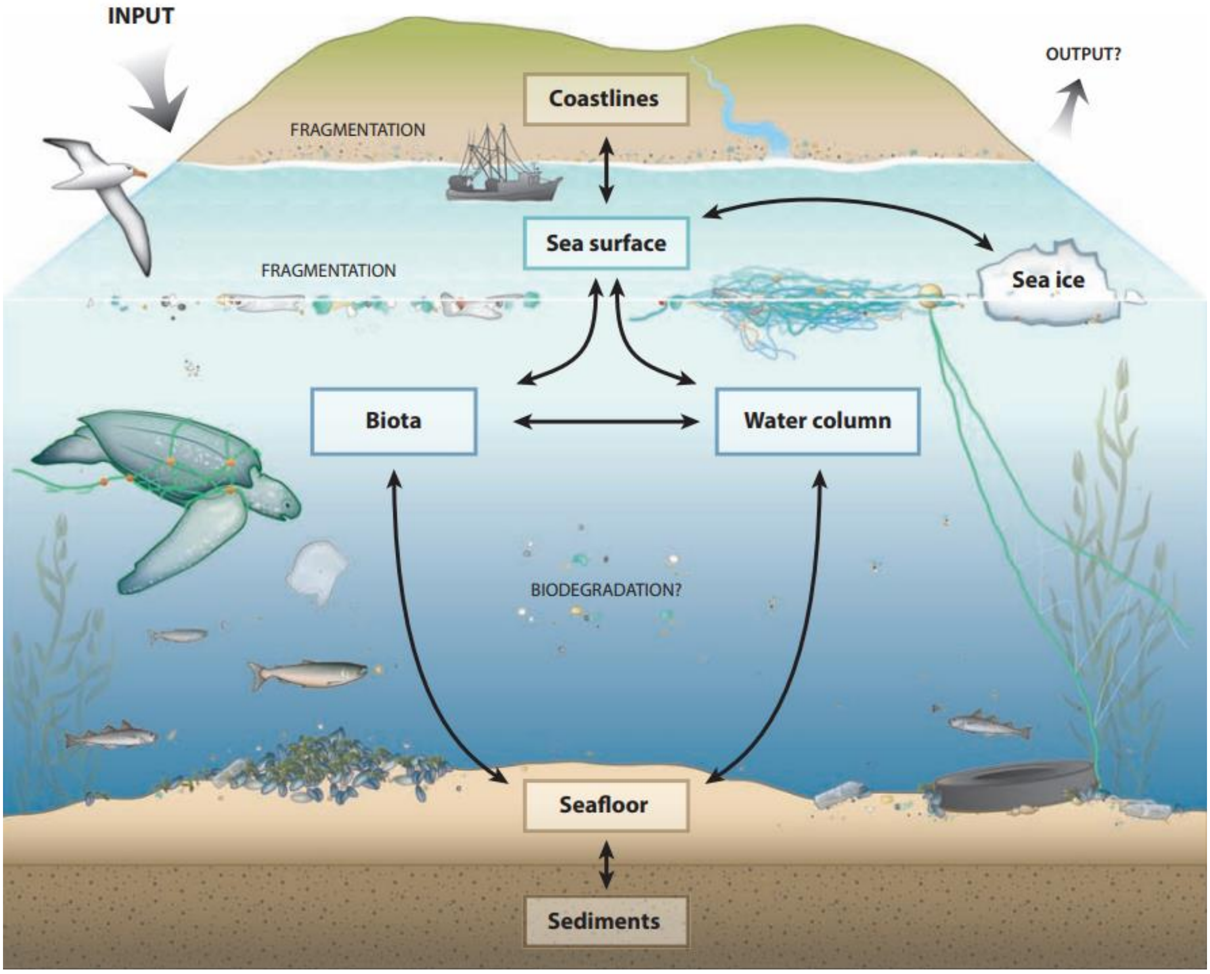

Figure 1.2: The mass balance of plastics in the marine environment. Source: Law, 2016.

The large gray arrows indicate fluxes into and out of the marine environment, including potential biodegradation of plastics. The boxes indicate reservoirs of plastic debris, and the black arrows indicate potential pathways of plastics between reservoirs. Fragmentation of plastics caused by weathering and biological processes can occur in all reservoirs, especially when exposed to sunlight (at the sea surface and along coastlines).

The importance of plastic debris in the marine and coastal environment was first noticed visually as physical direct impacts on marine biota and seabirds, such as entanglement in ropes, netting, severe harm and death (Figure 1.3) (Martins and Sobral, 2011). Nowadays, main focus is set at the ingestion of microplastics (Figure 1.4). Their ingestion by fauna and their accumulation in lower trophic levels could potentially lead to cascading effects in marine and coastal food webs (Frias *et al.*, 2014).

Figure 1.3: Common dolphin entangled in plastic. Source: Stothra Bhashyam *et al.*, 2021.

Figure 1.4: Microplastics found inside a fulmar. Source: Stothra Bhashyam *et al.,* 2021.

Plastics are increasingly toxic over time as they absorb compounds on their hydrophobic surfaces while drifting in the sea (Hirai *et al.*, 2011), serving as vectors of contaminants to marine organisms (Carbery *et al.*, 2018). Plastic debris may contain, accumulate or adsorb organic toxic substances, including persistent organic pollutants and heavy metals, which may leach to the seawater or may be ingested by organisms together with the plastic (Rochman *et al.*, 2013). Toxic, carcinogenic and mutagenic sorbed compounds or plastic additives and plasticizers can be transferred and bioaccumulated in organisms (Rochman *et al.*, 2013).

More widespread ecological impacts are expected from microplastics rather than bigger plastics (Rochman *et al.*, 2013), as their small size facilitates organisms' intake (Lusher *et al.*, 2013). The variation in sizes, shapes and colors of microplastics is of particular concern since they could easily be mistaken for food by marine organisms and seabirds (Hidalgo-Ruz *et al.*, 2012). Microplastics occur in size ranges that are similar to many organisms from benthos and plankton communities. This strong overlap between size categories highlights the potential for microplastic ingestion by a wide variety of organisms (Hidalgo-Ruz *et al.*, 2012).

Lower fitness and reproductive failure are common impacts on marine biota, which may lead to changes in biological community structure (Derraik, 2002). The direct effects of microplastics ingestion include reduced feeding, blocking of the intestinal tract leading to weight loss, impaired bodily functioning and starvation (Wright *et al.*, 2013). It could also disrupt the endocrine, reproductive and circulatory systems, increase toxic load in smaller organisms (Laglbauer *et al.*, 2014), cause cancers in fish (Rochman *et al.*, 2013) and shorten the lifespan of many organisms (Wright *et al.*, 2013).

The impact of plastic on organisms varies according to the type and size of the debris and can occur at different levels of biological organization (Figures 1.5 and 1.6), in a wide range of habitats. The severity of interactions between organisms and plastic litter depends on the physiology, feeding habit, size and behavior of the animal involved, the location of the animal compared to plastic and the physical characteristics of the plastic itself (Werner *et al*., 2016). More than 690 species have encountered marine plastic debris and at least 17% of impacted species are listed on the IUCN Red List as near threatened or above (Gall and Thompson, 2015).

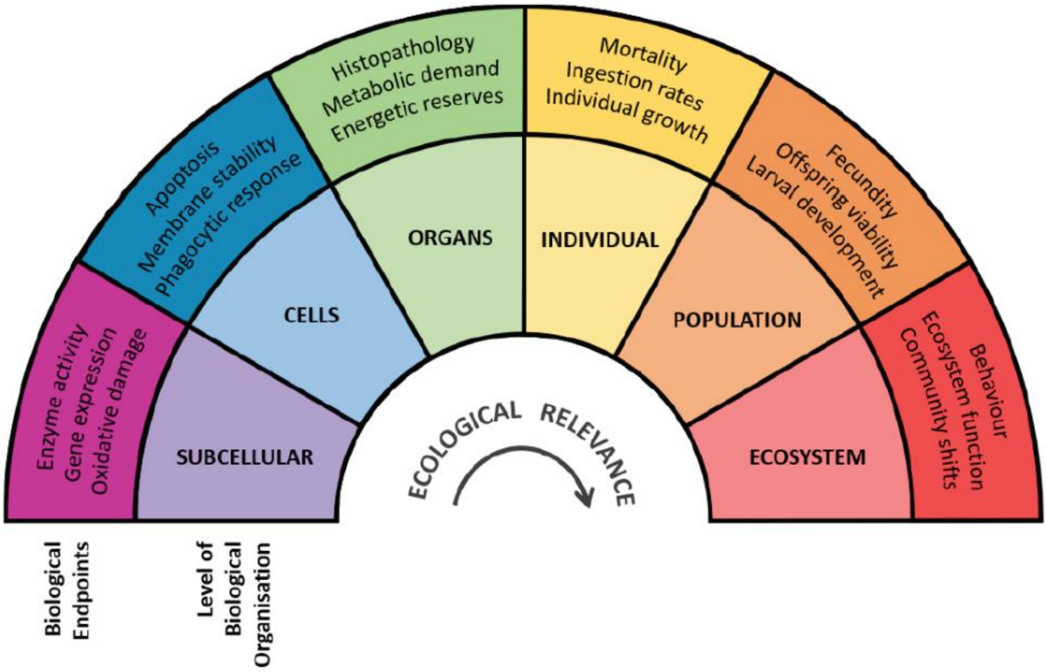

Figure 1.5: Impacts of microplastics on biota reported at various levels of biological organization. Source: SAPEA, Science Advice for Policy by European Academies, 2019.

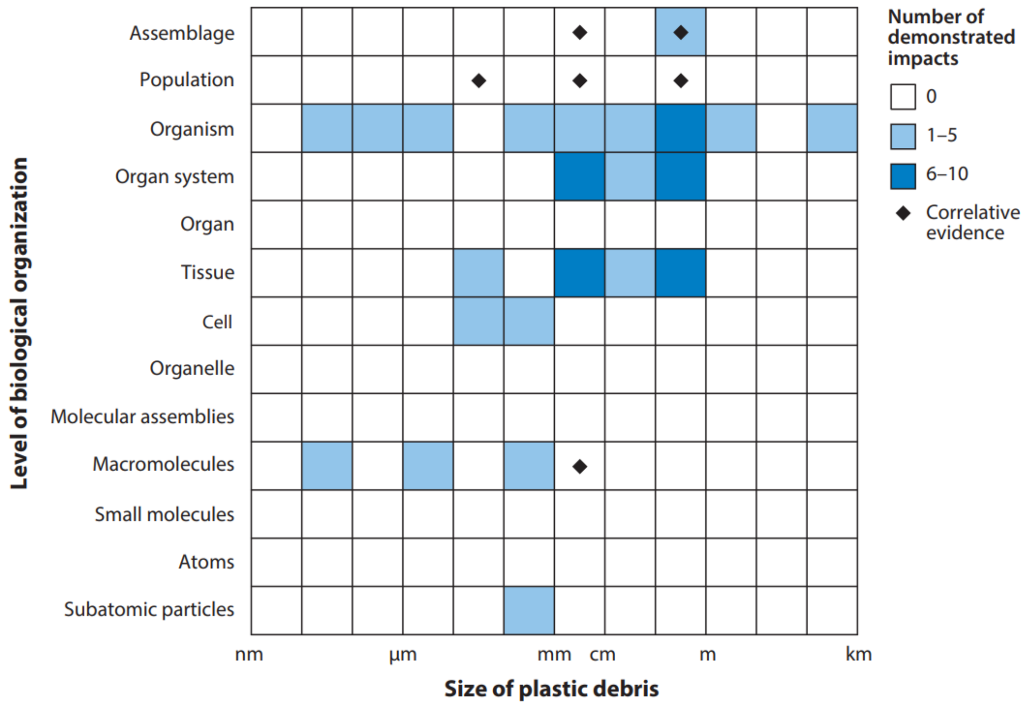

Figure 1.6: Demonstrated impacts of plastic marine debris as a function of debris size and affected level of biological organization. Source: Law, 2016.

Each matrix cell represents the number of impacts caused only by plastic marine debris. Diamonds in cells indicate correlative evidence supporting at least one impact.

Microplastics are highly bioavailable to organisms, either through direct ingestion or indirectly by trophic transfer from contaminated prey. Microplastics enter the food web from the lower levels (Figure 1.7) (Frias *et al.*, 2014), with consequences on the pelagic biota (Kedzierski *et al.*, 2019).

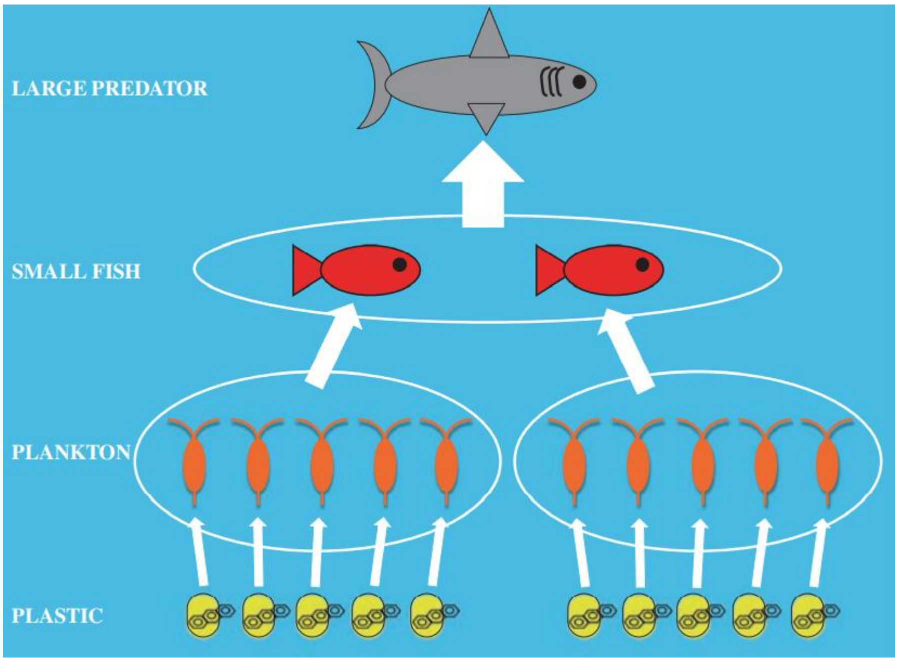

Figure 1.7: A scenario whereby organic chemicals from plastic may be transferred into lower trophic level organisms (e.g. zooplankton) via ingestion. Source: Rochman, 2015.

The accumulation at much greater concentrations via biomagnification in higher trophic level organisms (e.g. small fish and sharks) may ultimately lead to contaminated seafood for humans as a result of plastic contamination in marine food webs. The size of the arrows depicts how the body burden (i.e. bioaccumulation of chemicals) may magnify in predators as compared to their prey.

Trophic transfer represents an indirect, yet potentially major, pathway of plastic ingestion for any species whose feeding ecology involves the consumption of whole prey, including humans (Nelms *et al.*, 2018). Humans could suffer adverse health effects due to the exposure to microplastics (Figure 1.8) through unintentional ingestion via the food chain or inhalation and the consequent leaching of polycyclic aromatic hydrocarbons (Wright and Kelly, 2017). The trophic transfer of microplastics could also have significant consequences for seafood as a source of protein (Carbery *et al.*, 2018).

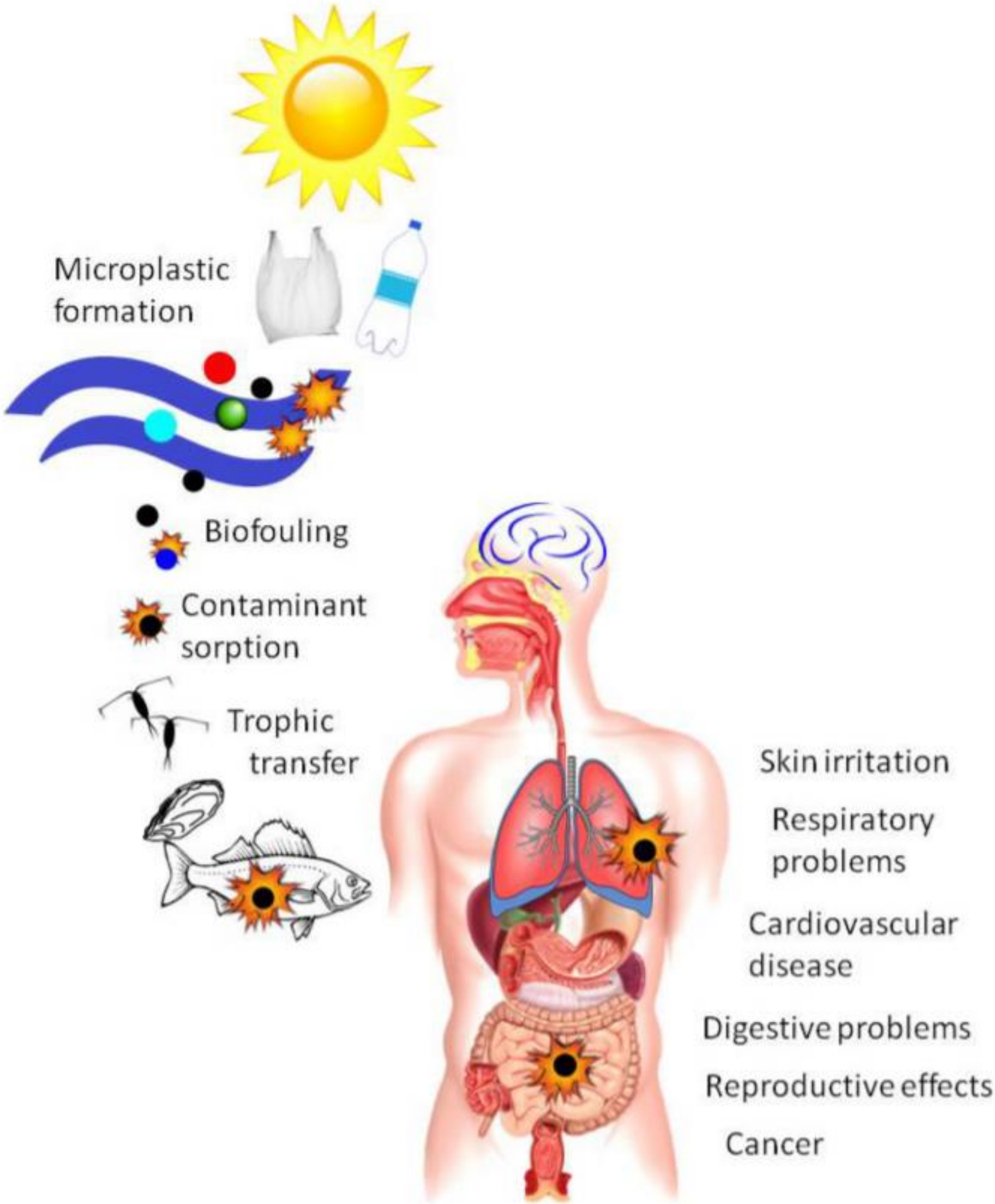

Figure 1.8: Potential human health effects resulting from the ingestion of microplastics. Source: Carbery *et al*., 2018.

