MEDICAL UNIVERSITY

"PROF. DR. PARASKEV STOYANOV" - VARNA

FACULTY OF PUBLIC HEALTH

DEPARTMENT OF HYGIENE AND EPIDEMIOLOGY

Dr. Yavor Hristov Chenkov

POLLUTION OF THE VARNA REGION OF THE BLACK SEA WITH PLASTIC WASTE AND POSSIBLE HUMAN HEALTH RISKS

ABSTRACT

on

dissertation work

for awarding the educational and scientific degree "Doctor"

Supervisor:

Prof. Dr. Teodora Dimitrova, dm

Varna, 2023

The dissertation contains 168 pages and is illustrated with 21 figures, 2 tables and 2 schemes. The appendices contain an archive of photographic evidence, as well as an author's questionnaire from the attached survey. 337 literary sources are cited.

Supervisor:
Prof. Dr. Teodora Dimitrova, MD
Reviewers:
1. Prof. Dr. Emil Vlaikov Vodenicharo, MD
2. Prof. Dr. Magdalena Stefanova Platikanova, MD

Jury
External members
1. Prof. Dr. Emil Vlaikov Vodenicharo, MD
2. Prof. Dr. Magdalena Stefanova Platikanova, MD
3. Associate Professor Angel Mario Jambazov, Ph.D.
Spare external member
Prof. Dr. Penka Dimitrova Gatseva, MD
Internal members
1. Prof. Dr. Tsonko Paunov Paunov, MD
2. Assoc. Dr. Rositsa hristova Stancheva – Chamova, MD
Spare internal member
Prof. Dr. Darina Naydenova Hristova, MD

The defense of the dissertation will take place on February 29, 2024.

of ……… in auditorium ……………………………………….

Introduction

Anthropogenic pollution of the environment has probably occurred throughout human history, but its scale and severity increased significantly after the Industrial Revolution in the 18th and 19th centuries. During this period, there was a rapid increase in the use of fossil fuels, accompanied by the growth of individual industrial sectors (Mohajan, 2019). All this ultimately leads to increased emissions of pollutants into the air, water and soil (Fowler, 2020). Human civilization is growing more and more dependent on technology and modern conveniences, while at the same time there is a lack of awareness among the general public about the various aspects of the planet's pollution. Moreover, new sources of pollution appear over time, whose long-term effects on nature have yet to be assessed.

Plastics are materials that are made by mixing different polymer molecules with other additives. Depending on the base polymer and the presence of additives, plastics with a wide variety of qualities are obtained (Odian, 2004; Bhattacharjee, 2020). The most common plastics in our daily life are derivatives of polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), polycarbonate (PC) and many others. Despite their undoubted benefits, however, plastics also pose significant challenges for wildlife. Uncontrolled disposal of plastic waste can lead to significant environmental pollution, which is the focus of the current scientific work.

Along with air pollution and global warming, the problem of plastic pollution of water bodies has become one of the most significant environmental challenges of modern times, raising concerns not only for the well-being of ecosystems in nature, but also carrying potential risks to human health. Currently, the majority of studies on plastic pollution of the environment examine the various compartments of the water systems of the Earth's hydrosphere. However, it has been confirmed that the majority of plastic pollution in aquatic environments originates from terrestrial sources (Xu, 2020), highlighting the need to focus research efforts on this issue in terrestrial environments as well. The present scientific work will focus on the various aspects of plastic pollution along some coastal areas in the Varna region. An approximate snapshot assessment of the quantities and types of larger-sized plastic waste (so-called "macroplastics") will be carried out. This is a problem of extreme importance, in view of the limited amount of data on this kind of pollution at these latitudes and the potential negative effects that could occur for marine ecosystems and humans.

Although empirical data show the presence of plastic pollution in almost every part of the planet – hydrosphere, lithosphere, atmosphere, etc., (Moore, 2023; Zhang, 2022; Bergmann, 2019; Zylstra, 2013; Ronda, 2021; Xu, 2020), the majority of research on the topic is focused on the study of water basins of the hydrosphere (Jambeck, 2015; Chiba, 2018; Lebreton, 2018; Eriksen, 2014). The results of these studies show that massive amounts of plastic are present in high abundance in both saltwater and freshwater basins. The ocean is the final destination for much of the plastic that has ended up in the environment for one reason or another. Plastic debris is found throughout the ocean, including coastal regions, the sea surface, deep-sea areas and polar sea ice. This is not accidental, in view of the fact that due to the general circulation of substances in nature, almost all pollutants from land, including plastics, sooner or later enter freshwater basins and from there into seas and oceans (Rochman, 2020; Jambeck, 2015). Their further fate still remains poorly understood, but due to their proven slow natural degradation, it is assumed that they would persist for tens to hundreds of years in an almost unchanged form or in varying degrees of fragmentation depending on multiple factors (Andrady , 2003; Barnes, 2009).

Plastics are extremely difficult to degrade in the natural environment due to the complex set of their physicochemical characteristics. Such characteristics are, for example, their hydrophobicity, the presence of stable covalent bonds, different functional groups and additives (Liu, 2022). Different types of plastic derived from them have different degrees and periods for degradation in the environment. The duration and extent of natural degradation can also be affected by additional factors (Tosin, 2012; Chamas, 2020). The main parameters of the environment, most significantly affecting the processes of plastic degradation, are light, temperature, humidity and the presence of microorganisms. All these factors affect the susceptibility and subsequent fragmentation of the various plastic materials (Andrady, 2022). Fragments generated after oxidation and subsequent exposure to mechanical loads include secondary micro- or even nanoparticles, which represent an emerging class of contaminants. Furthermore, in nature, microplastics (size < 5 mm) are more likely to attract other substances i.e. they possess sorption capacity, due to their large specific surface area and physicochemical characteristics, which further affects their degradation (Lee, 2014). On the other hand, the complex action of different meteorological and environmental parameters of the environment can influence the rate of natural polymer degradation.

Considering the potentially long lifetime of plastics, the methods used in laboratory conditions to simulate natural degradation and the achieved short-term experimental results to predict long-term degradation pathways, are insufficiently relevant and applicable to more accurately and objectively determine their lifetime fragmentation in nature. But they certainly fragment into smaller particles. By this point, it is clear that much of the discarded plastic waste is already fragmented to such an extent that it is difficult to pinpoint the immediate origin of the smaller fragments and the primary items from which they are derived. By applying spectroscopic, chromatographic and other techniques and equipment, it is possible to determine with approximate accuracy the type of polymer from which the pollutant particles are made, their quantity, as well as the additives emitted by them or the toxic agents sorbed from the environment (Araujo, 2018).

Plastic waste can enter the environment as a result of a large number of terrestrial and aquatic human activities (Pruter, 1987; United States Senate, One Hundred Fourteenth Congress, 2016; Coe, 2012). Regarding plastic pollution in the marine environment, it is generally accepted that land-based sources account for 60 to 80 % of marine litter (OSPAR Commission, 2007), while the remaining 20-40 % originates mainly from marine/ocean sources. It has been estimated that approximately 1 million plastic bottles are purchased every minute somewhere in the world and up to 5 trillion plastic bags are used each year (UNEP, 2018). Some of the waste enters European seas, where approximately 626 million “floating items” (or 3382 tons of waste) accumulate annually (González-Fernández, 2021).

The main sources of plastic in water bodies include:

1. Shipping activity - fishing, military, research and tourist-cruise.

2. Tourism - sea and land.

3. Household activities - microplastics from various household products and materials migrating to the marine environment through urban and rural sewage systems.

4. Production activities - improper disposal, incineration and recycling of a huge number of plastic products and their waste products entering the environment immediately after their production.

5. Agriculture and other sectors of the economy.

Currently, there is a lack of in-depth data on the specific sources of plastic pollution in the Bulgarian Black Sea water area. Some initial estimates indicate that plastic waste originates mainly from activities such as tourism, fishing and agriculture (Bobchev, 2018; Berov, 2020), with the majority of marine litter – about 70% – originating from land-based sources (Bekova, 2023).

Due to the specific degradation and distribution characteristics of plastic waste in aquatic environments, it can be assumed that the majority of large plastic debris is almost intact from its entry into nature or has undergone a low degree of fragmentation. The microplastic particles detached from them have a smaller contribution to the pollution of nature with fractions of plastic < 5mm, compared to the contribution of primary microplastic entering the environment through sewage systems, the net amount of which is assumed to be greater (Wang, 2020). In other words, the majority of microplastics entering the seas and oceans originate directly from human domestic activities (as primary microplastics through cosmetics and clothing), while a smaller fraction enters the environment after fragmentation and separation from macro- and mesoplastic waste. Polyethylene, polypropylene and polystyrene make up almost 83% of the total microplastic particles.

There are reasons to assume that the large number of chemical substances added to plastics already during their production processes (plasticizers, stabilizers, dyes, etc.), once found in nature, can be released from the polymer matrix to their surrounding environment (Gunaalan , 2020; Bhunia, 2013; Yousif, 2013; Burgos-Aceves, 2021; Gunaalan, 2020). Their fate after that is not sufficiently well understood, but there is reason to suppose that a part of them undergoes transfer in the environment, with the potential for migration to other matrices or living organisms.

In the last 2 decades, there has been increasing talk about the potential risks that plastic pollution poses to natural ecosystems (Browne, 2008; López-Martínez, 2021; Werner, 2016). They can be affected in mechanical, toxic or other ways by plastic pollution. These processes likely occur at many levels of the food web (Tuuri, 2023). The person, as an integral part of this web, is also exposed to various health risks (Anbymani and Kakkar, 2018, Galloway, 2015; Banerjee, 2021; Blackburn, 2022).

Research on plastic pollution in Bulgaria and related ecotoxicological and epidemiological aspects is still at a very early stage. The empirical data asset is still insufficient to make specific quantitative and qualitative assessments of the various parameters of plastic pollution in individual regions of the country. These circumstances, as well as the growing importance of the problem of plastic pollution in general, led to the need to conduct the present study.

Literature review

Nature of plastics and terminology

The term "plastic" comes from the Greek word "**πλαστικός**" (plastikos), which means "easily formed" or "able to be modeled", "moldable".

Plastics are synthetic materials obtained chemically (most often through the processes of polymerization and polycondensation) by connecting thousands to millions of repeating molecules - the so-called monomers, leading to the formation of linear, branched and network-like chains called polymers. The binding of monomers is done by covalent chemical bonds, and apart from the main backbone of the polymer chain, individual other chemical elements and radicals can be added, thus producing different types of plastics (Odian, 2004). The production of synthetic polymers include various raw materials, the most commonly used being processed petroleum products (ethylene, propylene, etc.), gas, carbon fibers, biomass, i.e. at an elementary level, plastics are primarily carbon structures. In the process of the production of plastics, in addition to the main polymer backbone, various additives and products are included - catalysts, additives (so-called plasticizers), fillers, solvents, etc. (Andrady, 2019). Thanks to them, plastics acquire unique, specific properties that distinguish them from natural materials - elasticity, thermal and chemical resistance, ductility, hardness, etc.

Polyethylene and polypropylene are the main representatives of the so-called polyolefins - the most widely used thermoplastic polymers in mass production (Wypych, 2018). They belong to semi-crystalline thermoplastics. They are characterized by easy processing, good chemical resistance and electrical insulation properties. Other polyolefins of industrial importance are polymethylpentene (PMP), polyisobutylene (PIB) and polybutylene (PB). As they are the most widely used industrial and household plastics, they are also the most common types of pollutants in the environment.

The specific properties of different plastics are due not only to the spatial configuration of their polymer molecules, but also to the presence of various additives. These substances are added to the polymer structure to improve certain properties of the material, such as impact resistance, heat resistance, transparency, flexibility, color and other characteristics (Hahladakis, 2018).

Plastic particles added to personal care products (cosmetics, face/hair/body products, toothpastes, etc.) are referred to as microbeads (Guerranti, 2019; Nawalage, 2022). They are very small polymer-based particles that are used to achieve certain textures, exfoliate (remove dead skin cells), add decorative effects such as glitter, or simply as fillers. We could relate them to the "primary microplastic" category, as they enter the environment not by weathering and separation from larger fragments, but directly in their primary form.

The life cycle of plastics includes three phases: production, use and disposal. In manufacturing, carbon-based raw materials - coal, gas and oil - are transformed through energy-intensive, catalytic processes into a vast array of products. The use of plastic occurs in every aspect of modern life and results in widespread human exposure to the chemicals contained in plastic. Although nowadays waste management strategies are greatly optimized and biodegradable polymer materials are increasingly entering the household, if the net amount of plastics in circulation continues to rise, the environment, and water bodies in particular, will be faced with an ecological catastrophe of colossal proportions (Eriksen, 2023).