Another concern related to plastic pollution in the marine environment is that small marine organisms such as barnacles or mollusks may grow on plastic debris and then use the lightweight material as means of transport (Figure 1.9). This allows them for travelling to new locations and eventually invading existing ecosystems (Allsopp *et al.*, 2006).

Figure 1.9: Barnacles colonizing a plastic cup. Source: Stothra Bhashyam *et al.*, 2021.

Tangible damages to humans caused by marine plastic debris are difficult to be estimated (Laglbauer *et al.*, 2014). The tourism industry faces monetary loss due to both a decrease in activity on polluted beaches and the costs of beach cleaning (Sheavly and Register, 2007). Safety issues arise from fishing lines, medical waste, discarded syringes and possibly from bacterial contamination of discarded hygiene waste (Sheavly and Register, 2007). Fishermen may also face damage to fishing gear, propeller entanglement and time losses due to gear cleaning as a result of macroplastic pollution (van Franeker *et al.*, 2005). It is still uncertain, though, whether marine debris can reduce fish quality through debris ingestion or tainting (van Franeker *et al.,* 2005). Moreover, indirect economic impacts result from the degradation of the marine environment (Laglbauer *et al.*, 2014).

Regarding the polymer types, it is a real fact that Polystyrene is found abundantly at sea, contains hazardous chemicals, and also is one of the six major polymers most produced and consumed, contributing to environmental pollution (Rochman *et al.*, 2013). It is likely the huge quantities of Polystyrene plastic waste scattered throughout oceans to generate copious quantities of degraded and eluted products, which may dissolve in any body of water or adsorb on the surface of sandy soil (Saido *et al.*, 2014). According to Kwon *et al*. (2015) Polystyrene plastic marine and coastal pollution is an environmental concern.

Polystyrene is a polymer that is low-cost, easy to process and it can be easily converted into a large number of semi-finished products like foams and films. It is not biodegradable (Saido *et al.*, 2003). It is the material of choice for many applications including food-packaging and disposable consumer plastic goods. Various foamed products, like drinking cups, egg cartons, trays, fast-food containers, cushioned packaging, thermal insulation, housewares, toys, cosmetic containers, covers, fixtures and also many medical applications are made of Polystyrene (Polymer database, 2021).

In addition, it has been shown that Styrofoam, which is expanded Polystyrene, can accumulate mercury if it is present in the environment (Abidli *et al.*, 2018).

Low-density Polyethylene is also a very common polymer in the natural environment. Carryout, grocery and mattress bags, squeezable bottles, food and bubble packaging, industrial, trash and can liners, pallet sheets, mulch, agricultural and construction film, waste bins, stretch- and shrink-wraps, shipping sacks and outdoor furniture are made of it (Crawford and Quinn, 2017).

Polypropylene is used to make fishing nets (Vianello *et al*., 2013) and it is very common to end on the beach. Polypropylene is characterized by low price and ease of processing, chemically inertness and many other attractive properties. The packaging industry is by far the largest consumer of Polypropylene followed by the textile and automotive industry. Products made of Polypropylene include disposable cups and cutlery, drinking straws, bottle caps, flexible food packaging, garbage bags, houseware articles, crates, tapes, labels, rope, toys, drainage pipes, pump parts, automotive bumpers, chemical tanks, gas cans, medical components, carpet fibers, sanitary products, filters and outdoor furniture among countless other products (Polymer database, 2021).

Ethylene-Vinyl Acetate copolymers are used for a myriad of applications in the packaging and plastic goods industries. Important applications include sealants in meat and dairy packaging structures, footwear, wire and cable insulation, pipes, toys, corks, photovoltaic encapsulation, medical packaging, hot melt adhesives, and lamination of glass to improve impact resistance (Polymer database, 2021).

Polystyrene, Polypropylene, low-density Polyethylene and Ethylene-Vinyl Acetate are low density plastics. According to Graca *et al.* (2017), low density polymers are constantly washed ashore and offshore which potentially favor their fragmentation in coastal zone. Low density microplastic concentration in beach sediments may be underestimated using current methods of microplastics separation due to their potentially very small size (Graca *et al*., 2017).

Polyvinyl Chloride finds extensive use is in the building and construction industry. It is used for water and sewage pipes, sidings, window frames, flooring, and wire and cable insulations. Other important applications are footwear, sporting goods, toys, and automotive parts like upholstery, floor mats, auto tops, and automotive wires and plastic films (Polymer database, 2021).

In conclusion, a huge concern is whether plastics represent a risk to marine and coastal ecosystems and also to human health (Campanale *et al.*, 2020). With the continued growth of plastics production worldwide, the impact on the natural environment warrant concern and stimulate new research, not only to quantify plastics contamination and its biological, social and economic impacts, but also to inform management solutions (Law, 2016).

2. Literature Review

The Mediterranean Sea is one of the most heavily polluted seas worldwide, especially with regard to plastics (Figure 2.1) (Deudero and Alomar, 2015). Plastic concentration in the basin is similar to that of the inner accumulation zones of the subtropical ocean gyres (Pedrotti *et al.*, 2016). Mediterranean has been proposed as the sixth greatest accumulation zone for marine litter and the most affected regarding to microplastics (Expósito *et al.*, 2021).

According to Suaria and Aliani (2014), plastic debris accounts for 82% of observed marine litter in the Mediterranean basin and constitutes the most important part of floating marine litter, comprising sometimes up to 100% of collected items. Microplastics have been found in all Mediterranean coastal countries (Fytianos *et al.*, 2021). Published cases for microplastic occurrence in some Mediterranean countries, sampling beach sediment, are shown in Table 2.1.

Being the Mediterranean Sea an important basin within the European waters, representing one of world's main shipping routes and due to its morphological and oceanographic features as a closed basin surrounded by densely populated countries, the evaluation of plastic pollution is mandatory to establish solid data in order to apply mitigation measures (Baini *et al.*, 2018). There is little information on trends of microplastics in the Mediterranean Sea and it is not clear whether they are transported in the same manner as larger plastics, especially for the Eastern part of the basin (Pedrotti *et al.*, 2019).

In a recent study (Lots *et al.*, 2017) on the whole Mediterranean Sea, the western area of the basin was observed to be less contaminated than the eastern one. In the eastern Mediterranean, relatively higher levels of microplastics contamination were observed in the sampling stations of Greece and Turkey than those measured in Israel.

Duncan *et al.* (2018) showed that the beaches of Cyprus are exposed to very high microplastic abundances, with the majority of them coming from industrial spills, followed by fragments from the breakdown of larger plastics. Microplastics were found in all sampling points, at all locations and depths, with particularly high abundance in superficial sand.

The Adriatic Sea in the most northern arm of the Mediterranean Sea, has been estimated to be affected by one of the most severe litter pollution among Mediterranean regions (Martellini *et al.*, 2018).

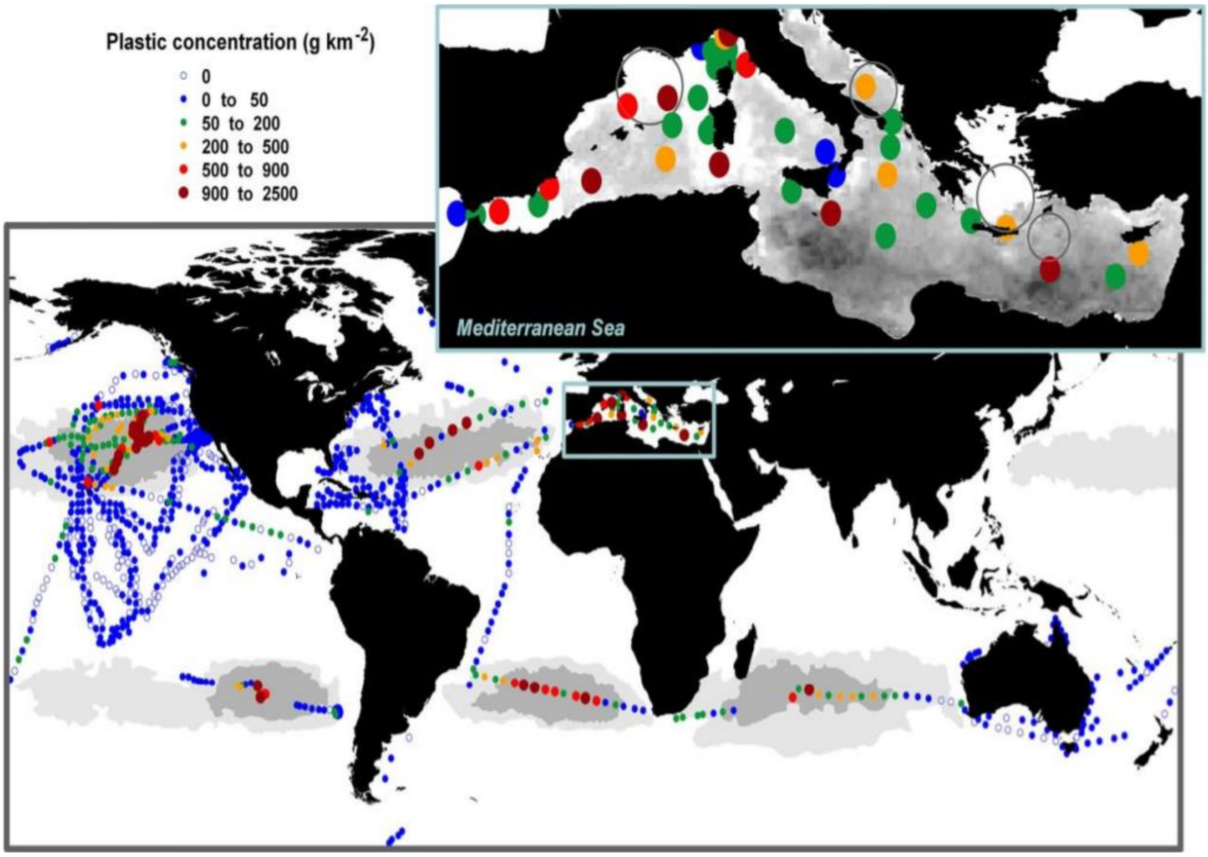

Figure 2.1: Concentrations of plastic debris in surface waters of the Mediterranean Sea at basin scale, zoomed in the top right corner inset, and compared to the plastic concentrations reported for oceans globally. Source: Fytianos *et al.*, 2021.

Table 2.1.: An overview of studies examining beach sediment microplastic contamination in some Mediterranean countries. The sampling location, sampling year, size definition of microplastics, mean, maximum and minimum abundance, the dominant shape, color and polymer type, and references are noted. (D.W.: dry weight, PE: Polyethylene, PET: Polyethylene Terephthalate, PP: Polypropylene, PS: Polystyrene.)

Location	**Year**	**Size**	**Mean Abundance**	**Min Abundance**	**Max Abundance**	**Dominant Shape**	**Dominant Color**	**Dominant Polymer Type**	**Reference**
Cyprus	2016	<5 mm	45.5 items/m^3	(no data available)	(no data available)	fragments & pellets	(no data available)	(no data available)	Duncan *et al.*, 2018
Dikili, Aegean Sea, Turkey	2015, 2017	<5 mm	248 items/kg D.W.	(no data available)	(no data available)	fibers	black & blue	(no data available)	Lots *et al.*, 2017
Datça Peninsula, South Aegean Region, Turkey	2018	100 nm-5 mm	1,154.4 items/kg D.W.	(no data available)	(no data available)	fragments	white	PE	Yabanli *et al.*, 2019
Lebanese coastline, Levantine Basin	2018	<5 mm	2,433 items/kg D.W.	(no data available)	4.68 items/g D.W.	fragments	blue & red	PP	Kazour *et al.*, 2019
Tel Aviv, Israel	2015, 2017	<5 mm	168 items/kg D.W.	(no data available)	(no data available)	fibers	black & blue	(no data available)	Lots *et al.*, 2017
Bosnia	2015, 2017	<5 mm	76 items/kg D.W.	(no data available)	(no data available)	fibers	black & blue	(no data available)	Lots *et al.*, 2017
Telaščica bay, Adriatic Sea, Croatia	2015	≤ 5 mm	(no data available)	(no data available)	377.8 items/kg D.W.	fibers	clear	(no data available)	Blaskovic *et al.*, 2017
Gulf of Trieste, Adriatic Sea, Slovenia	2012	≤ 5 mm	177.8 items/kg D.W.	(no data available)	444.4 items/kg D.W.	fibers	(no data available)	(no data available)	Laglbauer *et al.*, 2014
Slovenian coast, Adriatic Sea	2017	20 µm-5 mm	9 items/kg D.W.	0 items/kg D.W.	82.1 items/kg D.W.	fibers	white	PET, PE & nylon 6	Korez *et al.*, 2019

Caorle area, Northern Adriatic Sea, Italy and Slovenia	2016	≤ 5 mm	254.6 items/kg D.W.	137 items/kg D.W.	703 items/ kg D.W.	fibers	black & blue	(no data available)	Renzi *et al.*, 2018
Lagoon of Venice, Adriatic Sea, Italy	2012	≤ 1 mm	(no data available)	672 items/kg D.W.	2,175 items/kg D.W.	fragments	(no data available)	PE & PP	Vianello *et al.*, 2013
Lido di Dante, Italy	2015, 2017	<5 mm	1,512 items/kg D.W.	(no data available)	(no data available)	fibers	black & blue	(no data available)	Lots *et al.*, 2017
Central Adriatic Sea, Italy	2015	1-5 mm	28.4 items/m^2	0 items/m^2	75 items/m^2	fibers	red, orange, green & blue	nylon	Mistri *et al.*, 2017
Cecina, Tuscany, Ligurian Sea, Italy	2017	63 µm-5 mm	(no data available)	72 items/kg D.W.	191 items/kg D.W.	fragments	white, blue & tan	(no data available)	Blaskovic *et al.*, 2018
Southern Tuscany, Tyrrhenian Sea, Italy	2012	≤ 5 mm	316.8 items/kg D.W.	42 items/kg D.W.	1,069 items/kg D.W.	fibers	black, blue & clear	(no data available)	Cannas *et al.*, 2017
Maremma Regional Park (marine area), Tyrrhenian Sea, Italy	2015, 2016	≤ 5 mm	349.6 items/kg D.W.	45 items/kg D.W.	1,069 items/kg D.W.	fibers	white & clear	(no data available)	Guerranti *et al.*, 2017
Aeolian Archipelago's islands, Southern Tyrrhenian sea, Italy	2016	1 µm-5 mm	371.7 items/kg D.W	0 items/kg D.W	1,037 items/kg D.W	fibers	green & black	(no data available)	Fastelli *et al.*, 2016
San Mauro, Italy	2015, 2017	<5 mm	84 items/kg D.W.	(no data available)	(no data available)	fibers	black & blue	(no data available)	Lots *et al.*, 2017
Sicily, Italy	2015, 2017	<5 mm	160 items/kg D.W.	(no data available)	(no data available)	fibers	black & blue	(no data available)	Lots *et al.*, 2017

Malta	2015, 2016	1-5 mm	4.81 items/1.000 cm^3 (wet)	0.72 items/1.000 cm^3 (wet)	10.81 items/1.000 cm^3 (wet)	fragments	blue, white, cream & opaque	PE	Axiak *et al.*, 2017
Northern Tunisian coast	2017	0.1-5 mm	316.03 items/kg D.W.	141.2 items/kg D.W.	461.25 items/kg D.W.	fibers	black, clear, blue & white	PE & PP	Abidli *et al.*, 2018
Complex Lagoon-Channel of Bizerte, Tunisia	2016	0.3-5 mm	7,960 items/kg D.W.	3,400 items/kg D.W.	18,000 items/kg D.W.	fibers	clear, white & blue	(no data available)	Abidli *et al.*, 2017
Gulf of Annaba, Algeria	2017, 2018	<5 mm	(no data available)	182.66 items/kg D.W.	649.33 items/kg D.W.	fibers	black, white & blue	PE	Tata *et al.*, 2020
Cassis, France	2015, 2017	<5 mm	124 items/kg D.W	(no data available)	(no data available)	fibers	black & blue	(no data available)	Lots *et al.*, 2017
Gulf of Lion, France	2016	<5 mm	112 items/kg D.W.	12 items/kg D.W.	798 items/kg D.W.	fibers	(no data available)	PE & PP	Constant *et al.*, 2019
Spanish Mediterranean continental shelf	2014, 2015	<5 mm	113.2 items/kg D.W	45.9 items/kg D.W	280.3 items/kg D.W	fibers	transparent & blue	PS	Filgueiras *et al.*, 2019
Barcelona, Spain	2015, 2017	<5 mm	148 items/kg D.W	(no data available)	(no data available)	fibers	black & blue	(no data available)	Lots *et al.*, 2017
Tarragona, Spain	2018	0.5-5 mm	10.7 items/kg D.W	0.7 items/kg D.W	42 items/kg D.W	fragments	(no data available)	PE & PP	Expósito *et al*., 2021
Balearic Islands, Spain	2013	<5 mm	(no data available)	100.8 items/kg D.W	897.4 items/kg D.W	fibers & fragments	black & blue	(no data available)	Alomar *et al.*, 2016
Denia, Spain	2015, 2017	<5 mm	156 items/kg D.W	(no data available)	(no data available)	fibers	black & blue	(no data available)	Lots *et al.*, 2017

In 2004, Katsanevakis and Katsarou investigated the abundance and composition of debris in shallow coastal areas of Greece. They showed that plastic debris were the most dominant and they indicated that plastic pollution is more intense in coastal areas. They also found greater abundance of debris in bays than in open areas. Especially in the Saronic Gulf, the abundance of marine debris was higher than the rest of the Greek areas surveyed.

Indeed, Politikos *et al*. (2017) demonstrated that the Saronic Gulf is a main receptor of plastic, using modeled transport pathways of floating litter based on the dominant sea currents. In addition, Ioakeimidis *et al*. (2014) had already found that the Saronic Gulf has very high link to fisheries plastic litter sources (e.g. synthetic ropes, fishing nets, fishing gear, etc.). They had also assumed that the enclosed character of the Saronic Gulf and the relatively steep bottom topography favor the accumulation of plastic litter there.

Tziourrou *et al.* (2019) examined samples from two beaches of Salamina Island, Saronic Gulf. The results of microplastic characterization agreed with their predictions based on the land uses both locally and from across the Greek mainland. The authors concluded that microplastic distribution is related to the increased anthropogenic and industrial activity, but also to fishing activities in this area.

Seary *et al.* (2013) carried out a multiple phase microplastic assessment of the Greek marine environment. All 114 sites which were sampled in 2009, found contaminated with microplastic fibers. The Attica peninsula and the island of Ikaria, Aegean Sea were the most contaminated locations. In a second phase of this study in 2011, all 49 sampled locations exhibited again fibrous contamination. The island of Sifnos, Aegean Sea displayed the highest microplastic contamination. Rhodes and Ikaria islands (Aegean Sea), which were sampled both in 2009 and 2011, showed an increased mean microplastic level.

Kaberi *et al.* (2013) assessed densities of microplastics along the shoreline of Kea Island, Aegean Sea. They showed a direct relation to beach orientation and wind regime rather than to proximity to land based sources. They concluded that the island is very vulnerable to microplastic pollution transported from the open Aegean Sea. In addition, the authors underlined the role of water circulation as the major mechanism of microplastic dispersion worldwide.

De Ruijter *et al.* (2019) studied the occurrence and spatial distribution of microplastics in Samos Island, Aegean Sea along a land-sea transect. The highest concentration of microplastics was recorded on the beach. They indicated that transport by hydrodynamics and *in situ* deposition by humans may be important processes. In relation to the different shapes, fragments were more abundant on the beach, while fibers were more abundant in the intertidal zone, suggesting a distribution probably governed not only by size but also by morphology and perhaps by chemical composition.

Karkanorachaki *et al.* (2018) examined the temporal and spatial distribution of plastic pellets and fragments along the width of four sandy beaches, from shoreline to the upper parts, in Northern Crete during 2013. Their densities varied throughout the year in each beach, with highest densities during the summer.

Digka *et al.* (2018) studied microplastic pollution in the Northern Ionian Sea. Microplastics were found in all beach sediment samples. The authors showed that microplastic particles which are abundant in surface seawater, tend to accumulate on sediment.

According to Seary *et al*. (2013), all Greek beaches are potentially polluted with microplastics, showing a trend of increasing microplastic contamination over time. Examples of published cases for microplastic occurrence in Greek beaches, examining beach sediment, are shown in Table 2.2

Table 2.2: An overview of studies examining beach sediment microplastic contamination in Greece. The sampling location, sampling year, size definition of microplastics, mean, maximum and minimum abundance, the dominant shape and polymer type, and references are noted. (D.W.: dry weight, PE: Polyethylene, PP: Polypropylene).

Location	**Year**	**Size**	**Mean Abundance**	**Maximum Abundance**	**Minimum Abundance**	**Dominant Shape**	**Dominant Polymer Type**	**Reference**
Attica peninsula	2009	≤ 5mm	20.13 items/50 ml	(no data available)	(no data available)	fibers	(no data available)	Seary *et al.*, 2013
Ikaria Island			19.79 items/50 ml	(no data available)	(no data available)		(no data available)	
Sifnos Island	2011		112.08 items/50 ml	(no data available)	(no data available)		(no data available)	
Samos Island	2017	<5 mm	11.5 items/kg D.W.	37.2 items/kg D.W.	1.1 items/kg D.W.	fragments & fibers	(no data available)	De Ruijter *et al.*, 2019
Kea Island	2012	1 mm ≤ x < 2 mm	329.13 items/m^2	300 items/m^2	0 items/m^2	fragments	PE	Kaberi *et al.*, 2013
		2 mm ≤ x < 4 mm	275.75 items/m^2	(no data available)	(no data available)			
Northern Crete	2015, 2016	<5 mm	(no data available)	85 items/kg D.W.	5 items/kg D.W.	fragments & films	(no data available)	Piperagkas *et al.*, 2019
Northern Ionian Sea	2014-2015	< 1 mm	1,760 items/m^2	(no data available)	(no data available)	filaments	PE	Digka *et al.*, 2018
		1 mm ≤ x ≤ 5mm	56.7 items/m^2	95 items/m^2	17 items/m^2	fragments		
Thermaic Gulf	2017	≤ 5mm	(no data available)	0.1 items/g D.W.	0.02 items/g D.W.	fragments	PE & PP	Sarigiannis *et al.*, 2019
Pilion	2015, 2017	< 5 mm	232 items/kg D.W.	(no data available)	(no data available)	fibers	(no data available)	Lots *et al.*, 2017

3. Research Objectives

The aim of the present study is a quantitative and qualitative study of microplastics in ten (10) beaches in Attica coastal area and three (3) beaches in Andros Island. In order to fulfill this aim, the following objectives have been set:

- To examine the occurrence, abundance and spatial distribution of large microplastics (1-5 mm).
- To record their morphologic characteristics, such as shape (type) and color.
- To identify their polymer type.
- To compare and possibly correlate the granulometry of sampling sites with the occurrence/abundance of microplastic pollution.
- To make some remarks about the possible origin of microplastics.

4. FT-IR Analysis

The analysis of microplastics in various environmental samples requires their identification (Song *et al.*, 2015). Confirming the polymer types of microplastics can provide additional information such as the origin and further behaviors (Song *et al.*, 2014). Knowledge of the polymer composition is of significant importance, as sorption capacities for toxic chemicals change according to polymer type (Lee *et al*., 2014).

The use of spectroscopy is strongly recommended, as it can determine a chemical composition with high reliability (Hidalgo-Ruz *et al.*, 2012). Visual and stereoscopic sorting is much less reliable compared to this method.

Infrared spectroscopy for microplastic analysis is based on the comparison of the infrared spectrum of a sample with spectra of known polymers (Portolés Pérez, 2018). The infrared radiation excites the molecular vibrations, which depend on the composition and molecular structure of the substance and are specific for each wavelength (Portolés Pérez, 2018). The amount of energy transmitted by the sample is measured, thus obtaining the characteristic infrared spectra. These infrared spectra show different band patterns for each plastic polymer (Portolés Pérez, 2018).

Fourier Transform Infrared (FT-IR) spectroscopy is a technique from which particles of plastic polymers are precisely identified (Portolés Pérez, 2018). FT-IR can not only reliably classify the polymer forms of microplastics, but also provide details on microplastics' physicochemical weathering, by evaluating their oxidation strength (Corcoran *et al.*, 2009).

For microplastic analysis, attenuated total reflectance (ATR) is commonly used in FT-IR (Xu *et al.*, 2019). ATR is an infrared sampling technique that provides excellent quality data in conjunction with the best possible reproducibility of any infrared sampling technique (PerkinElmer, 2005) and affords well-resolved and less intense bands (Xu *et al.*, 2019).

According to the technical report of PerkinElmer in 2005, an ATR accessory operates by measuring the changes that occur in a totally internally reflected infrared beam when the beam comes into contact with a sample (Figure 4.1). An infrared beam is directed onto an optically dense crystal with a high refractive index at a certain angle. This internal reflectance creates an evanescent wave that extends beyond the surface of the crystal into the sample held in contact with the crystal. This evanescent wave protrudes only a few microns beyond the crystal surface and into the sample. In regions of the infrared spectrum where the sample transmits energy, the evanescent wave will be attenuated or altered. The attenuated energy from each evanescent wave is passed back to the infrared beam, which then exits the opposite end of the crystal and is passed to the detector in the spectrometer. The system then generates an infrared spectrum.

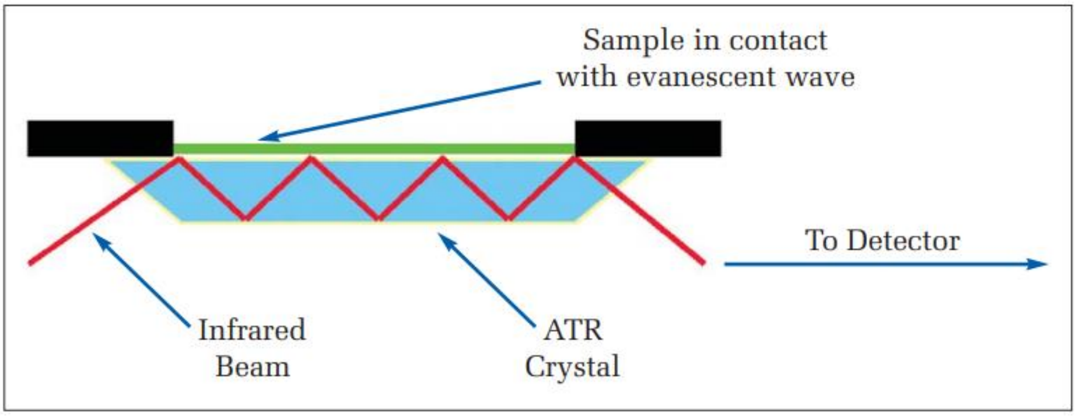

Figure 4.1: A multiple reflection ATR system. Source: PerkinElmer, 2005.

For the technique to be successful, the following two requirements must be met; the sample must be in direct contact with the ATR crystal and the refractive index of the crystal must be significantly greater than that of the sample or else internal reflectance will not occur (the light will be transmitted rather than internally reflected in the crystal).

A baseline correction method allows an acceleration history to be modified to minimize the overall drift of the displacement obtained from the time integration of the given acceleration. An ATR correction function is also included. It simply applies a linear ramp to the ATR spectrum in order to approximate the relative band intensities that would be found in a transmission experiment.

In general, identifying unknown particles from field samples using an automated mapping of ATR FT-IR is a difficult process. The spectra of particles are difficult to match with those of the scientific literature with high percentages, due to the surface condition of microplastics (Song *et al.*, 2015). The more degraded due to the environmental conditions microplastics are, the more peaks in infrared spectra are found, formed of new functional groups on polymer surface (Tziourrou *et al.*, 2019).

5. Materials and Methods

This study was conducted during July and August 2021, sampling ten sandy beaches in Attica coastal area and three sandy beaches in the island of Andros, Cyclades.

5.1. Environmental Setting of Sampling Areas

The Saronic Gulf, located in the South Aegean Sea, is a semi-enclosed gulf which practically constitutes the marine gateway of the Athens greater metropolitan area and the alongshore outskirts. It is characterized by extreme maritime navigation, tourism, fisheries and industrialization. In the northern part of the gulf, Ilisos and Cephissus rivers flow, resulting in the creation of large riverine deposits.

The southern coast of Athens is usually referred to as the Athens Riviera. These beaches are famous destinations for both local people and tourists. Their proximity to Athens means that they are often crowded, especially during summer. Agios Kosmas, Edem, Loutra of Alimos, Faliro - Naftikos Omilos, Palaio Faliro, Phloisbos, Glyfada - Coast A, Glyfada - Coast B, Asteria and Voula beaches were selected for sediment sampling.

Andros is one of the closest islands in Athens and constitutes a very famous tourist destination in the summer. Three beaches; Gialia, Liopesi and Fellos were selected to be sampled.

In 2011, heavy rain caused an informal waste disposal site to collapse in Andros Island, with most of the material tumbling into the sea. In fact, divers found a reef of plastic bags on the bottom where the landfill had crumbled into the waters.

Figure 5.1.1 shows a map of the sampling sites, taken from Google Earth. Figure 5.1.2 shows a set of 6 photographs which are examples of beaches where sediment sampling took place. Tables 5.1 and 5.2 present data for each sampling station.

Figure 5.1.1: Map of sampling sites. Source: Google Earth.

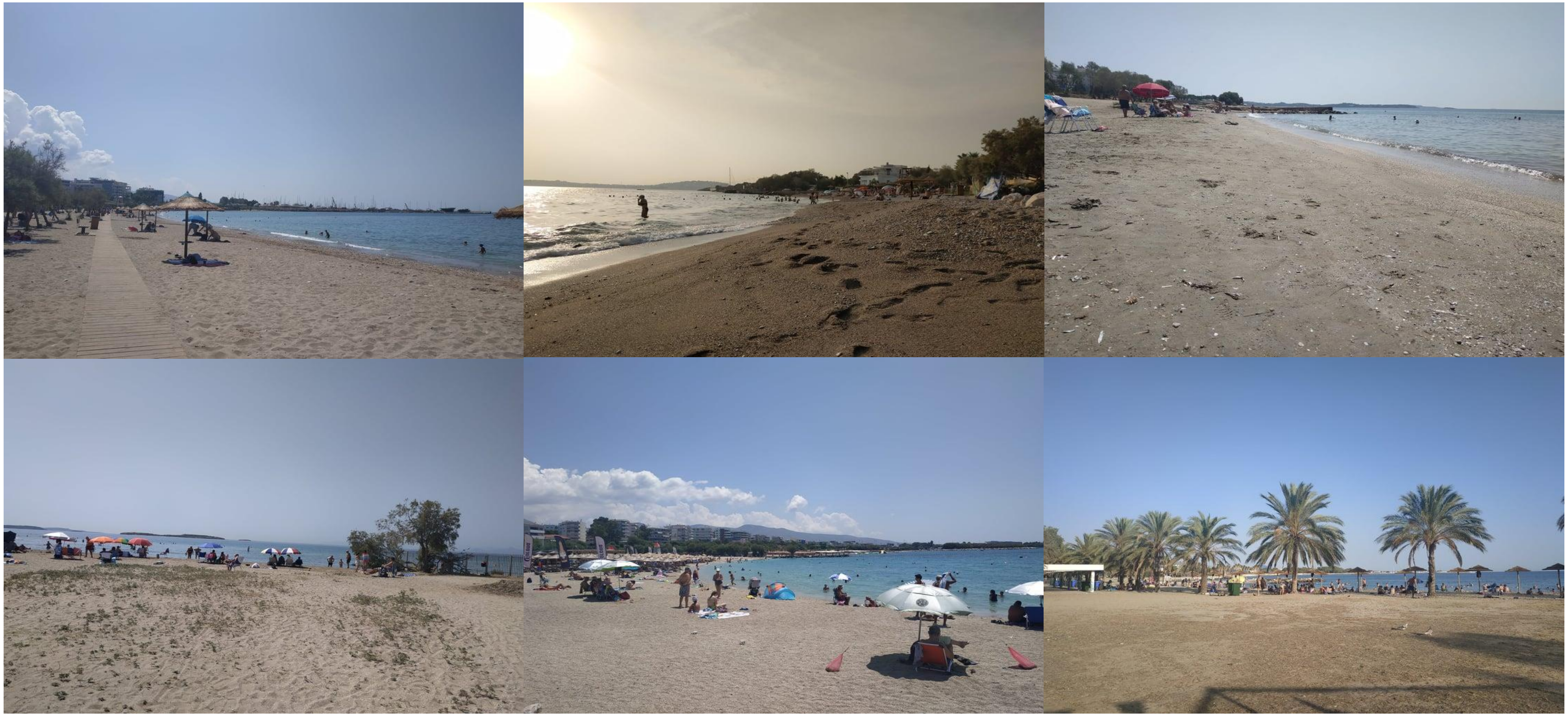

Figure 5.1.2: Examples of beaches where sediment sampling took place.

Table 5.1: Data for the sampling sites in Attica.

Sampling Stations Attica Saronic Gulf	**Date**	**Location**	**Latitude Coordinate**	**Longitude Coordinate**
SS1	16/7/2021	Agios Kosmas	37.890689	23.719108
SS2	16/7/2021	Agios Kosmas	37.890357	23.720342
SS3	16/7/2021	Agios Kosmas	37.889997	23.721407
SS4	19/7/2021	Edem	37.92092281	23.69599442
SS5	19/7/2021	Edem	37.91991309	23.69867207
SS6	19/7/2021	Edem	37.91811388	23.70051623
SS7	19/7/2021	Loutra Alimou	37.90493102	23.71772854
SS8	19/7/2021	Loutra Alimou	37.90389251	23.71863312
SS9	19/7/2021	Loutra Alimou	37.90236376	23.71928261
SS10	30/7/2021	Faliro - Naftikos Omilos	37.921167	23.695608
SS11	30/7/2021	Faliro - Naftikos Omilos	37.921444	23.695233
SS12	30/7/2021	Faliro - Naftikos Omilos	37.922239	23.693855
SS13	4/8/2021	Palaio Faliro	37.922529	23.693446
SS14	4/8/2021	Palaio Faliro	37.92295	23.693106
SS15	4/8/2021	Phloisbos	37.924352	23.69172
SS16	4/8/2021	Phloisbos	37.924919	23.691267
SS17	9/8/2021	Glyfada – Coast A	37.873907	23.731399
SS18	9/8/2021	Glyfada – Coast A	37.873446	23.732663
SS19	9/8/2021	Glyfada – Coast A	37.872677	23.733466
SS20	9/8/2021	Glyfada – Coast B	37.86851	23.73634
SS21	9/8/2021	Asteria	37.866043	23.739747
SS22	9/8/2021	Asteria	37.865282	23.740671
SS23	11/8/2021	Voula	37.850427	23.748221
SS24	11/8/2021	Voula	37.84939	23.750483
SS25	11/8/2021	Voula	37.848099	23.752253

Table 5.2: Data for the sampling sites in Andros Island.

Sampling Stations Andros Island	**Date**	**Location**	**Latitude Coordinate**	**Longitude Coordinate**
SS1	23/7/2021	Gialia	37.851983	24.938983
SS2	23/7/2021	Gialia	37.854467	24.93935
SS3	23/7/2021	Gialia	37.856683	24.940383
SS4	24/7/2021	Liopesi	37.8799	24.741617
SS5	25/7/2021	Fellos	37.8962	24.711233

5.2. Sediment Sampling

Beach sediment was collected at the high tide line. GPS coordinates were noted, pictures were taken and general observations were made. Sampling was performed *in situ* at the high tide line of each beach.

In Attica coastal area, a wooden quadrat of 50×50 cm (0.25 m^2) was used. The top 1 cm of sand was scooped from each quadrat area using a steel scoop (Figure 5.2.1). Then, 3 liters of seawater were added to each sample using a glass bottle. The supernatant was filtered through a 1 mm mesh. This process was repeated three times.

In Andros Island, a wooden quadrat of 25×25 cm (0.0625 m^2) was used. The top 2 cm of sediment were scooped.

Each sample was kept in a paper bag and each bag was labeled properly. Then, all bags were transferred to the Oceanography and Marine Geochemistry Laboratory of the University of Piraeus to be analyzed.

Figure 5.2.1: Photographs taken during sampling process.

5.3. Sediment Analysis

Samples were dried at room temperature for days. Then, they were visually examined in order to separate the organic debris from sand and investigate the presence of macroplastics or mesoplastics. All samples were examined by naked eye twice.

Dried samples were sieved again, using two metallic sieves with 1 mm and 5 mm mesh size respectively. In this way, most of the fine sand was discarded and the grain size class 1–5 mm was separated.

The dried sediment was weighted in a high precision balance (0.1 mg). After this process, 1 gram of each sieved and homogenized sample was selected in order to be examined under the ZEISS Stemi 508 Stereo Microscope. The number of microplastics found and their morphological characteristics were noticed. This process was repeated five times. Pictures of microplastics were taken using the microscope camera ZEISS Axiocam ERc5s, attached on the stereoscopic microscope (Figure 5.3.1).