According to the classification adopted by the National Oceanic and Atmospheric Administration (NOAA), plastics found in water bodies can be classified based on their size (Lippiatt, 2013; Frias, 2019). Thus, three main size classes are distinguished: micro- (≤5 mm), meso- (5 mm to 2.5 cm) and macroplastics (>2.5 cm). Macroplastics can be identified by article type or by plastic type using the International Resin Coding System (ASTM D7611). The abundance and global distribution of microplastic particles has increased over the past few decades, and the average amount of plastic waste found in the environment appears to be decreasing (Barnes, 2009). Plastic microbeads falling under the category of microplastics can be used as ingredients in personal care and cosmetic products, leading to the direct introduction of these particles into wastewater streams from households, hotels, hospitals and sports facilities (Boucher, 2017). In recent years, scientists have begun to investigate the fragmentation of plastics down to smaller scales than microplastics. In 2014, the fragmentation of expanded polystyrene (EPS) granules to nanosized particles in laboratory conditions was reported for the first time (Shim, 2014). The term "nanoplastics" is currently debated in scientific circles, but there is still disagreement regarding the definition of the upper limit of the size of these particles. Some authors take their size as an upper limit of 1000 nm, while according to others, an upper size limit of 100 nm should be taken (Gigault, 2018; Piccardo, 2020). Laboratory evidence shows that the formation of nanoscale particles from larger plastic fragments is very likely to occur in the environment as well (Song, 2017).

One of the main physical factors that influence the degradation of plastics in the environment is sunlight (Eales, 2022). Ultraviolet radiation causes photooxidative degradation of polymer molecules, leading to the rupture of their chains and the formation of free radicals. This process, initiated by light in the presence of oxygen, is also called oxidative photodegradation or photooxidation (Yousif, 2013). Thus, it reduces the molecular weight of the polymer material, causing a deterioration in its mechanical properties (Bottino, 2003; Vasile, 2000). Given the heterogeneity of natural UV radiation, ranging from no exposure (in sediments) to full UV exposure (in floating or beach litter, as well as airborne plastics), it is argued that degradation/fragmentation rates, induced by UV will also vary dramatically between different environmental niches (Feldman, 2002; Yousif, 2013; Eales, 2022).

Plastic pollution in seas and oceans

The internationally agreed definition of "marine litter", based on the definitions that have been used for many years in the context of marine and ocean pollution, was created by the United Nations (United Nations Environment Programme, Regional Seas Program (2005): Marine Utter - An analytical overview). According to this definition, "marine litter" is any persistent, manufactured or processed solid material discarded or abandoned in the marine and coastal environment'. Additionally: “Marine litter consists of items that have been made or used by humans and intentionally dumped into the sea, rivers or beaches; brought indirectly to the sea by rivers, sewage, rainwater or winds; accidentally lost, including materials lost at sea in bad weather (fishing gear, cargo); or intentionally left by people on beaches and shores."

Marine litter thus includes all items that are not of natural origin and would not occur naturally in the marine and coastal environment, but are nevertheless found there (OSPAR Commission (2007). It consists of items that have been or used by humans and at some point, regardless of where they were first dumped or lost, ended up in the coastal or marine environment.

From studies concerning plastic pollution in the seas and oceans, it is clear that waste is widely dispersed not only on the sea surface, but it is also now known that it is spatially concentrated in specific deep-sea environments, especially in canyons, deep ocean trenches, sedimentary drift deposits and below surface water zones (Peng, 2018; Harris, 2020). Other places where significant accumulation of plastic debris has been found are the subsurface water column, shores, sea ice and marine organisms (Hardesty, 2017). There are estimates that 70% of marine litter ends up on the seabed, 15% floats in the marine column or on the sea surface, and 15% is located along the coast (OSPAR Commission 2007).

Plastic pollution in the Black Sea

Research on plastic pollution in the Black Sea is still at a very early stage. There are a limited number of publications on the subject (Suaria, 2015; González-Fernández, 2022; Aytan, 2016; Oztekin, 2017; Çevik 2022), but research interest in this direction has begun to grow in recent years. The results of the available published reports show that the concentration of plastic near the mouth of the Danube River is significantly higher than in the coastal areas along the Romanian and Bulgarian coasts. This can be explained by the import of plastic from the Danube River into the western part of the Black Sea (Pojar, 2021). The analyzes showed an average concentration of 7 plastic particles/m³, dominated by fibers (~76%), followed by foils (~13%) and fragments (~11%). Very few spheres and granules were found. The results of the verification of polymer types by pyrolysis and spectroscopic analyzes show that the dominant types of plastic are PP and PE, which is consistent with other studies analyzing the surface waters of other seas and the world's oceans.

One of the most significant studies of plastic pollution in the waters of the Black Sea, conducted and published by an all-Bulgarian research team, is the expedition on board the "Rainbow warrior", conducted between 08.08.2017 and 08.10.2017 in coastal waters between Burgas Bay and Cape Kaliakra (Berov, 2020). The Rainbow Warrior is a Greenpeace sailing vessel that was visiting Bulgarian waters as part of their "Plastic Free" campaign. In sampling during the expedition itself, two environmental condition criteria were covered - amount of plastic litter > 2.5 cm floating on the sea surface, as number/km^2, and marine plastic litter <5 mm floating on the sea surface, as number and weight per km^2 (microplastics). The amounts and type of floating marine debris > 2.5 cm were determined using the visual transect method (Vlachogianni, 2016). The average number of floating marine debris found in this expedition was 41.5 ± 30.05 items/km2. The highest amounts were observed west of Cape Kaliakra - 93.8 elements/km^2, north of Cape Emine - 77.4 elements/km^2 and Varna Bay - 60.9 elements/km^2. In general, these concentrations of anthropogenic debris in the open sea are very similar to the concentrations of floating debris calculated after expeditions in the Pacific Ocean (Hinojosa, 2009), the southeastern part of the Atlantic Ocean (Ryan, 2014) and a section of the western Black Sea coast of the Romanian waters (Suaria, 2015). The most common anthropogenic litter included bags (7–53%), plastic pieces (unidentified debris) 2.5–50 cm (20–83%), packaging (7–27%), polystyrene pieces 2.5–50 cm (3–43%) and bottles (3–9%). In most transects, predominant litter sizes ranged between 10 and 30 cm.

To date, large-scale areas of dense plastic accumulation similar to the accumulation sites in the oceans (eg, the Pacific north of Hawaii) have not yet been observed in the Black Sea. The chaotic nature of marine flows and currents makes it difficult to theoretically predict the transport and possible accumulation of anthropogenic debris, but in general, the available data indicate that the specific characteristics of the circulation in the Black Sea are not favorable for the concentration of floating dense marine beds (Stanev, 2019). However, certain seasonal trends of transfer and potential predominance of marine debris in certain areas of the Black Sea water area have been established (Miladinova, 2020), which does not exclude scenarios of dense accumulation under certain conditions over time. In view of the unique physico-chemical features of the Black Sea, distinguishing it from any other water basin on Earth, it can be assumed that the mechanisms of distribution, degradation and influence of plastic pollution on marine ecosystems differ from those in the oceans and the rest closed and semi-closed type seas, despite some similarities in the observed results. Thanks to the increasing number of reports from scientific teams from all countries bordering the Black Sea, the white spots in this area of knowledge are gradually being filled (Suaria, 2015; González-Fernández, 2022; Aytan, 2016; Oztekin, 2017; Pojar , 2021; Berov, 2020; Miladinova, 2020; Bat, 2022).