Figure 5.3.1: The stereoscopic microscope during observation.

Then, 1 gram of each sample was grinded with a porcelain mortar and pestle for further analysis by the use of Attenuated Total Reflectance - Fourier Transform Infrared (ATR FT-IR) spectroscopy.

5.4. FT-IR Analysis

Beach sediment was examined using FT-IR analysis for the presence of microplastics, but only in a very limited quantity of each grinded sample, which was less than 1 gram. This amount was subjected to the source of the infrared light.

Some microplastic particles which had been separated during the stereoscopic observations, were analyzed in this way. Fibers were totally excluded from this analysis.

Spectra of sediment and microplastic samples were obtained using a Perkin Elmer Spectrum Two FT-IR spectrometer with Universal ATR Accessory, at the Oceanography and Marine Geochemistry Laboratory of the University. The accessory was supplied with a flat top-plate Zinc Selenide (ZnSe) crystal allowing simple sampling of powder solids. PerkinElmer's Spectrum™ FT-IR software was used which utilizes a "Preview Mode" and allows the quality of the spectrum to be monitored in real-time while fine tuning the exerted force.

5.5. Contamination Minimization

During all processes, contamination by airborne microplastics was minimized. The wooden quadrat, the metal scoop, the sieves and the rest equipment were cleaned and wrapped prior to sampling. Sediment samples were stored only in paper bags. People undertaking the sampling and examination avoided any synthetic clothing. All glassware used in the laboratory was rinsed thoroughly with purified distilled water before its use. During FT-IR analysis, precautions to avoid possible microplastic contamination were taken.

6. Results

6.1. Analysis of Beach Sediment

Sediment grain size was characterized in order to assess whether microplastic concentrations are linked to granulometry. Sediment was categorized according to the Wentworth (1922) grain-size classification. Due to the sieving process, three categories of sediment size existed; “very coarse sand”, “granule gravel” and “pebble gravel” (Figure 6.1.1).

Figure 6.1.1: Wentworth (1922) grain-size classification for 1-8 mm sediment size. Source: Wentworth, 1922.

In tables 6.1 and 6.2 below, sediment from each sampling station in the Attica and Andros studying areas, is characterized by a Wentworth size class.

Table 6.1: Wentworth size class categorization for sampling stations in Attica.

Sampling Stations Attica Saronic Gulf	**Location**	**Wentworth Size Class**
SS1	Agios Kosmas	Granule gravel
SS2		Very coarse sand
SS3		Granule gravel
SS4	Edem	Granule gravel
SS5		Very coarse sand
SS6		Granule gravel
SS7	Loutra Alimou	Pebble gravel
SS8		Granule gravel
SS9		Granule gravel
SS10	Faliro - Naftikos Omilos	Granule gravel
SS11		Granule gravel
SS12		Pebble gravel
SS13	Palaio Faliro	Pebble gravel
SS14		Pebble gravel
SS15	Phloisbos	Pebble gravel
SS16		Pebble gravel
SS17	Glyfada – Coast A	Pebble gravel
SS18		Granule gravel
SS19		Pebble gravel
SS20	Glyfada – Coast B	Pebble gravel
SS21	Asteria	Granule gravel
SS22		Pebble gravel
SS23	Voula	Very coarse sand
SS24		Very coarse sand
SS25		Very coarse sand

Table 6.2: Wentworth size class categorization for sampling stations in Andros Island.

Sampling Stations Andros Island	**Location**	**Wentworth Size Class**
SS1	Gialia	Very coarse sand
SS2		Very coarse sand
SS3		Pebble gravel
SS4	Liopesi	Very coarse sand
SS5	Fellos	Very coarse sand

In Attica, sediment was finer at Agios Kosmas, Edem and Voula beaches. Pebbles were found at Loutra Alimou, Faliro - Naftikos Omilos, Palaio Faliro, Phloisbos, Glyfada and Asteria beaches. Attica coastal area was found enriched in granule gravel and pebble gravel sediment (40% of each). A lower proportion of very coarse sand sediment was noticed (20%) (Figure 6.1.2).

In the island of Andros, Liopesi and Fellos were characterized by coarser sediment, while pebbles were found at the sampling station 3 of Gialia beach. It was also found that the majority of sampling stations are composed of very coarse sand. Granule gravel sediment was not noticed at all (Figure 6.1.3).

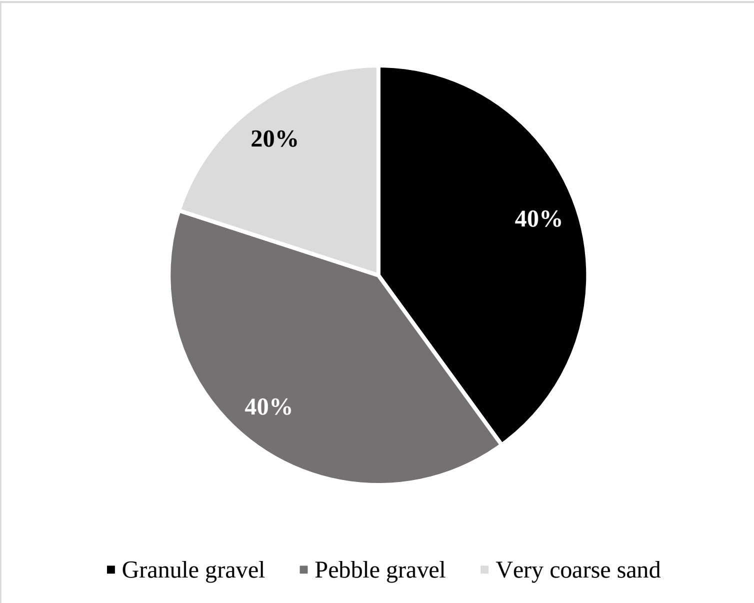

Figure 6.1.2: Proportion of each grain size class from samples collected in Attica.

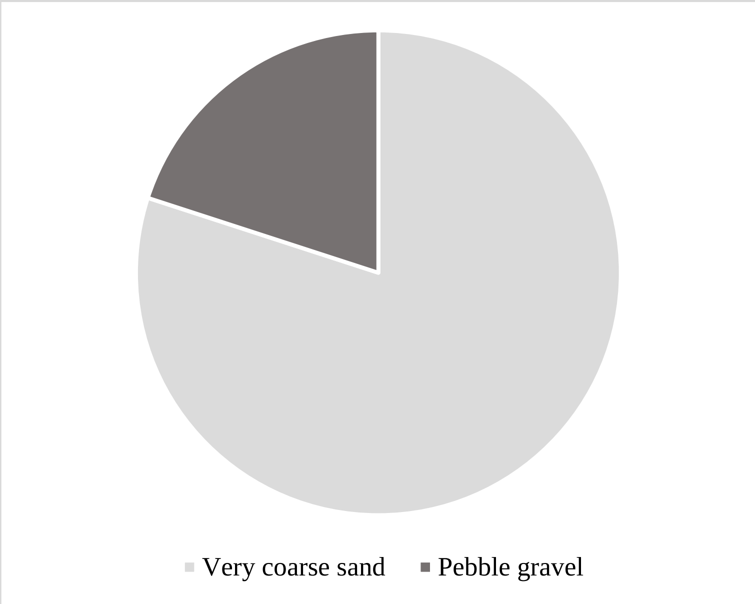

Figure 6.1.3: Proportion of each grain size class from samples collected in Andros Island.

The dry weight of sediment samples was also calculated and showed variability, ranging from 104 g/m^3 found at sampling station 25 (Voula) to 1,782 g/m^3 found at sampling station 16 (Phloisbos). The average value of dry weight for beaches of Attica was 706 g/m^3.

Regarding samples from Andros, the minimum value of dry weight was 35 g/m^3 found at sampling station 1 (Gialia), the maximum value was 2,480 g/m^3 found at sampling station 3 (Gialia) and the average value was calculated equal to 680 g/m^3.

More details about all values of dry weights are presented in Tables 6.3 and 6.4.

Table 6.3: Dry sediment weight per volume (g/m^3) for samples from Attica.

Sampling Stations Attica Saronic Gulf	**Dry weight per Volume (g/m^3)**
SS1	561
SS2	137
SS3	411
SS4	571
SS5	160
SS6	488
SS7	939
SS8	436
SS9	489
SS10	690
SS11	748
SS12	945
SS13	900
SS14	1,094
SS15	1,461
SS16	1,782
SS17	811
SS18	509
SS19	1,096
SS20	1,457
SS21	495
SS22	881
SS23	365
SS24	126
SS25	104

Table 6.4: Dry sediment weight per volume (g/m^3) for samples from Andros Island.

Sampling Stations Andros Island	**Dry weight per Volume (g/m^3)**
SS1	35
SS2	483
SS3	2,480
SS4	316
SS5	87

6.2. Abundance of Microplastics

The number of microplastics per 5 grams of each sample detected during stereoscopic observations is presented in Tables 6.5 and 6.6. Microplastic contamination was not present in all sediments.

The maximum concentration of microplastics found in sediment from Attica coastal area was 8 items/5 g (station 23, Voula beach) and the average value was calculated equal to 1.44 items/5 g. The maximum abundance found in sediment from the island of Andros was 2 items/5 g (stations 1 and 3, Gialia beach) and the average value was calculated equal to 1 item/5 g.

Table 6.5: Number of microplastics detected in 5 g of each beach sediment sample from Attica.

Sampling Stations Attica Saronic Gulf	**Number of microplastics per 5 g**
SS1	2
SS2	4
SS3	1
SS4	1
SS5	2
SS6	1
SS7	1
SS8	2
SS9	1
SS10	0
SS11	0
SS12	4
SS13	0
SS14	0
SS15	0
SS16	0
SS17	0
SS18	1
SS19	3
SS20	1
SS21	0
SS22	0
SS23	8
SS24	2
SS25	2

Table 6.6: Number of microplastics detected in 5 g of each beach sediment sample from Andros Island.

Sampling Stations Andros Island	**Number of microplastics per 5 g**
SS1	2
SS2	0
SS3	2
SS4	1
SS5	0

6.3. Morphology of Microplastics

Microplastic types and colors were recorded during stereoscopic observations. Microplastic particles were divided into four groups with regard to their types as; fragments, fibers, foams and films. Regarding their color, they were characterized as black/grey, blue, green, purple, red, white/yellow and also transparent and colorful. Tables 6.7 and 6.8 show information about the number, the type and the color of microplastics detected at each sampling station.

In Attica coastal area, fragments were dominant (50%) (Figure 6.3.1). The majority of microplastics (all types) was green (28%) (Figure 6.3.2). More specifically, the majority of fragments was blue (Figure 6.3.3), while the majority of fibers was green (Figure 6.3.4). A small number of foams and films was detected totally; three foams which were black/grey, white/yellow and blue, and two films which were colorful and transparent respectively. The highest number of fragments was detected at the sampling stations 2 (Agios Kosmas) and 23 (Voula) and the highest number of fibers was detected at the sampling sites 12 (Faliro - Naftikos Omilos) and 23 (Voula).

In the island of Andros, a very small amount of microplastics was recorded; in total three fibers and two fragments. The fibers were white/yellow and transparent and the fragments were blue and green. More fibers were detected at the sampling station 1 (Gialia).

Table 6.7: Number, type and color of microplastics detected in samples from Attica.

Sampling Stations Attica Saronic Gulf	**Number of items per 5 g**	**Type**	**Color**
SS1	2	Fragment	Blue
			Green
SS2	3	Fragment	Blue
			Red
			Transparent
	1	Fiber	Purple
SS3	1	Fragment	Purple
SS4	1	Fragment	Colorful
SS5	2	Fragment	Blue
			Green
SS6	1	Fragment	Red
SS7	1	Fragment	Black/Grey
SS8	1	Film	Colorful
	1	Fragment	Blue
SS9	1	Fiber	Blue
SS12	4	Fiber	Green
SS18	1	Fragment	Green
SS19	2	Fiber	Transparent
	1	Foam	Black/Grey
SS20	1	Film	Transparent
SS23	2	Fiber	Transparent
	1		Green
	1		Red
	3	Fragment	Black/Grey
			Blue
			Green
	1	Foam	White/Yellow
SS24	1	Fiber	Green
	1	Fragment	Purple
SS25	1	Foam	Blue
	1	Fragment	Blue

Table 6.8: Number, type and color of microplastics detected in samples from Andros Island.

Sampling Stations Andros Island	**Number of items per 5 g**	**Type**	**Color**
SS1	2	Fiber	White/Yellow
SS3	1	Fiber	Transparent
	1	Fragment	Green
SS4	1	Fragment	Blue

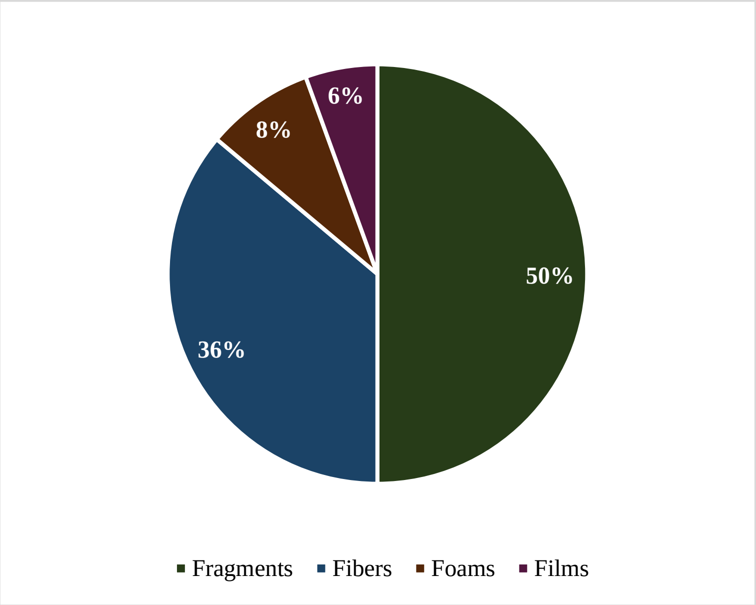

Figure 6.3.1: Proportion of each type of microplastics found in samples from Attica.

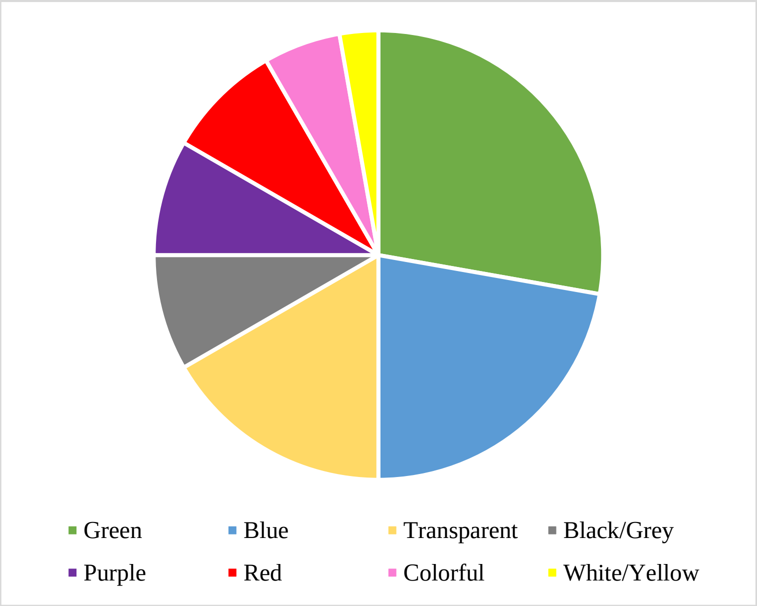

Figure 6.3.2: Proportion of colors of microplastics found in samples from Attica.

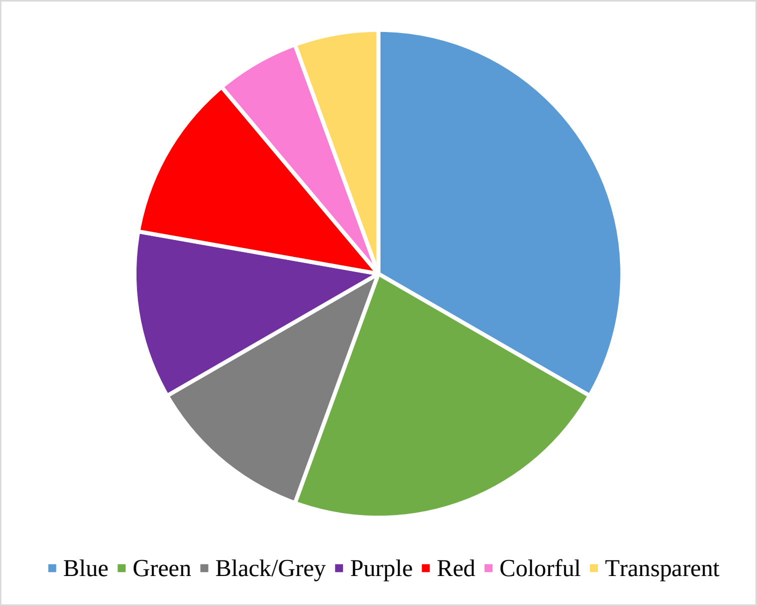

Figure 6.3.3: Proportion of colors of fragments found in samples from Attica.

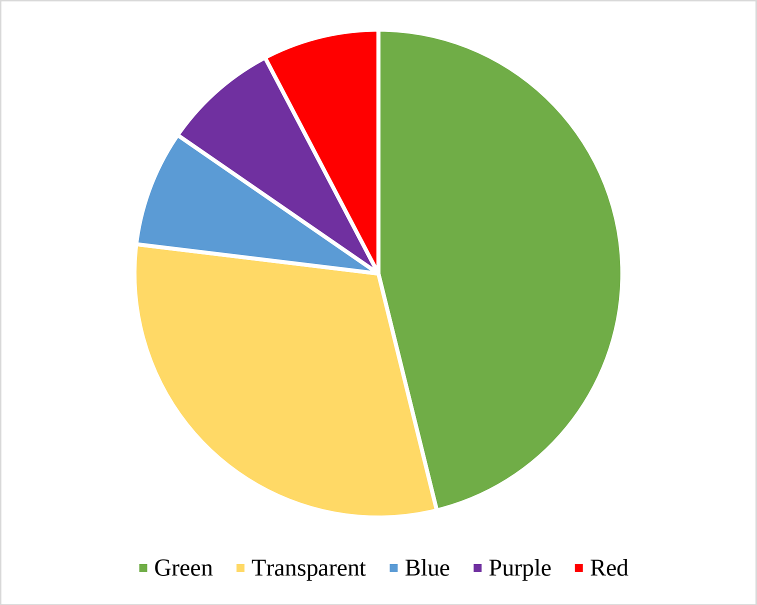

Figure 6.3.4: Proportion of colors of fibers found in samples from Attica.

Some pictures of detected microplastics taken by the external camera attached on the stereoscopic microscope are showed in Figure 6.3.5.

Figure 6.3.5: Examples of microplastics detected in the sediment samples.

6.4. Relation Between Granulometry & Abundance of Microplastics

The relation between the occurrence of microplastics and the grain size classes of sediment samples was investigated. The majority of microplastics was found at stations with very coarse sand, both in Attica and Andros Island (Figures 6.4.1 and 6.4.2).

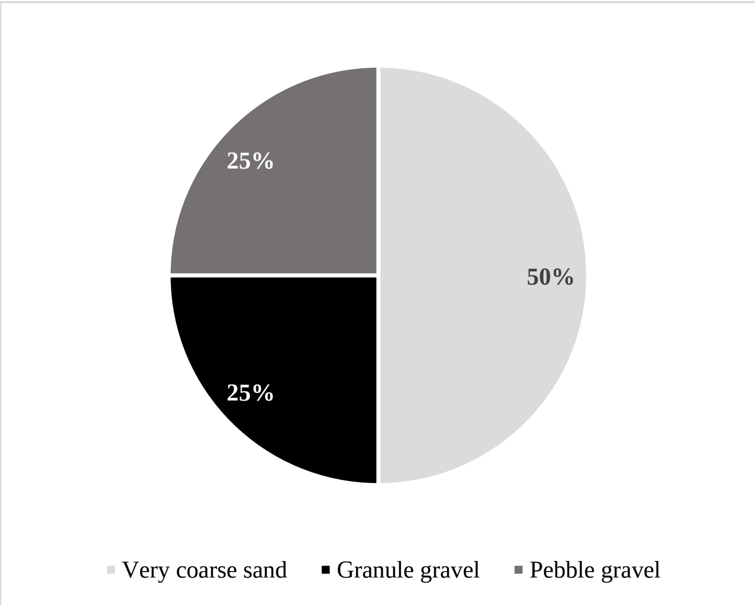

Figure 6.4.1: Proportion of microplastic occurrence in each grain size class in samples from Attica.

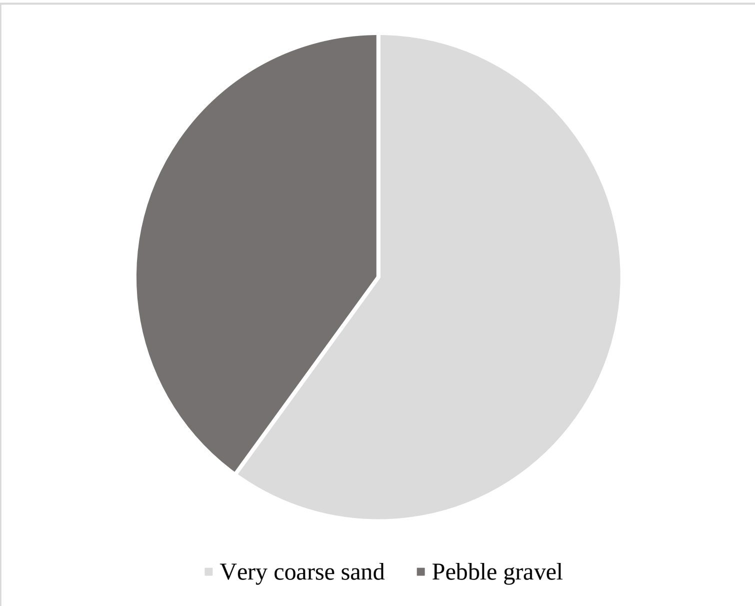

Figure 6.4.2: Proportion of microplastic occurrence in each grain size class in samples from Andros Island.

In Attica, the greatest microplastic abundance was found at the sampling station 23 (Voula), where sediment is very coarse. In addition, high abundance was noticed at the sampling station 2 (Agios Kosmas) which is also consisted of very coarse sand. In Andros Island, microplastic presence was also recorded at sampling stations with very coarse sandy sediment (sampling stations 1 and 4).

Microplastic fragments, fibers and foams were found in all sediment types, but higher concentrations were observed in coarser sand. The only microplastic type that was not found in very coarse sediment is the category “films”, but its abundance was too low.

6.5. FT-IR Analysis

Spectra were similar to known spectra for beach sediment samples. Any polymer presence was not detected. The ATR FT-IR transmittance spectra of some selected sediment samples are shown in Figures 6.5.1 to 6.5.11, noting their dominant peaks.

In total, seven fragments, two films and two foams were checked under FT-IR analysis. These eleven particles gave clear spectra, comparable to spectra of specific polymer types. The rest of microplastics that were detected during our observations, either did not have discernible peaks in their spectra, even after several trials, or their quantity and density did not allow this analysis.

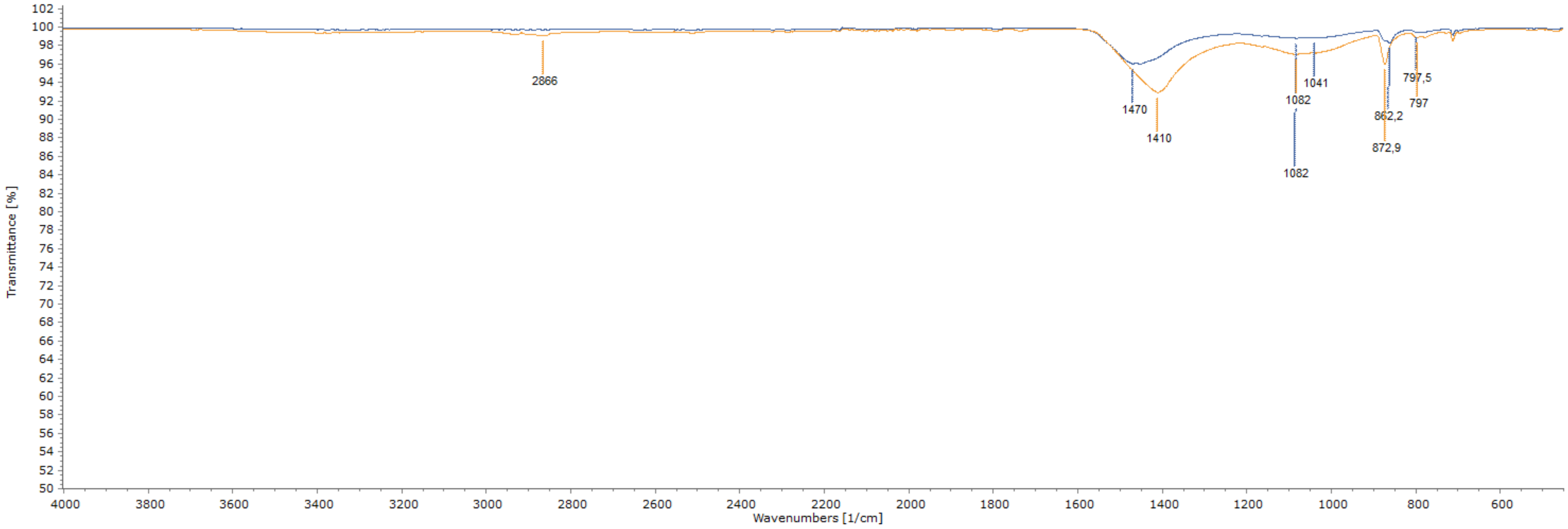

Figure 6.5.1: Result of ATR FT-IR analysis for beach sediment from Agios Kosmas (Saronic Gulf).

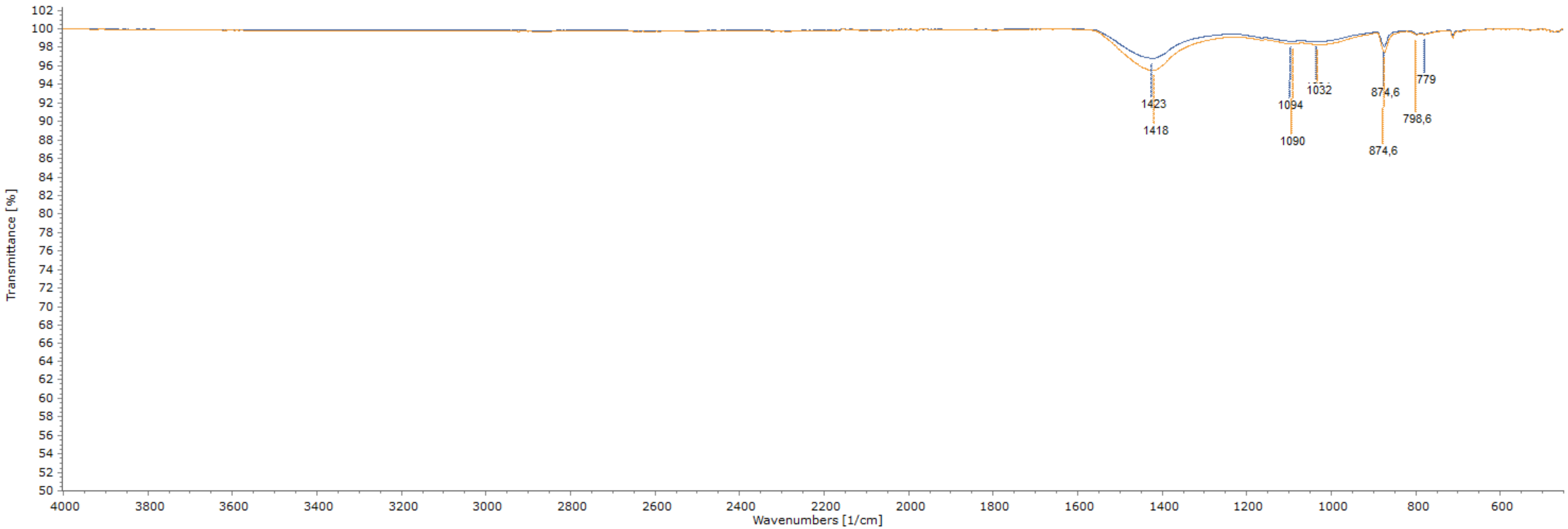

Figure 6.5.2: Result of ATR FT-IR analysis for beach sediment from Edem (Saronic Gulf).

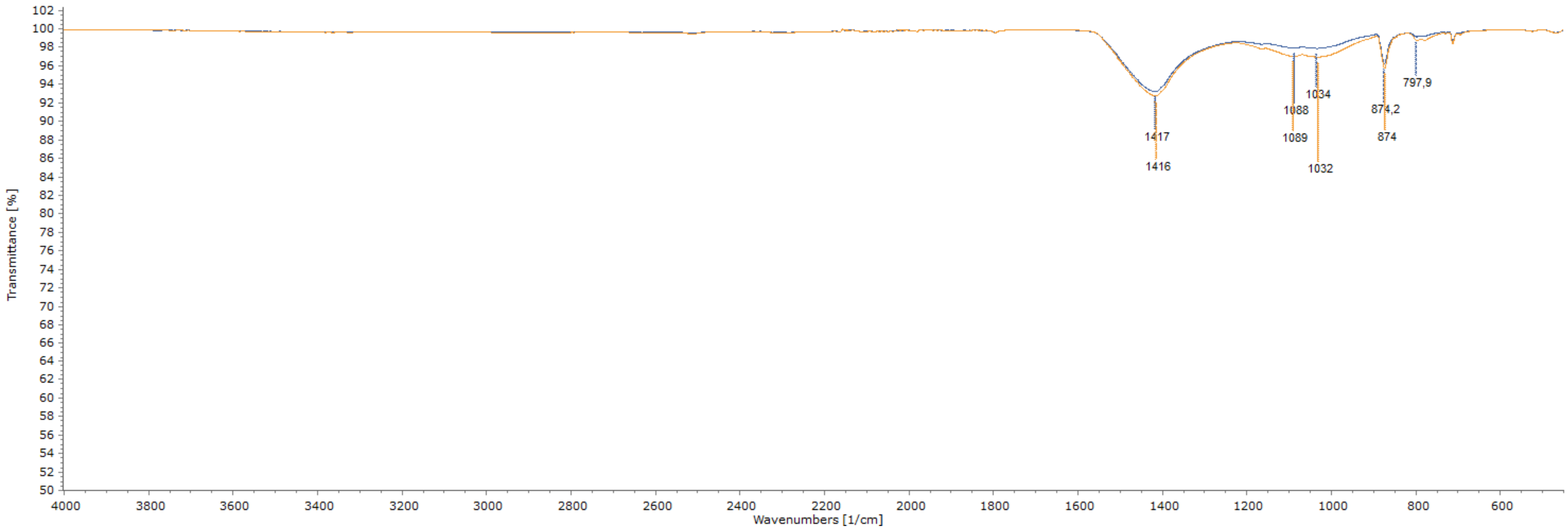

Figure 6.5.3: Result of ATR FT-IR analysis for beach sediment from Loutra Alimou (Saronic Gulf).

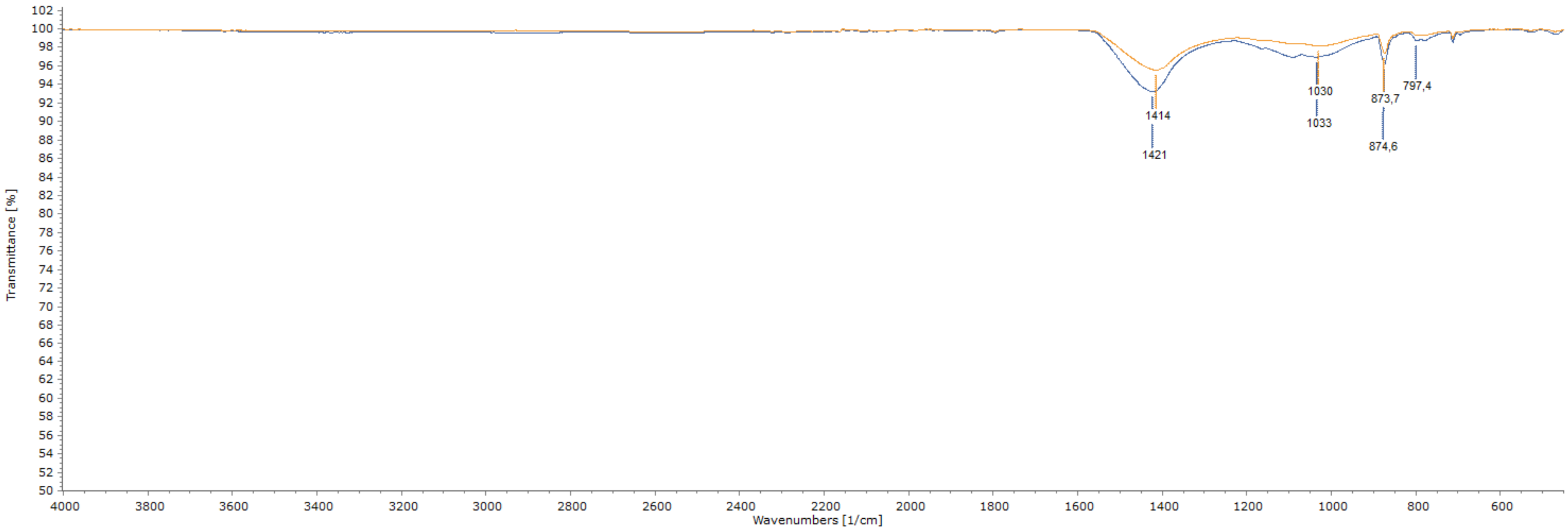

Figure 6.5.4: Result of ATR FT-IR analysis for beach sediment from Faliro – Naftikos Omilos (Saronic Gulf).

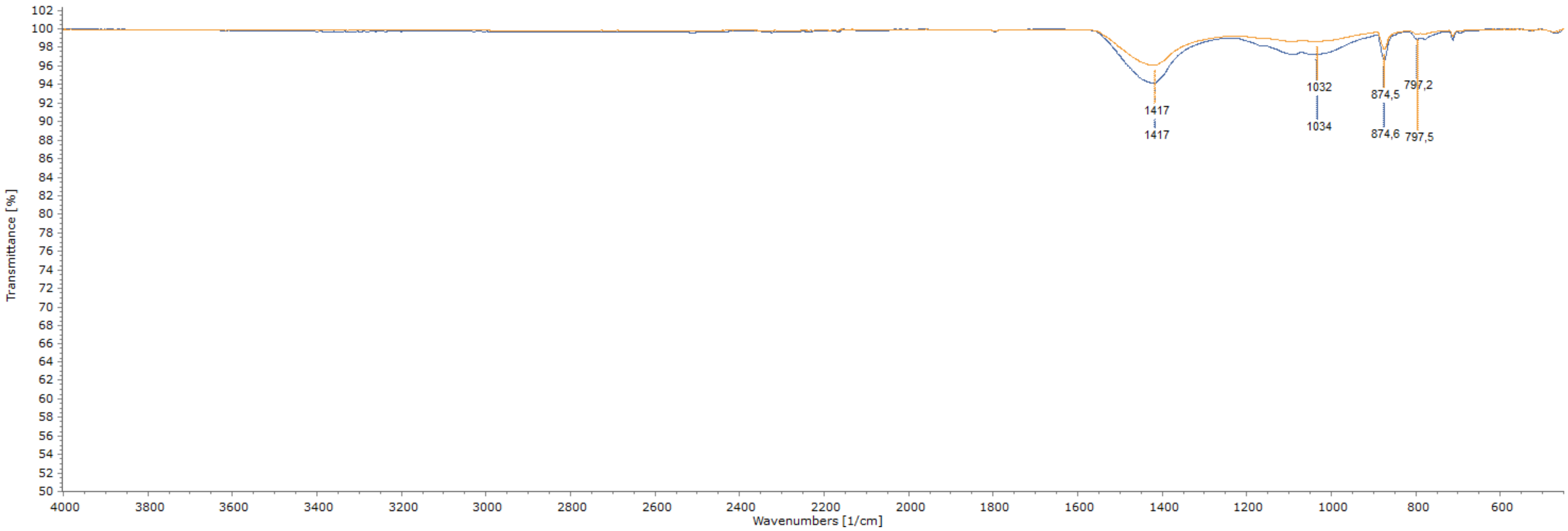

Figure 6.5.5: Result of ATR FT-IR analysis for beach sediment from Palaio Faliro (Saronic Gulf).