Plastic pollution in rivers and lakes

Plastic pollution in freshwater basins is a serious problem that affects aquatic ecosystems and even the welfare of the animals and humans that use these aquatic resources. Rivers eventually flow into seas and oceans, so they contribute much of the plastic pollution in saltwater basins. It has been proven that plastic waste can be retained for a certain period of time on the banks of rivers. Sometimes over years, they accumulate, degrade and fragment, which can dramatically reduce global estimates of plastic emissions from rivers to the ocean (Delorme, 2021).

Currently, the scientific literature on plastic pollution in rivers and lakes is scarcer than that describing the state of the seas and oceans, but in recent years the research interest of scientists has begun to focus more and more in this direction as well (Eerkes-Medrano, 2015; Wang , 2021; Dusaucy, 2021). There is great heterogeneity across studies, not only in terms of hydrological differences between individual freshwater basins, but also in terms of methodology used and criteria for comparing results (Al-Zawaidah, 2021). Some of the studies examine surface water pollution, others focus on the analysis of coastal and bottom sediments, and still others focus on the transfer and accumulation of plastic particles in various organisms and the potential risks to the inhabitants of freshwater ecosystems. This subsection will focus primarily on estimates from analyzes of plastic pollution in surface water from rivers and lakes.

It is estimated that just over 1,000 rivers on the planet contribute to around 80% of global annual emissions of plastic waste (Meijer, 2021). Estimates vary between 0.8 million and 2.7 million metric tons per year, with small urban rivers among the most polluting. Other estimates based on a projected calibrated global model of plastic input from rivers to oceans based on waste management, population density and hydrological information estimate that between 1.15 and 2.41 million tonnes of plastic waste currently enter the ocean each year from rivers, with over 74% of emissions occurring between May and October (Lebreton, 2017). The 20 most polluting rivers, located mostly in Asia, account for 67% of the total global volume. Third estimates, using mismanagement of plastic waste as a predictor, estimate global inputs of plastic waste from rivers to the sea to range between 0.41 and 4×10^6 t/y (Schmidt, 2017).

Based on the source of waste in rivers, pollution is classified into point and non-point sources (Khan, 2021). Point sources are industrial, domestic sewage plants and known sources that discharge waste directly into water bodies, while non-point sources refer to those sources that indirectly discharge their pollutant into water bodies. Such are agricultural runoff, discharge of air pollutants through rain or the process of precipitation of impurities in the air, etc.

Plastic pollution of coastal areas

The majority of plastic pollution in aquatic environments is known to originate from terrestrial sources (Xu, 2020). The life of plastic waste in the terrestrial environment still remains poorly understood, but due to its proven slow natural degradation, it is assumed that it would remain there for tens to hundreds of years, either almost unchanged or in varying degrees of fragmentation, depending on multiple factors (Fei, 2022; Darabi, 2021). The meteorological and geological parameters of the environment play an essential role in the residence and possible migration of plastic waste between the different matrixes on land and water basins. Depending on the different combinations and intensity of action of these parameters, the waste can remain on land for long periods of time or pass into the aquatic environment. Having passed into the water bodies, they can remain on their surface or settle to the bottom depending on their size and density, and they can also be thrown back onto land, after which the described cycle can be repeated an unlimited number of times (García Rellán, 2022).

Nowadays, the coasts of rivers, seas and oceans around the world are visibly littered with plastic debris of different scales and consistency, varying in different reports on this topic (Oigman-Pszczol, 2007; Corcoran, 2009; McDermid, 2004; Díaz-Mendoza, 2020; Mesquita, 2022; Mitchell, 2021; Lee, 2013). Plastic waste is dumped directly on site as a result of tourism and other human activities, or is transported to the coast by rivers, wind, man-made drainage systems or directly from the seas and oceans. Beaches are some of the most studied coastal areas in terms of plastic pollution. The types and amounts of plastic waste on beaches depend mainly on topography, weather activity, proximity to sources of waste and the extent and type of beach exploitation (Storrier, 2007). The deposition and retention of this waste on beaches, however, is largely controlled by the composition and degradation rates of the plastic debris itself.

Currently, studies have been published on plastic pollution of coastal areas from almost every continent on the planet, and their number continues to grow (Critchell, 2019; Al Nabhani, 2022; Li, 2018; Ghaffari, 2019; Rabari, 2022). Here, only some summary results of studies of plastic pollution on beaches in different parts of the planet will be presented. Quantitative and some qualitative aspects of individual pollutants will be presented, which will serve as a basis for subsequent comparative analyzes with the results of our studies on the subject.

Автори и година на публикация	**Локация**	**Количествена оценка**	**Качествена оценка**
Oyebamiji Abib Abayomi et al., 2017	Qatar, Persian Gulf, Indian Ocean	36-228 items /m^2	LDPE, PP, PET
Sanaz Ghaffari, Alireza Riyahi Bakhtiari, 2019	Iran, Caspian Sea	24,90 ± 1,74 items /m^2	Foam, pellets, fragments
Clara Álvarez-Hernández et al., 2019	Canary Islands, Atlantic Ocean	2–115,5 items /m^2	PE, PP, PS
Gabriel Enrique De-la-Torre et al., 2020	Peru, Pacific Ocean	174,25 items /m^2	HDPE, IPP, PS
Carlos Edo et al., 2019	Canary Islands, Atlantic Ocean	178-3504 items /m^2	PE, PP, PS
Kiani M. Pérez-Alvelo et al., 2021	Puerto Rico, Atlantic Ocean	52–432 items /m^2	PE, PP, PVC
Lamtiur Junita Bancin, 2019	Taiwan, Indian Ocean	96.8 items /m^2	PE, PP, PS

Tab. 1 *Concentrations and polymer composition of plastic debris found on beaches at different locations around the world. The table also shows the authors of the publications, the years of publication and the locations of the beaches surveyed.*

Risks to living organisms and humans

Although this scientific work does not include biomonitoring studies, this subsection will discuss the impact that plastic materials can have on living organisms, as well as the potential risks to them and to human health. This is necessitated by the paucity of scientific literature on the topic in Bulgarian academia.

Plastic pollution of aquatic ecosystems is a concern for a growing contingent of scientists from different fields of knowledge - ecology, hydrobiology, oceanology, zoology, toxicology, even medicine. Plastics pose a variety of mechanical, toxicological and epidemiological risks, not only to ecosystems in the environment, but also potential risks to human health.