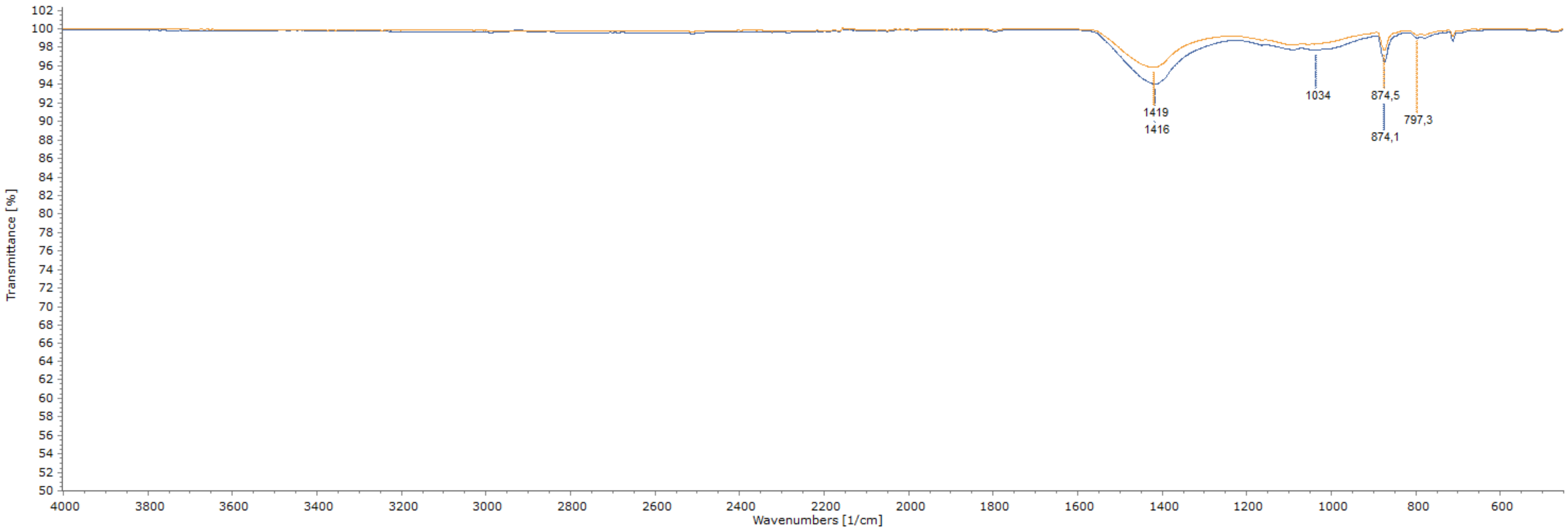

Figure 6.5.6: Result of ATR FT-IR analysis for beach sediment from Phloisbos (Saronic Gulf).

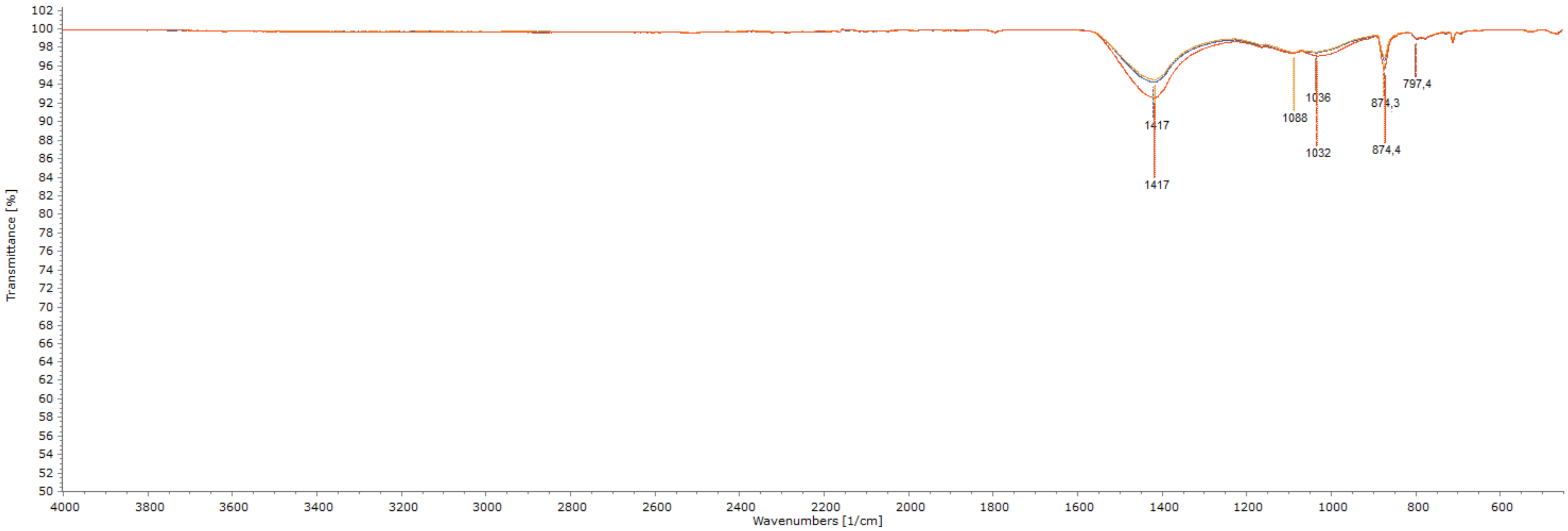

Figure 6.5.7: Result of ATR FT-IR analysis for beach sediment from Glyfada (Saronic Gulf).

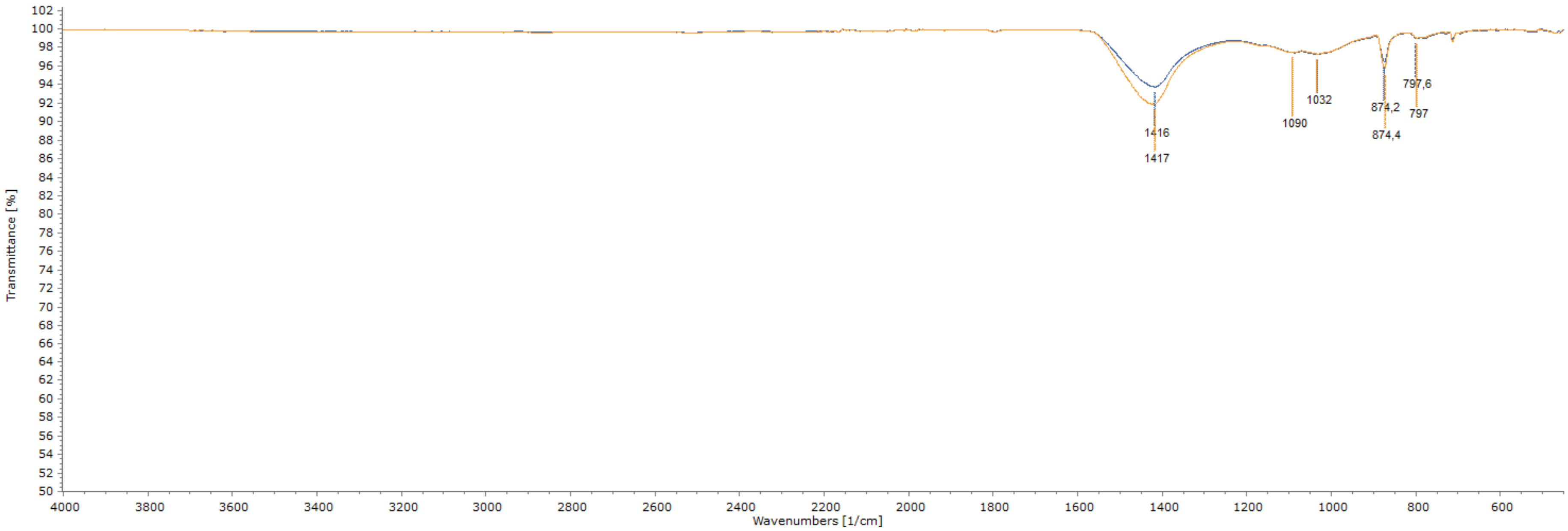

Figure 6.5.8: Result of ATR FT-IR analysis for beach sediment from Asteria (Saronic Gulf).

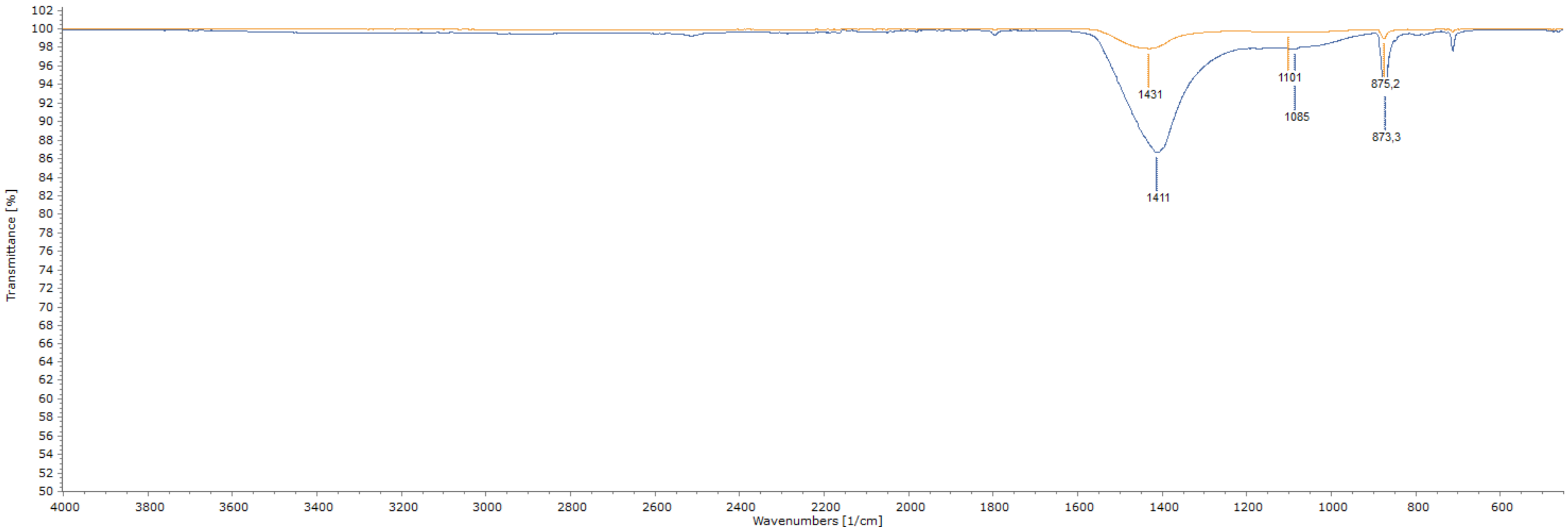

Figure 6.5.9: Result of ATR FT-IR analysis for beach sediment from Voula (Saronic Gulf).

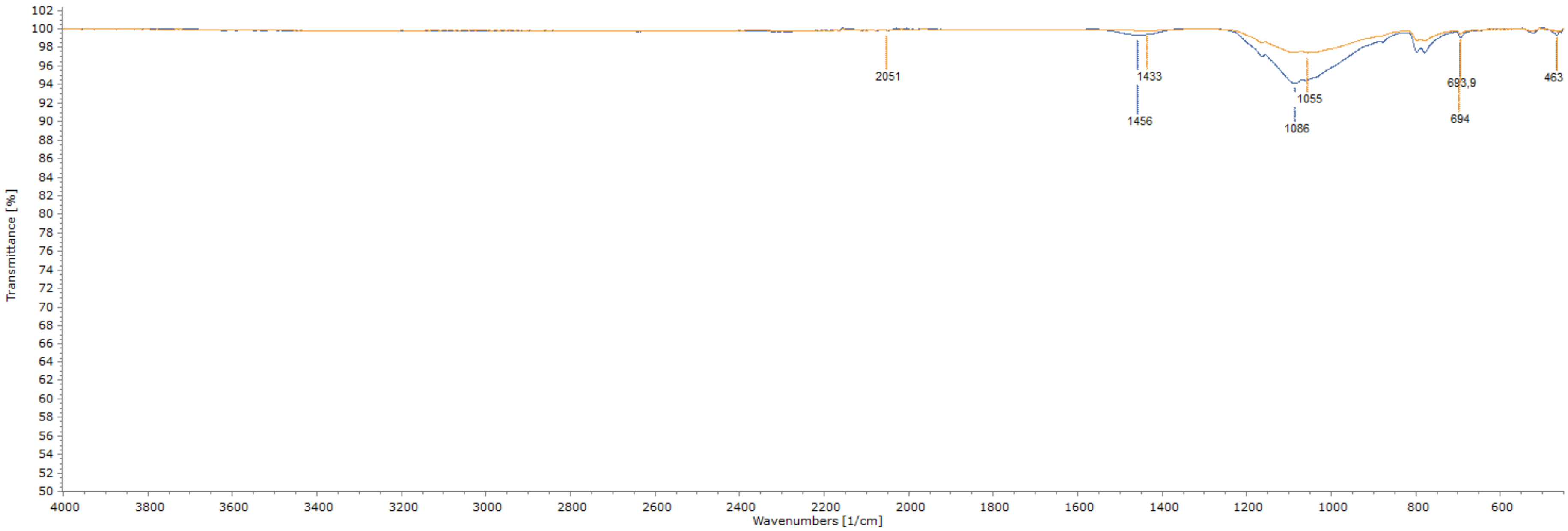

Figure 6.5.10: Result of ATR FT-IR analysis for beach sediment from Gialia (Andros Island).

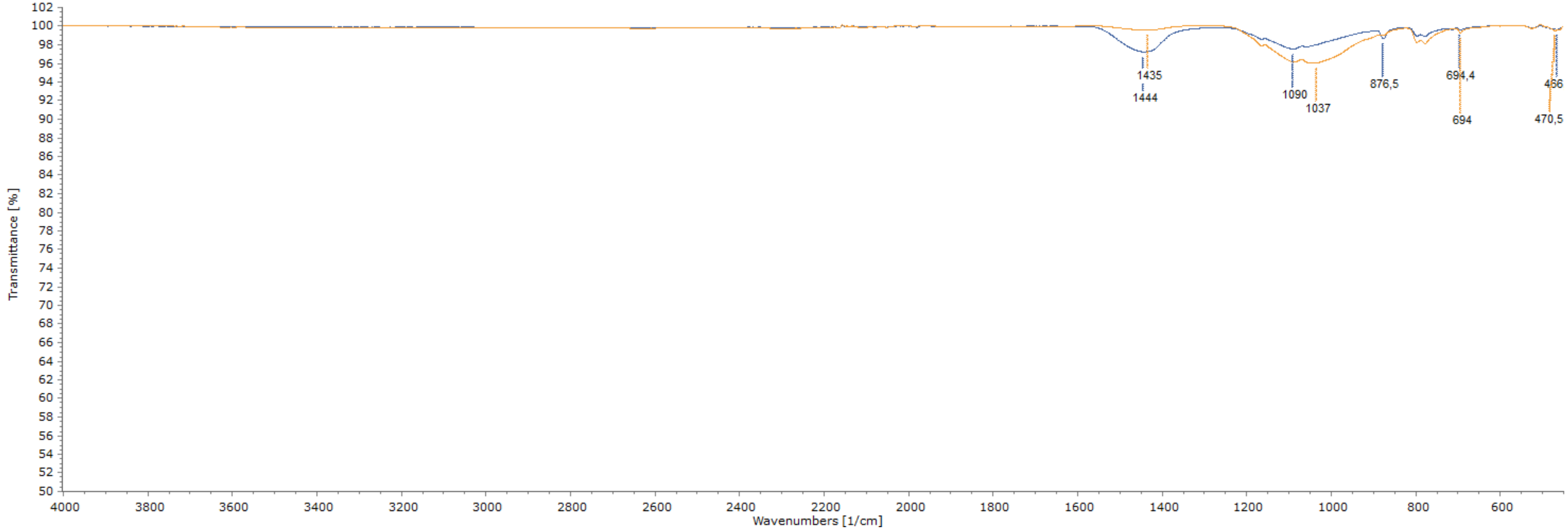

Figure 6.5.11: Result of ATR FT-IR analysis for beach sediment from Liopesi (blue line) and Fellos (orange line) (Andros Island).

The characteristic bands at 1,085, 800 and 460 cm^{-1} correspond to stretching, bending and out of plane of Si-O bonds of silica (SiO_2) (Shokri *et al.*, 2009). Spectral features related to Si–O stretching vibrations of clay minerals are between 1,050 and 1,000 cm^{-1} (Madejová and Komadel, 2001). Peaks at 470 cm^{-1} and 1,100 cm^{-1} are caused by asymmetric bending and stretching vibrations of the SiO_4 tetrahedron (Meyer-Jacob *et al.*, 2014). Peak at 695 cm^{-1} is related to symmetric bending vibrations of the SiO_4 tetrahedron (Meyer-Jacob *et al.*, 2014). Peak at 465 cm^{-1} corresponds to the mineral of quartz (Sivakumar *et al*., 2012).

Common vibrations, such as -CH stretching (2,980-2,780 cm^{-1}), -CO stretching (1,760-1,670 cm^{-1}) and -CH deformation (1,480-1,400 cm^{-1}), occur in nearly all organic matter (Xu *et al.*, 2019). Calcite ($CaCO_3$) is characterized by spectral transmittance around 876 cm^{-1} (Huang and Kerr, 1960).

Regarding the identification of microplastics, spectra were matched with known spectra (Veerasingam *et al.*, 2020) of the following polymers: Polypropylene, Polystyrene, Low-Density Polyethylene, Polyvinyl Chloride, Ethylene-Vinyl Acetate (Table 6.9, Figures 6.5.12 to 6.5.22). In total, the maximum ratio (45%) of analyzed microplastics was possibly identified as Polystyrene (PS).

Table 6.9: Shape, color and identified polymer type of some microplastics analyzed under ATR FT-IR, detected in samples from Attica and Andros Island.

Sampling Stations	**Shape**	**Color**	**Polymer Type**
Attica, Saronic Gulf			
SS1	Fragment	Green	PP
SS2	Fragment	Blue	EVA or LDPE
	Fragment	Transparent	PS
SS8	Film	Colorful	PS
	Fragment	Blue	LDPE
SS20	Film	Transparent	LDPE
SS23	Foam	White/Yellow	PS
SS24	Fragment	Purple	PS
SS25	Foam	Blue	PS
	Fragment	Blue	PP
Andros Island			
SS3	Fragment	Green	PVC

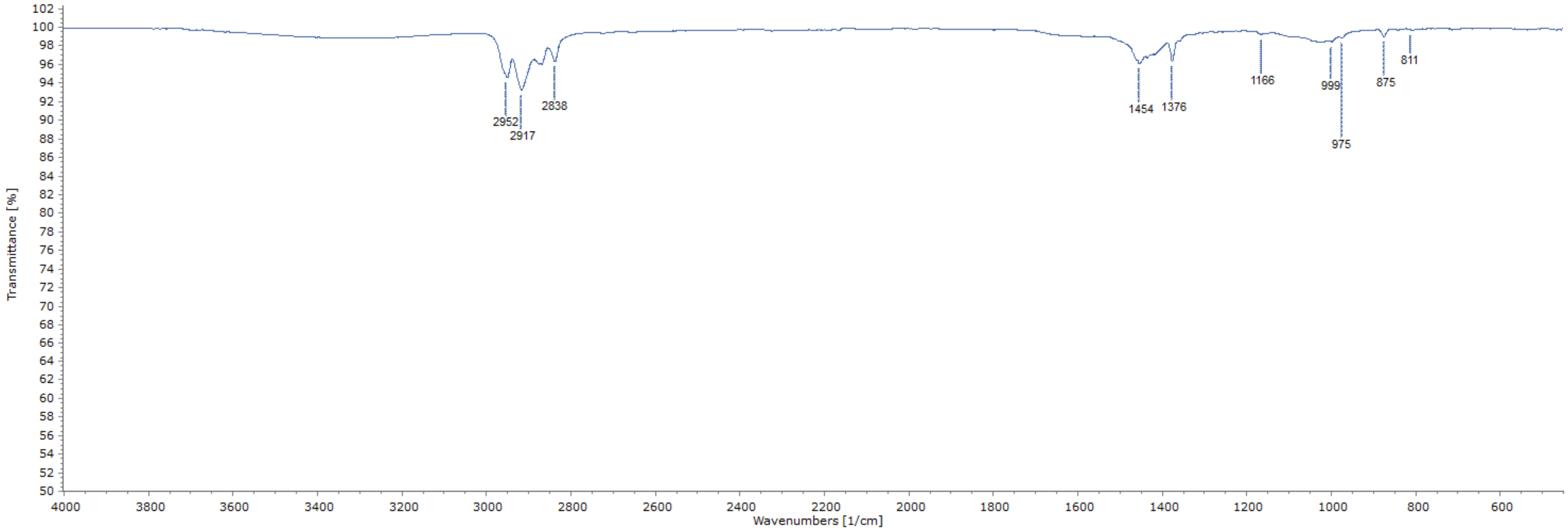

Figure 6.5.12: Result of ATR FT-IR analysis for the green fragment from the SS1 – Saronic Gulf.

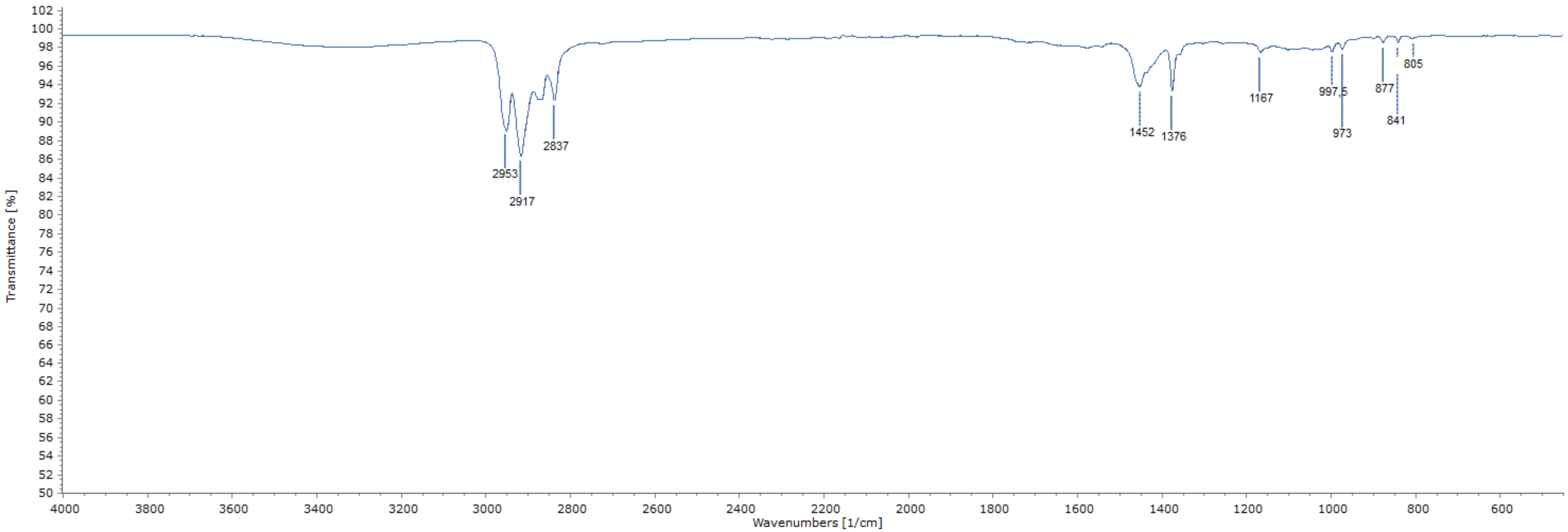

Figure 6.5.13: Result of ATR FT-IR analysis for the blue fragment from the SS25 – Saronic Gulf.

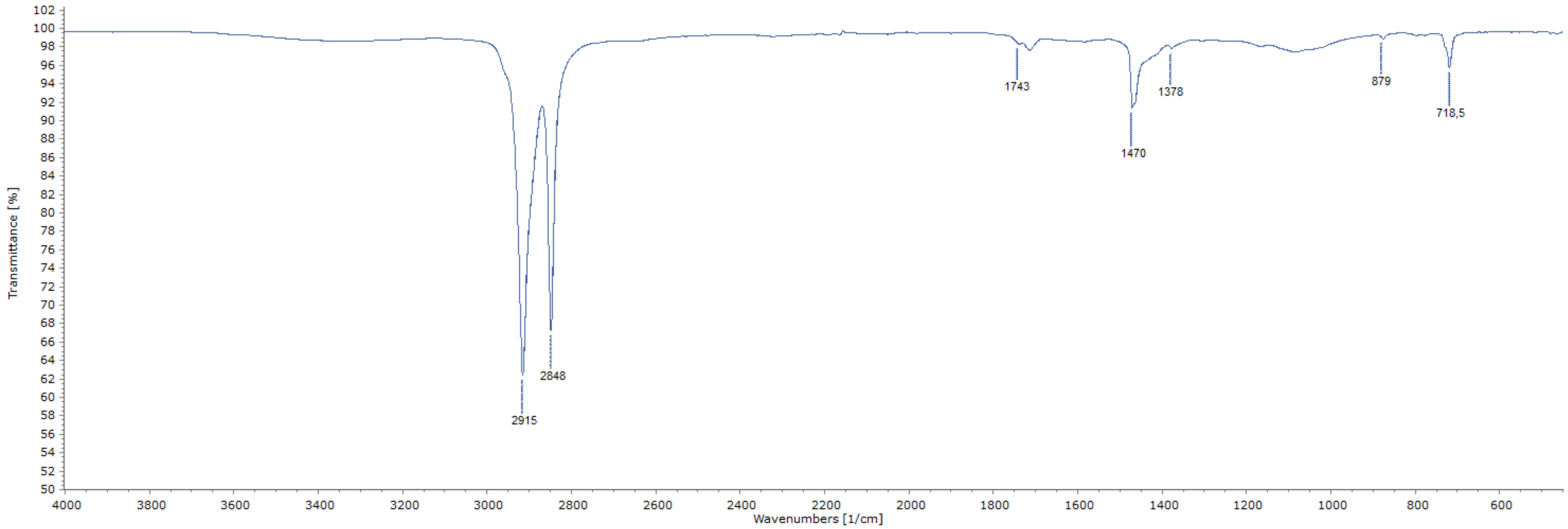

Figure 6.5.14: Result of ATR FT-IR analysis for the blue fragment from the SS2 – Saronic Gulf.

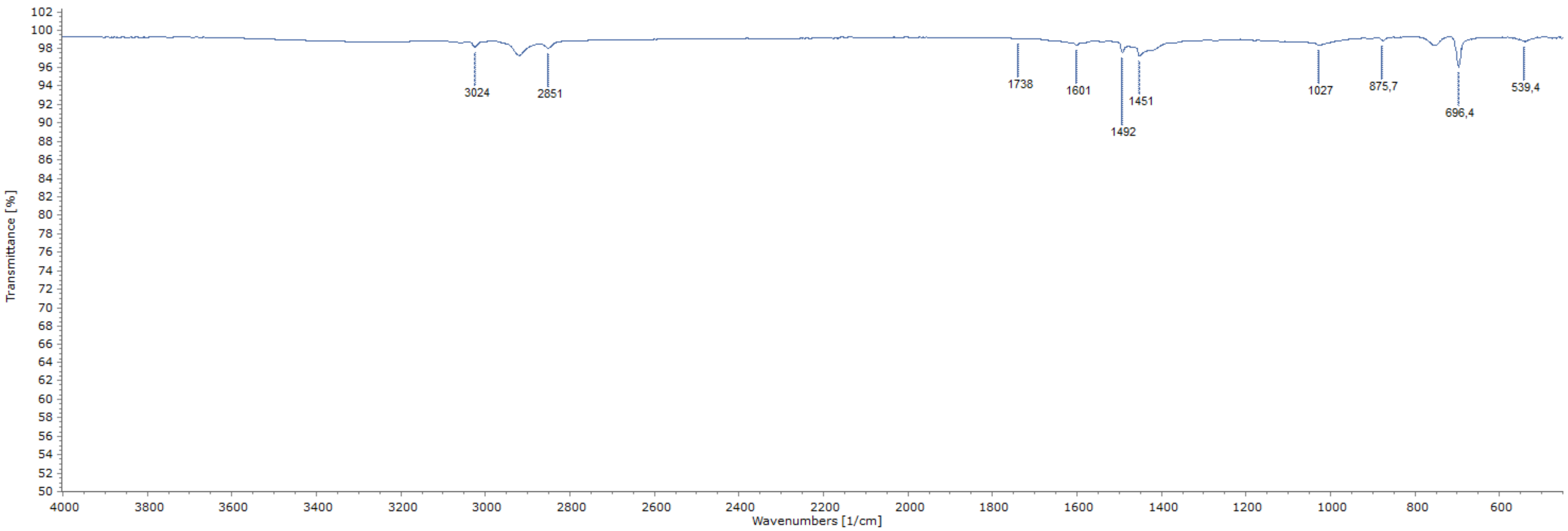

Figure 6.5.15: Result of ATR FT-IR analysis for the blue foam from the SS25 – Saronic Gulf.

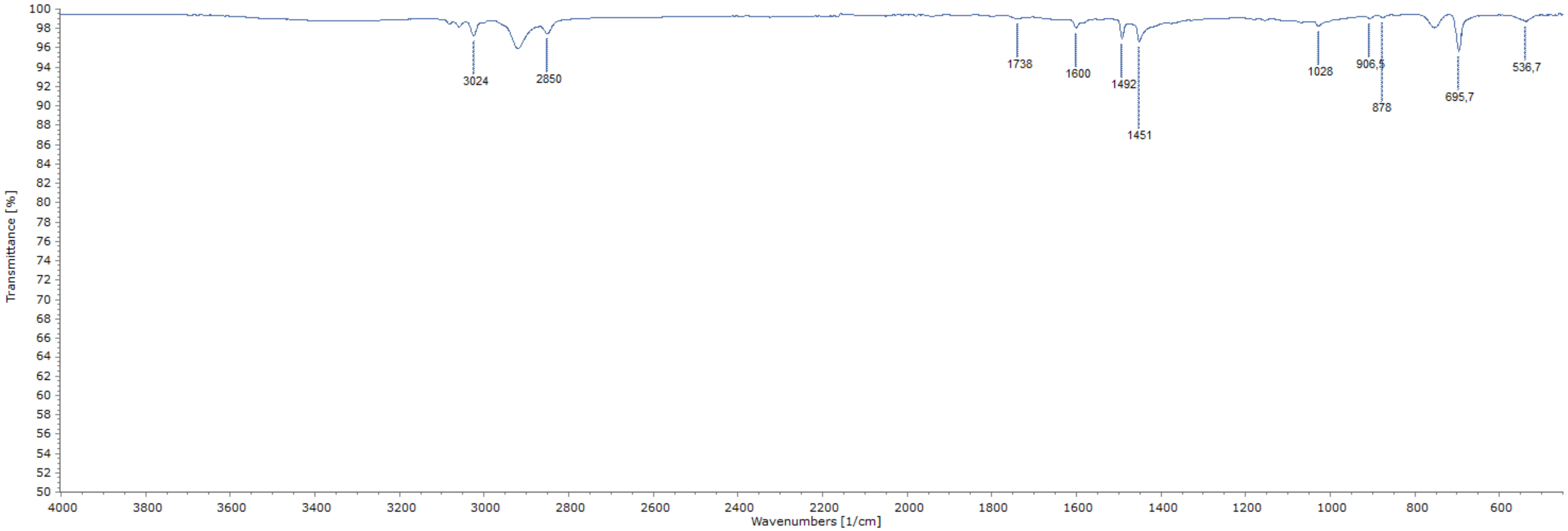

Figure 6.5.16: Result of ATR FT-IR analysis for the white/yellow foam from the SS23 – Saronic Gulf.

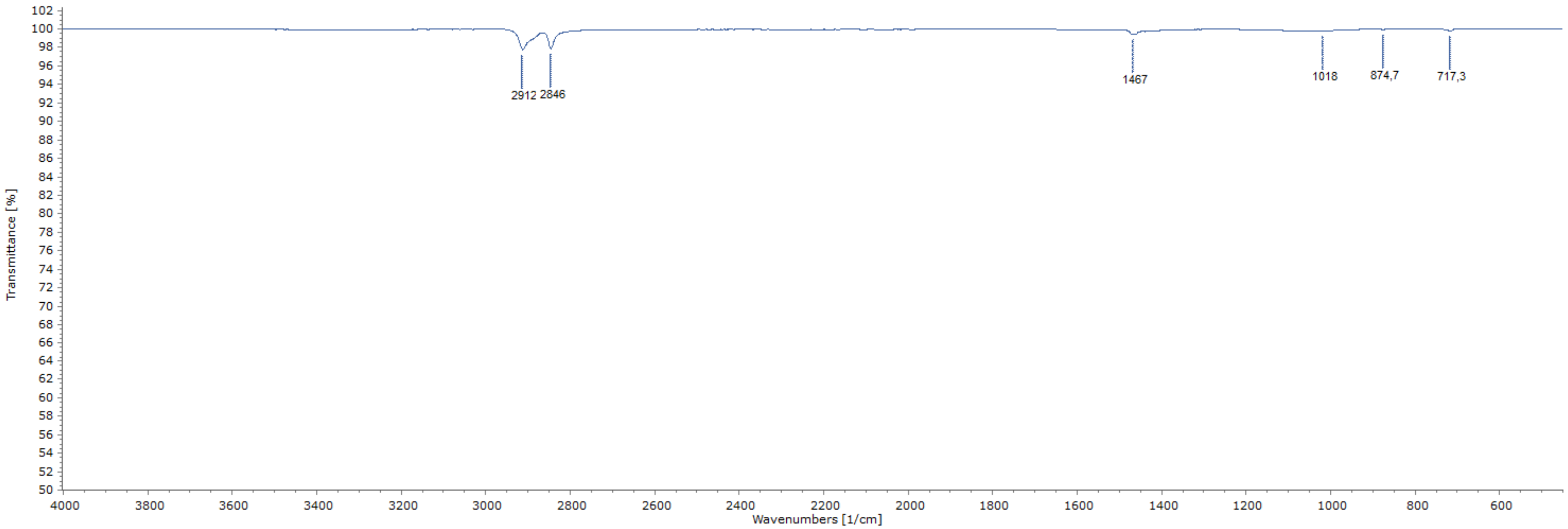

Figure 6.5.17: Result of ATR FT-IR analysis for the blue fragment from the SS8 – Saronic Gulf.

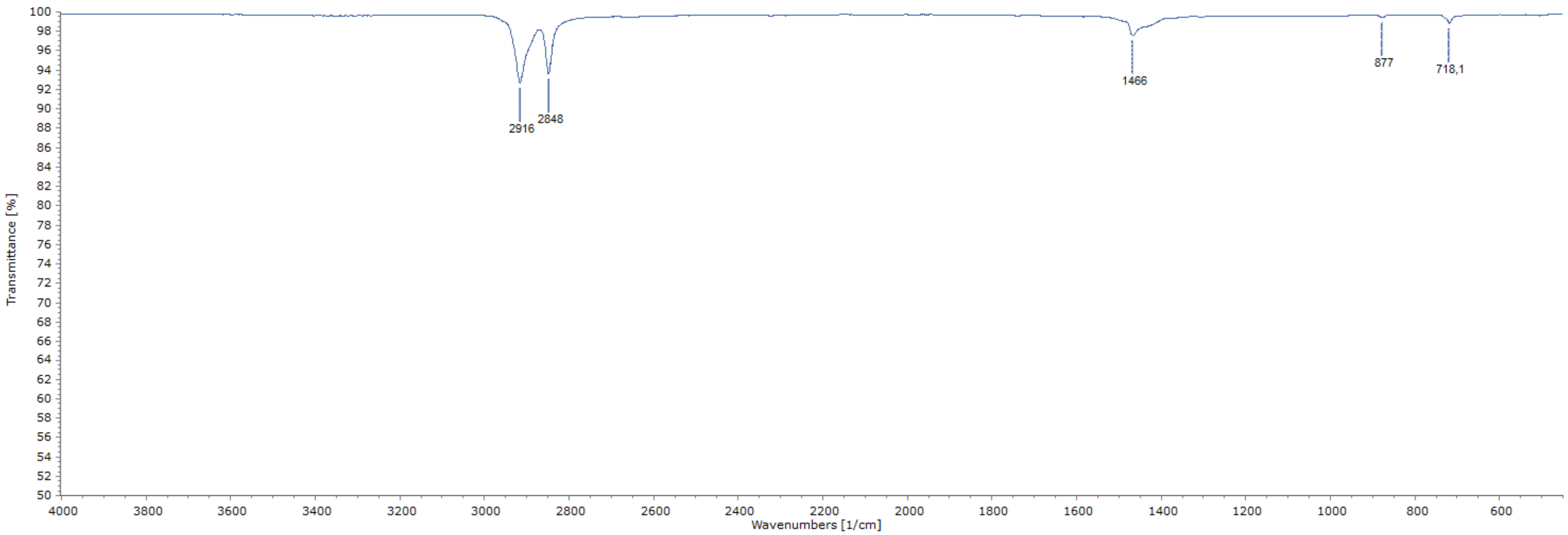

Figure 6.5.18: Result of ATR FT-IR analysis for the transparent film from the SS20 – Saronic Gulf.