Plastic litter in aquatic environments impacts organisms at different levels of biological organization and habitats in a number of ways, namely by entanglement in or ingestion of litter, by chemical transfer, as a vector for transport of biota, and by altering or modifying species assemblages, for example by providing artificial habitats (Werner, 2016,). Every year, millions of animal species inhabiting the oceans are depleted, maimed and even killed by anthropogenic marine litter, mostly of plastic origin (Butterworth, 2012). Thus, it seems inevitable that entanglement and ingestion of/by marine debris will alter the biological and ecological characteristics of individuals, compromising their ability to capture and digest food, sense hunger, escape predators, and reproduce. By 2016, over 817 species of marine organisms had been affected in one way or another by plastic pollution (Butterworth, 2012). Given the ubiquity and increasing amount of plastic waste in the seas and oceans, it is highly likely that there are now significantly more marine species affected directly or indirectly by anthropogenic marine plastic debris.

Plasticizers are additives to plastics that aim to increase the flexibility and torsional ability of the material. They are a heterogeneous group of chemical compounds that can be dissolved in polymer fabrics and affect their pliability and elasticity (Wypych, 2023). Harmful biological effects that some plasticizers exhibit towards living organisms and humans have been definitively proven, although most studies use In vitro cell and animal models and do not objectively account for actual exposure and possible transport pathways to and from the environment (Oehlmann, 2009). The best studied plasticizers are from the group of phthalates and bisphenol A derivatives. They have proven negative effects on a large number of living organisms including humans (Burgos-Aceves, 2021; Oehlmann, 2009; Eales, 2022; Chang, 2021; Rochester, 2013; Michałowicz, 2014). There is solid evidence of the negative effects of these substances on the endocrine system, reproductive and other organs, and therefore they can be grouped into a common terminological category - the so-called Endocrine Disruptors.

Aim and objectives

The aim of this dissertation is to contribute to a better understanding of the current problem of plastic pollution, taking into account the scarce and in many places missing data on the quantities, types and dynamics of this type of pollution in the Bulgarian Black Sea and adjacent coastal areas. Furthermore, adding our experience and data on different aspects of plastic pollution, the scientific work will outline a simplified conceptual framework for a phased and segmented study of this problem in the Varna area, by optimizing and applying different aspects of ecological and biological monitoring. This will pave the way towards the implementation of a comprehensive risk assessment and effective protection of marine ecosystems and human populations from possible ecological and health catastrophes.

The tasks to be set in order to achieve this objective are as follows:

1. To conduct a short questionnaire survey, applied to a sample of the population of the city of Varna, related to citizens' awareness of plastic pollution in the region. A key point in this task is to elicit information from the citizens about the most polluted coastal areas in the region.

2. On the basis of the opinions given by the residents of the city, to survey different geographical locations in and around the city and from them to identify "hot spots" / zones of anthropogenic pollution with plastic debris.

3. Collect, describe and categorize anthropogenic debris from the identified easily accessible hotspots/areas, then calculate and assess their quantity, type and approximate degree of degradation.

4. Examine the labelled contents of some of the commercially available personal care products and identify the most common components of potential microplastic nature.

5. To complement the existing recommendations and guidelines for environmental monitoring in relation to anthropogenic plastic pollution in the Varna region, adding value both to current environmental monitoring strategies and to future studies and analyses of plastic pollution.

Methods

The design of this research work applies several different methodologies, including not only the documentary method used to construct the literature review, but also the sociological method, field methods, microscopic analysis, statistical and graphical methods. The first stage of the applied set of methodologies involves a survey applied to a sample of the population of the city of Varna. Based on some of the responses from the survey, a plan was drawn up to crawl certain geographical locations in order to identify "hot spots/zones" with concentrations of plastic waste pollution.

Survey method

In order to study the awareness and opinion of the citizens of the city of Varna regarding some aspects of plastic pollution, the survey method was applied. Using a Google form, a short semi-structured questionnaire was prepared, including several closed and one open-ended question. It has been sent out on social networks for completion by people living in the city of Varna and adjacent municipalities. Sampling time is 7 days. The main criterion for inclusion in the survey is that the respondents live and/or work/study in the city and/or adjacent municipalities. The open-ended question had the greatest value from a research point of view, as it aimed to find out where, according to the respondents, the most polluted coastal areas in and around the city of Varna are. Their responses would be the starting point for pinpointing plastic pollution 'hotspots'. The complete set of questions in the survey card is presented in the "Appendices" section, after the photo material. The application of a survey method in the present scientific work did not require approval by the Research Ethics Committee (KENI), as no invasive methods and interventions were used, as well as identifying data for the respondents.

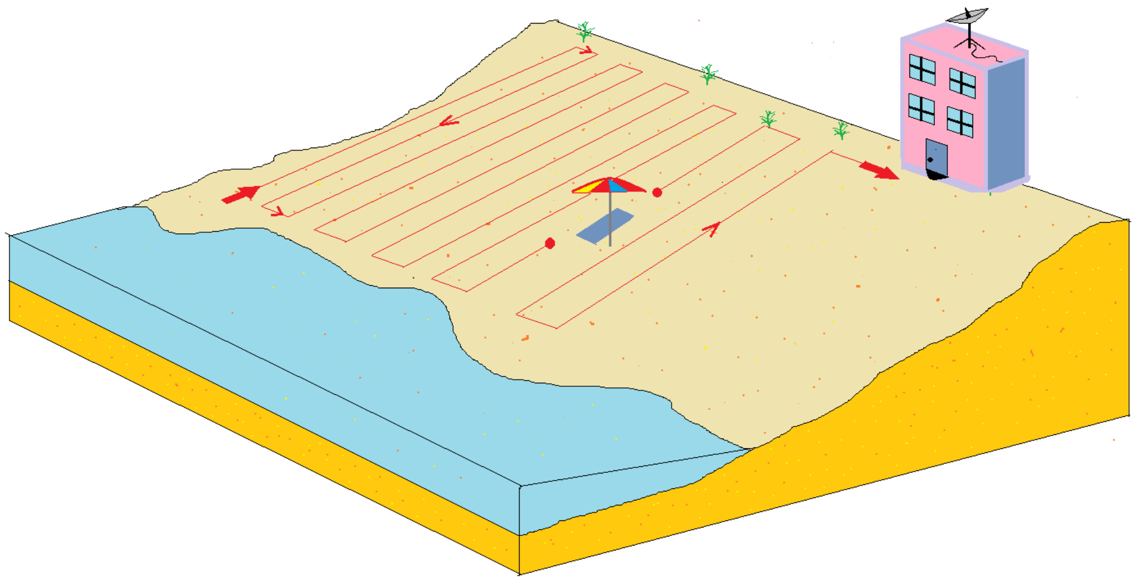
Locations and sampling

The selection of locations and sampling, as well as all site survey logistics, is consistent with some established guidelines for marine and coastal zone monitoring (Kershaw, 2019), with some additions and modifications added for the purposes of this paper.

Before the sampling tours, various locations in and around the city of Varna were inspected, which, according to the various respondents from the attached survey, represent areas with a greater than usual concentration of plastic waste. The geographical topography of these areas varies from sandy beaches (tourist, fishing) to hard-to-reach rocky beaches and landslide areas. The purpose of the preliminary inspection is to mark places that, during the next inspection, will be examined in more detail regarding their contamination with plastic waste, and accordingly to collect all possible debris.

On 20.07.2019 between 7:00 a.m. and 10:00 a.m., a distance of 600m was covered along the beach strip of the central beach, the city of Varna, with the starting and ending points at coordinates 43°11'46.0"N 27°55'16.6"E and 43 °12'04.2"N 27°55'25.2"E (Fig.1). The location was chosen in accordance with the Varna district named in the survey as the most polluted with plastic waste. The date is selected depending on the availability of favorable weather conditions. The early hour aims to ensure a reduced presence of beachgoers in view of unhindered sampling. A total of 5 students and NGO volunteers participate in the team that collects the samples. They all joined on a voluntary basis, motivated by the collective environmental convictions they each shared regarding plastic pollution in the seas and oceans. All volunteers are members of "Greenpeace - Bulgaria", a national branch of the international environmental organization "Greenpeace". Within 15 minutes before the start of the beach crawl itself, instructions are given to observe uniform rules when taking the samples. The instructions include: 1. Observance of a certain trajectory when moving along the beach; 2. Collecting only the potential plastic waste visible on the surface of the sand, even if part of it is buried deep; 3. Avoiding areas in close proximity to umbrellas and beachgoers, so as not to disturb their comfort.

Walking along the beach is carried out by the following method: Start from the tidal zone of the coastline and walk in a perpendicular direction until you reach the area of the beach bordering the beginning of vegetation or a building. It then takes a step to the side and returns in the opposite direction until reaching the intertidal zone of the shoreline. The crawl pattern is a vector with a zigzag trajectory. In this way, comprehensive coverage of the maximum area of the beach is ensured. The described method of beach crawling is outlined in diagram 1.



Scheme 1. Method of walking along the beach during sampling. The entire method is described in the text above.

On 15.05.2020, between 13.00 and 16.00, the same distance along the beach was covered with the starting and ending point, corresponding to the same coordinates as during the crawl from 20.07.2019 (43°11'46.0"N 27°55'16.6" E and 43°12'04.2"N 27°55'25.2"E). In this crawl, 4 volunteers participate in the sampling. The crawl pattern was the same as the first sampling, again collecting only surface debris and avoiding areas in close proximity to umbrellas and beachgoers. The ruler tool of Google Earth software was used to measure the parameters of the study areas. In both samplings, latex gloves and plastic garbage bags are used as support materials and personal protective equipment.

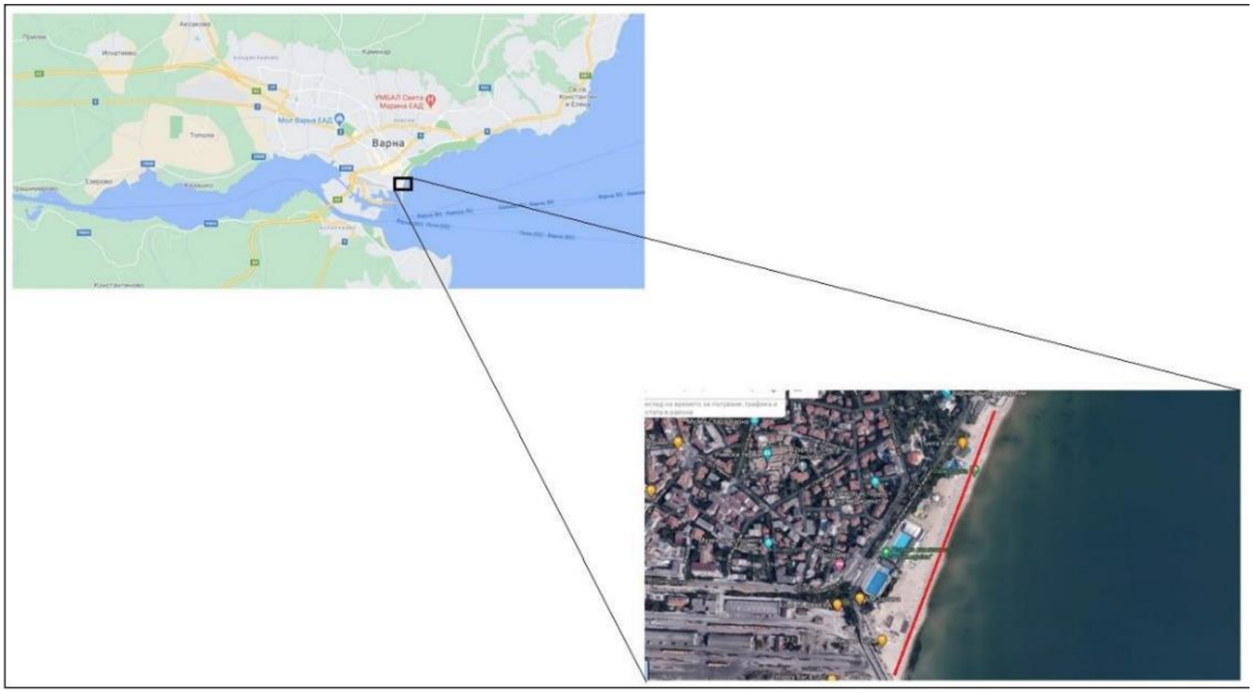


Fig. 1 Geographical map of the city of Varna and the section of the beach from which the samples were collected. The red line reflects the distance covered (600m) from the beach.

The walk along the northern shore of Lake Varna was conducted on the morning of February 11, 2021, in accordance with a preliminary study of suitable weather conditions. It starts at a point with coordinates 43°12'14.5"N 27°53'23.5"E continues along the coast and stops at a point with coordinates 43°12'16.0"N 27°53'21.7"E which represents a length of ~ 61 m. After this section, the terrain is a rocky coast, which makes walking very difficult, and in some places makes it impossible without specialized equipment (Fig.2). This is also the main reason for limiting this area to a single crawl. According to its structure, the coast is mainly composed of coarse sand and gravel, which after the shoreline, entering the water, gradually turns into a small rocky structure mixed with stones and sand.