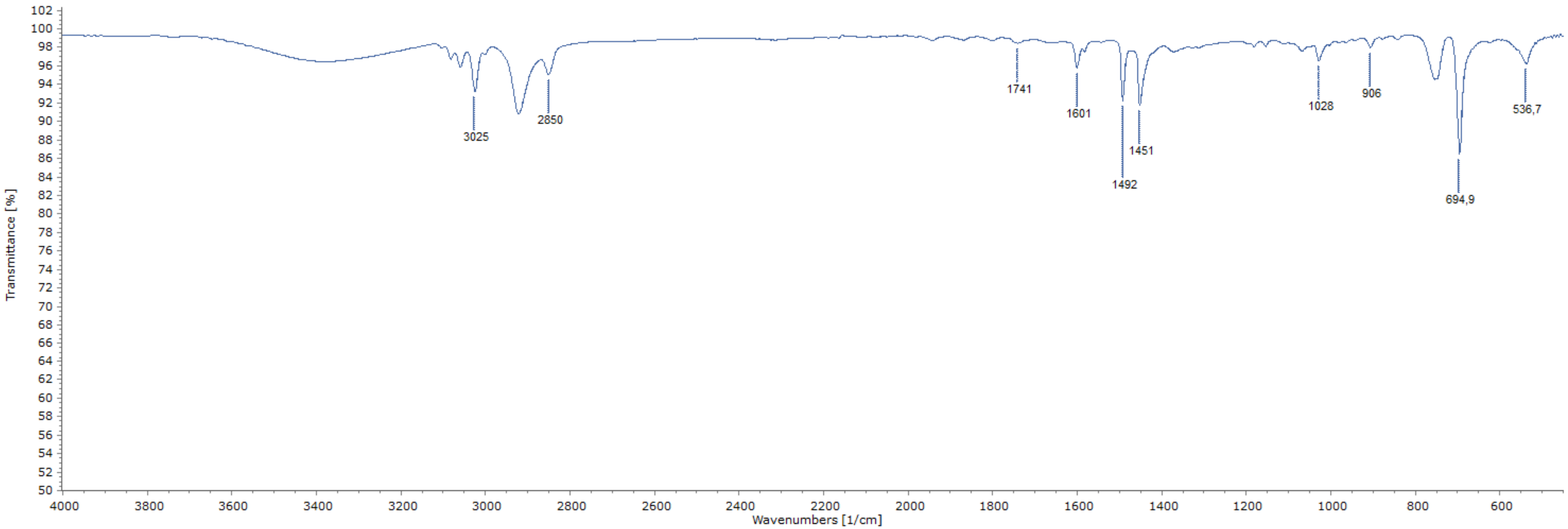

Figure 6.5.19: Result of ATR FT-IR analysis for the transparent fragment from the SS2 – Saronic Gulf.

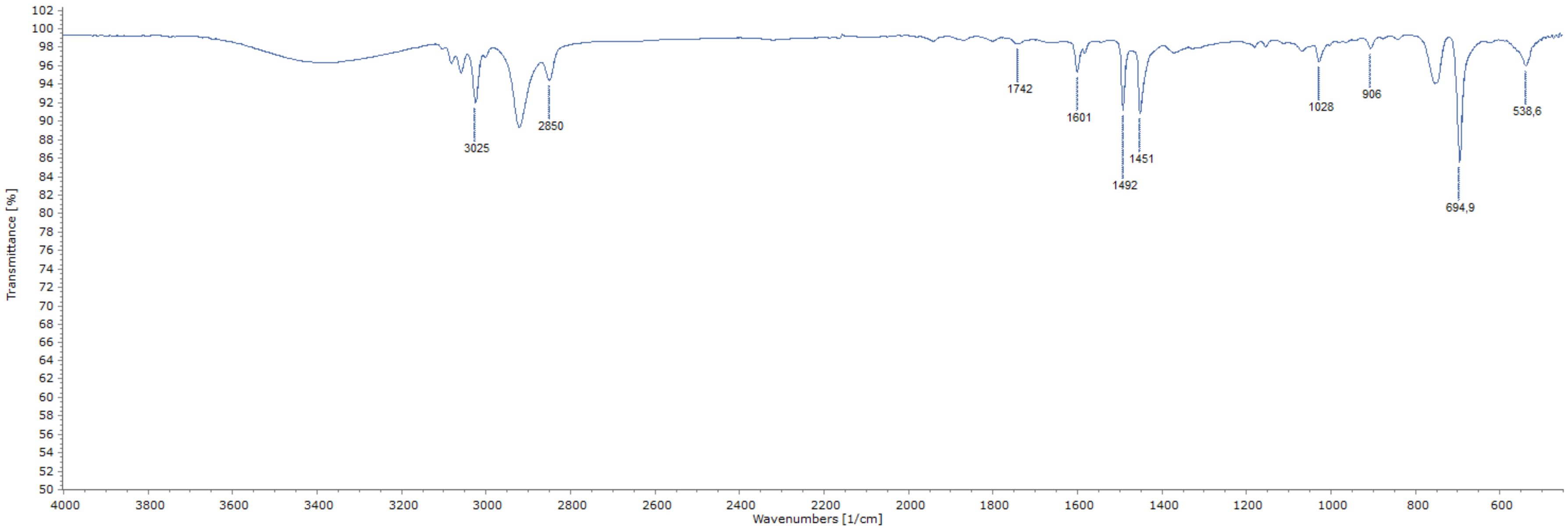

Figure 6.5.20: Result of ATR FT-IR analysis for the colorful film from the SS8 – Saronic Gulf.

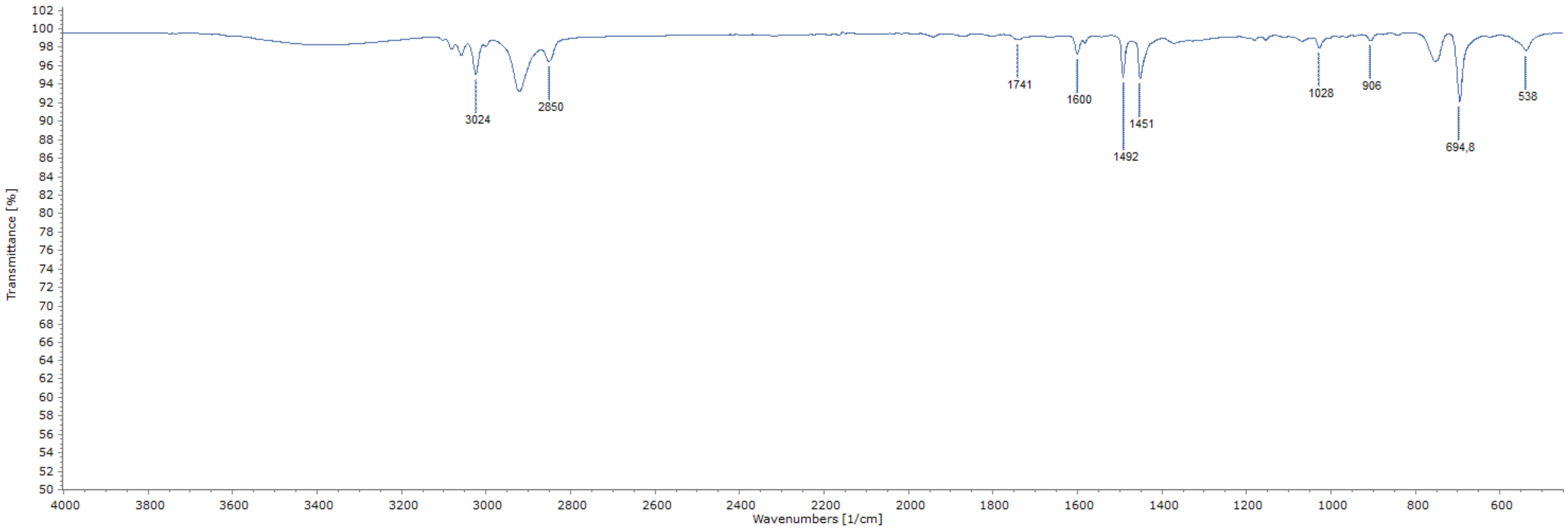

Figure 6.5.21: Result of ATR FT-IR analysis for the purple fragment from the SS24 – Saronic Gulf.

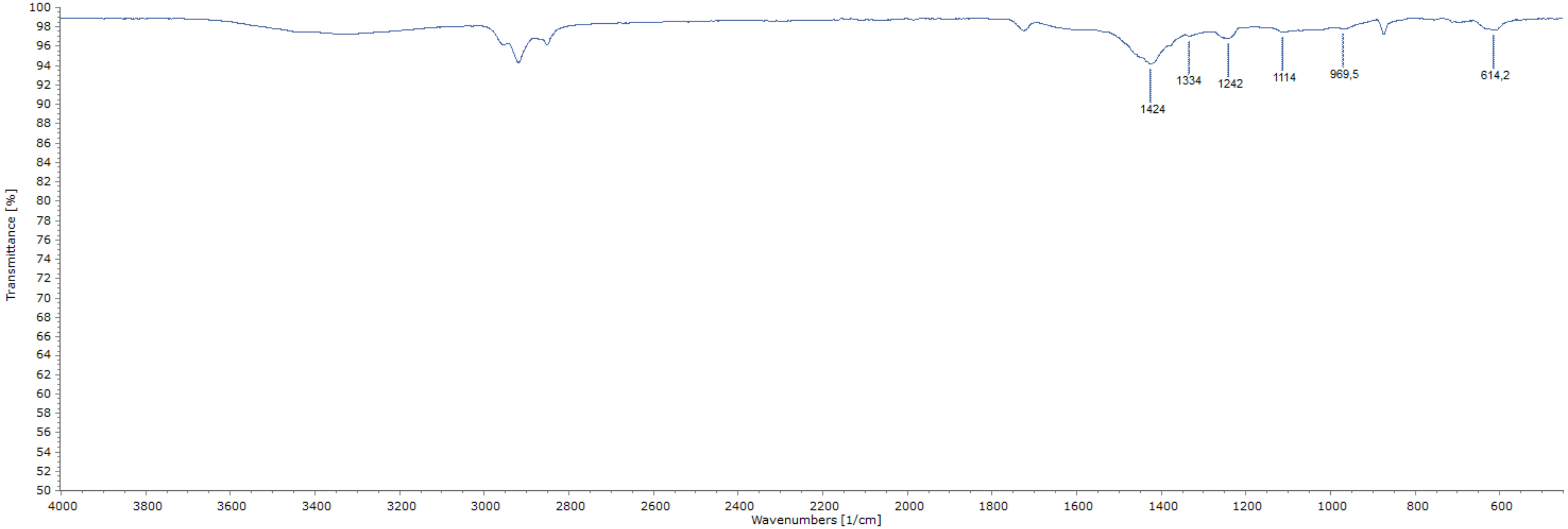

Figure 6.5.22: Result of ATR FT-IR analysis for the green fragment from the SS3 – Andros Island.

6.6. Macroplastics

The presence of macroplastics was also recorded. During the sampling process, it was macroscopically observed that Agios Kosmas, Loutra Alimou, Glyfada - Coast B and Voula beaches were the sites where a large amount of large plastic debris was deposited.

Macroplastics were detected in six sediment samples, at the stations; 3 (Gialia) of Andros Island and 1 (Agios Kosmas), 8 (Loutra Alimou), 20 (Glyfada - Coast B), 23 and 25 (Voula) of Attica. Three large fragments, a piece of Styrofoam, a cable and a piece of plastic wrap were found in total (Figure 6.6.1). More details for their length and their color are presented in Table 6.10.

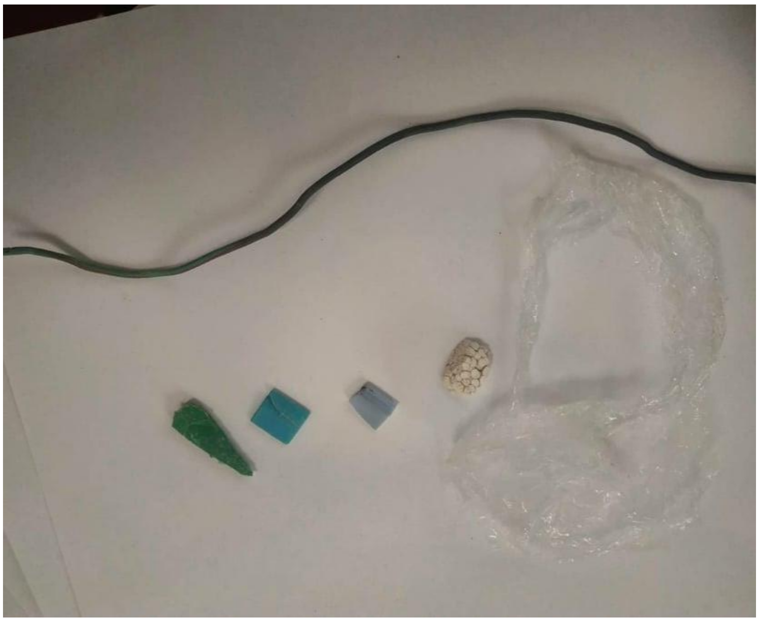

Figure 6.6.1: Macroplastics detected in samples from Attica and Andros Island.

Table 6.10: Category, length and color of macroplastics detected in samples from Attica, Saronic Gulf and the island of Andros.

Sampling Stations	Category	Length (cm)	Color
SS1 (Agios Kosmas)	Fragment	3	Green
SS8 (Loutra Alimou)	Fragment	1.4	Blue
SS20 (Glyfada - Coast B)	Plastic wrap	9	Transparent
SS23 (Voula)	Foam	1.5	White/Yellow
SS25 (Voula)	Fragment	2.7	Blue
SS3 (Gialia, Andros Island)	Cable	14	Green

7. Discussion

Sediment from Attica coastal area, Saronic Gulf presented variability in grain size classes. More than the 50% of microplastics was found in very coarse sediment, a result which matches with the global literature. According to Gregory (2009), the smaller the grain size of sand is, the more it favors microplastic accumulation. Smaller sandy particles have higher retention efficiency while large-sized ones can easily backwash microparticles (Digka *et al*., 2018).

The dominance of fragments in sediments collected from Attica could suggest that their source is more related to the breakdown of larger plastic debris (Abidli *et al.*, 2018), than to the release of primary microplastics from industrial activities.

The majority of found fragments was blue, a possible result of the decomposition of water bottles, bags, drinking straws, toys or fishing debris (Abidli *et al*., 2017). The majority of fibers was green and they might be derived by synthetic fabrics or fishing nets and ropes (Alomar *et al.*, 2016). The presence of colored microplastics is of high significance, since they could easily be mistaken for food by the biota (Kaberi *et al*., 2013). In addition, colored microplastics are considered as vectors of contamination (Browne *et al*., 2008).

Polystyrene might be the dominant identified polymer, which is in good accordance with results of another study (Ng and Obbard, 2006). However, Polyethylene and Polypropylene are frequently found as the most dominating polymers in microplastics according to Hidalgo-Ruz *et al*. (2012).

In any case, possible microplastic contamination in the Saronic Gulf is a fact about worry. According to Karapanagioti *et al*. (2011), plastic particles collected from Saronic beaches have demonstrated very high pollutant loading, comparable to heavily industrialized places of the world.

Regarding the samples collected from the island of Andros, sediment presented more homogenous granulometry and granule gravel was not found. Three of the five collected microplastics were microfibers that could derive from synthetic fabrics or the fragmentation of fishing ropes and nets (Thompson *et al*., 2004). The number of samples collected and the abundance of microplastics found were limited and any statistical analysis or conclusions related to their number, morphological characteristics and polymer identification, could not be possible.

It is a fact that irregular microplastic shapes were found in samples both from Attica and Andros Island. Fragments, fibers, foams and films were found, which are secondary microplastics. They usually arise from the fragmentation of bigger plastics through light, heat, chemical, or physical processes (Cole *et al*., 2011), or they are contributed to the transfer of land-based microplastics (Expósito *et al*., 2021).

A much higher number of microplastics was found in samples from Attica than from the island of Andros. Attica beaches might be much more polluted due to urban sources and the high population in this region (about 3.8 million inhabitants). Indeed, population density is positively correlated with microplastic abundance (Browne *et al*., 2011).

It is also expected that wind-driven circulation has an effect on microplastic accumulation at beaches, with higher concentrations reported in sheltered areas, like the Saronic Gulf, than in exposed ones, like the island of Andros, Aegean Sea (Vianello *et al*., 2013). Cephissus and Ilisos rivers could also affect the microplastic distribution in the Attica region. Indeed, several studies have attributed high microplastic concentrations to river discharge (Lots *et al*., 2017).

The diversity of microplastics found in both studying regions regarding shape, color and polymer composition could show different origins. Touristic, fishing and shipping activities are common both in Attica and Andros Island; as a result, the way and the extent that these activities may affect the microplastic presence there, cannot be safely assessed in the present study. In addition, several point sources that could spread microplastics along these coasts may include marinas, (illegal) trash disposal, urban runoff and strong winds, wastewater effluents and transportation from landfills due to weather conditions (Peters and Bratton, 2016).

8. Conclusions

This research aimed to assess microplastic pollution in beach sediments from the Attica coastal area and the island of Andros. Based on a quantitative and qualitative analysis of microplastics, it could be concluded that:

- The majority of microplastics was found in very coarse sandy sediment.
- Fragments were dominant in sediment from Attica beaches, while fibers consisted the majority of detected microplastics in sediment from Andros Island.
- The majority of microplastics found were colored, with green and blue being the dominant colors.
- Polystyrene was probably the most common polymer identified using FT-IR analysis.
- Greater abundance of microplastics was found in Attica coastal area than in the island of Andros.
- The most significant factors affecting microplastic pollution in these regions might be; tourism, fisheries, shipping activity, other anthropogenic factors and also some physical characteristics, for example the geographic location of each sampling site.

The results of this study indicated the presence of large microplastic particles (1-5 mm) in the majority of the examined samples, emphasizing their dispersion especially in the Attica coastal area.

The present study provides novel insight and original results for beach microplastic pollution of selected Greek coasts. It is anticipated that the outcomes of the present study will provide insights towards a better interpretation of beach sediment microplastics data. To better understand the implications of these results, future studies could be extended to assess the impacts of microplastic presence and its fate on the Greek coasts.

9. Acknowledgements

This thesis is the outcome of extensive work and research, in the context of the M.Sc. program "Sustainability and Quality in marine industry" of the University of Piraeus.

Foremost, I want to express my profound gratitude to my supervisor, Professor Fani Sakellariadou, whose expertise, support and guidance were invaluable. Her insightful feedback pushed me to sharpen my thinking and brought my work to a higher level.

I would like to acknowledge Professor Basil Stylianos Tselentis for his assistance through each stage of this process. I am extremely grateful. In addition, I warmly thank Dr. Danae Antivachis for her valuable help and guidance during FT-IR analysis. I also thank the members of the committee for their critical comments.

Finally, I could not have completed this thesis without the support of my inspirational family throughout the whole M.Sc. program.

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