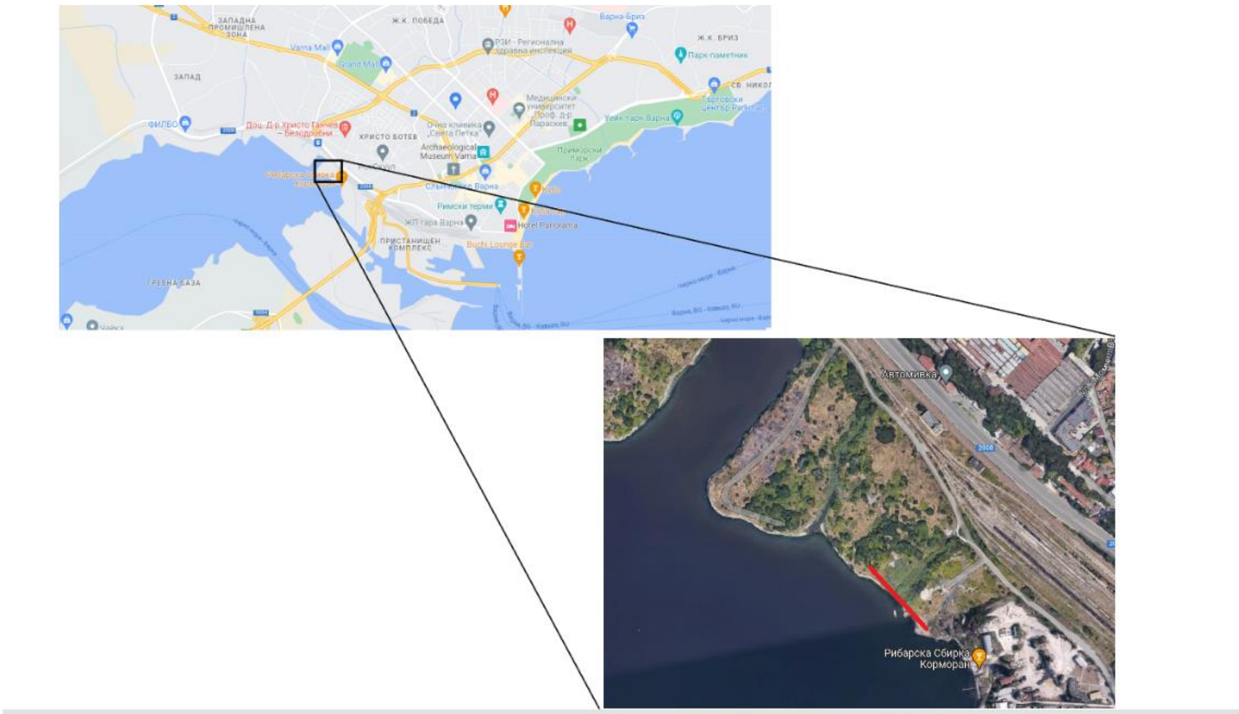


Fig. 2 Section of the shoreline of Lake Varna from which the samples were collected. The red line reflects the traveled distance (61m) from the coastal section. The ruler tool of Google Earth software was used to measure the parameters of the study areas.

A total of 5 people participated in the crawl on a voluntary basis. All possible plastic debris was collected along the 61m of the coast. Any waste on the earth's surface is considered plastic, for which organic, metal or glass origin is excluded. Verification is done on a visual basis based on consensus among all participants in the sampling. Only the debris visible on the surface was collected and no samples were taken from great depth in the sand, except for those fragments which were buried to varying degrees, but some of which were still visible on the surface. In this way, all possible plastic debris from the coast of the 61-meter sector up to 3 meters from the shoreline was collected in plastic garbage bags. After the third meter, vegetation begins and the concentration of waste drops sharply. The approximate covered area equals 146.25m^2.

Debris documentation and statistical analysis

After the two crawls of the first section of the central beach of the city of Varna (coordinates: 43°11'46.0"N 27°55'16.6"E and 43°12'04.2"N 27°55'25.2"E), all collected potentially plastic debris is weighed and photographically documented, then counted and categorized. The litter was arranged on a white background by the principal investigator up to 3 days after the completion of the crawl due to the need to dry some of it. They are then photographed in natural daylight with a professional Sony A7 III camera with a 35mm macro lens.

A similar methodology was used for the survey of the northern part of Lake Varna, but before being categorized, all samples were washed once with tap water to remove adhering sand and marine organisms. This step was not necessary when taking the samples from the central beach, since there they were dry and with no organic and other matter stuck to them. After drying, they are weighed, arranged on a flat light, drawn surface and photographed with a camera. Finally, each sherd was assigned to a specific category, after which a description was performed to identify the most common items. After analysis, all waste was collected in garbage bags and disposed of in a plastic waste container.

In order to make a quantitative and qualitative assessment of the potentially plastic waste found in all three searches, a simplified descriptive statistical analysis was performed, by arranging in spreadsheets the different categories and the number of waste for each category, using the Microsoft Excel program, part of the package MS Office 2019 version. The total amounts of waste and their weight were assessed. Each individual waste is assigned to a specific category and the percentage ratio of each waste category is calculated. In this way, the results are presented in a visual form by applying graphical methods of the pie chart type. In addition, the Clean-Coast Index (CCI) was calculated, which is an objective method developed to assess the level of cleanliness of coastal areas (Alkalay, 2007). The detailed description of this method is discussed in the Results section.

Microscopic analysis

Due to the huge amount of debris, a large part of which has similar morphological characteristics, only some of the debris found during the first two crawls of the central beach of the city of Varna were selected for microscopic examination. They were then examined at various magnifications with a low class digital microscope, model - Levenhuk DTX RC2. In the microscopic observation itself, with the help of metal tweezers, pressure was applied or passed over the surface of the fragments to determine to what extent their integrity would be disturbed. This stage of the study was entirely led by the principal investigator.

Detection of potential microplastics in commercial products

As a complement to the research work, a pilot study was conducted on the presence of microplastic particles in commercial household products. This study aims to give a more complete picture of plastic pollution in the area of the city of Varna, since the emphasis of the scientific work is on the larger waste in the environment. By examining the presence of potential plastic derivatives in products from the commercial network, we can also gain insight into the possible importation of some smaller plastic particles flowing through the sewage system into the marine environment. Using the smartphone application "Beat the microbead app", a total of 65 personal care products were scanned in a retail store to determine the presence of microplastics and other particles in their contents. This mobile application allows you to quickly and easily scan the contents on the packaging of various products, revealing whether they contain microplastic particles and what types they are. Items surveyed include hair (shampoos, conditioners) and body (shower gels) products. In the content of oral hygiene products (toothpastes), the presence of microplastic particles was also detected, but these were not scanned here because the aim was to pilot test the mobile application itself on a small scale. For more details about the application and its use, the following Internet address can be visited: https://www.beatthemicrobead.org/.

Results

The semi-structured questionnaire sent on social networks was completed by a total of 262 residents of the city of Varna and adjacent municipalities. About 51% of them (N=133) are in the age group of 19 to 30 years; approximately 29% (N=76) of the respondents are between 31 and 50 years of age, and in the age groups over 50 and under 19 there are respectively about 14% (N=37) and 6% (N=16) of them. Almost 2/3 of all respondents are female - 70.2% (N=184). In the following lines, the answers to some of the more interesting and significant questions in the survey will be presented. The results of all questions in the survey card, along with their answers, are presented in the "Appendixes" section.

There are 5 possible answers to the question "Which type of waste containing plastic is most often found on the beach of the city of Varna?": plastic bags, straws, cups, bottles and caps. 3% of respondents (N=9) answered that they thought it was the straws; according to nearly 8% of them (N=20) these are the caps, and an almost equal number of people indicated that the plastic waste that is most often found on the beach of the city of Varna are bags, bottles and cups (respectively N=71 , N=80 and N=82 i.e. about 30% each.

Asked how often they use single-use plastic products – bags, bottles, cups, utensils, etc., 32.1% (N=84) of respondents answered that they use such items once a day. More than once a day - 21% (N=55), while 42.4% (N=111) of respondents answered that they avoid using single-use plastic products. 4.6% (N=12) of respondents marked "Can't judge" as an answer.

To the question "After use, do you dispose of plastic products separately?", only 22.9% (N=60) of respondents gave a positive answer, 17.6% (N=46) answered "No", 35.9% (N=94) answered "I would like to, but there are no separate waste disposal containers nearby" and 23.7% (N=62) answered that they do it "Occasionally".

94.7% (N=248) of respondents believe that plastic pollution is a problem, while 5.3% (N=14) are not sure. None of the respondents answered that plastic pollution is not a problem – N=0.

To the question "Whom would you turn to for questions about protecting the cleanliness of the beach?" 59.5% (N=156) of the respondents answered "Regional Environmental and Water Inspection; 35.9% (N=94) would turn to the "Municipality", 21.8% (N=57) - to "Concessionaire", 21.4% (N=56) - to "Non-governmental organization", and 17 .2% (N=45) - to "Regional Health Inspection". 12.2% (N=32) of the respondents could not decide who they would turn to.

The survey card also included one open-ended question that had the greatest value from a research point of view. It was structured as follows: "Where on the beach in and around the city of Varna have you come across plastic waste piled up or floating in the water?" The majority of respondents gave more than one answer, with the most frequently given answers being "Central beach" (n=134), "South Beach" (n=79), "the shores of Lake Varna" (n=61), "Beach in Asparuhovo" (n=35) and others. It was some of the specified locations that were selected for preliminary crawling and subsequent sampling.

While walking along the beach on 20.07.2019. nearly 1,000 wastes were collected, of which only 856 were classified as "plastics" and remained for analysis. The rest was mostly metal (can-type aluminum cans) or paper and organic debris (food scraps and plant tissue), which after crawling were disposed of separately in waste containers.

The total weight of the collected plastic waste amounts to approximately 1040 g. The most common debris falls into the "Other" category (n=363). Packaging (n=153) is the second most common, followed by clamping devices (n=81), caps (n=63), chopsticks (n=54), utensils (including stirrers) (n=51), bags (n=38), straws (n=29). The least common litter turned out to be plastic cups (n=19) and bottles (n=5 or 0.6%). In fig. 3 shows photos of some of the listed debris. The rest of the photographic material, representing all categories of debris found, is placed in the "Appendices" section. The percentage distribution of the categories thus listed is presented in Fig. 4. The smallest size among the fragments is < 4mm, and the largest and most voluminous were plastic bags and bottles (>10 cm). The color range of the collected debris is diverse - the pieces are white, gray, brown, blue, pink, red, yellow and green.

Fig. 3 Photographs of some of the listed debris. The rest of the photographic material, representing all categories of debris found, is placed in the "Appendices" section.

Fig. 4 Percentage distribution of the categories of plastic waste during the first crawl of the beach.

During the second crawl on 15.05.2020. 938 pieces of debris were collected, which we assigned to the "plastics" category. All other debris belonging to the categories "metals", "paper" and "organic waste" were disposed of separately in the respective containers. The total weight of the collected plastic waste amounts to ≈ 960 grams. And in the second crawl, the most common plastic debris was from the "Other" category (n=685), followed by caps (n=63), plastic sticks (n=62), straws (n=41), packaging (n =36), utensils (n=17), cups (n=13), clamping devices (n=9). The least common waste is bottles (n=7) and bags (n=5). In fig. 5 shows photos of some of the listed debris. The rest of the photographic material, representing all categories of debris found, is placed in the "Appendices" section. The percentage distribution of the categories thus listed is presented in Fig. 6. For greater clarity, in Fig. 7 we present the percentage distribution of the categories, with the "Other" category removed. The color range of the debris collected here is also diverse - the pieces are white, blue, brown, gray, pink, red, yellow, green and other colors. In just under 2% (n=29) of the total amount of samples taken in the two crawls of a central city beach, it became possible to identify the type of polymers symbolically/literally indicated on the surface. Among them, varieties of PE (HDPE, PET) and PP were found.

Fig. 5 Photos of part of the waste found during the second crawl. More photographic material of the rest of the debris found can be found in the "Appendices" section.

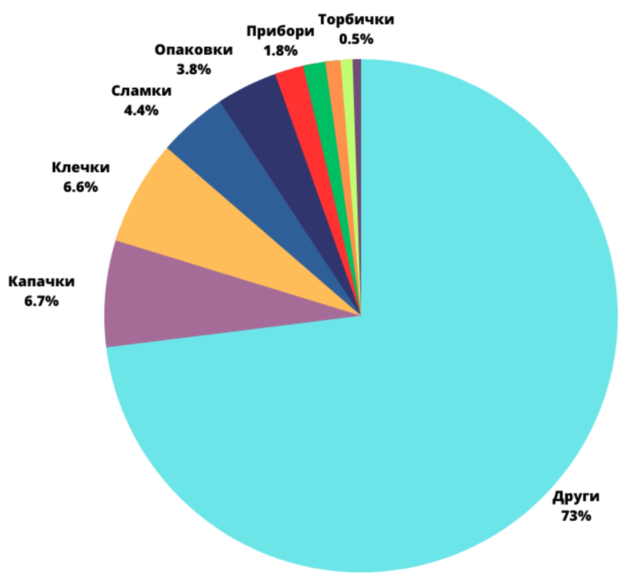


Fig. 6 Percentage distribution of the categories of plastic waste during the second crawl of the beach.

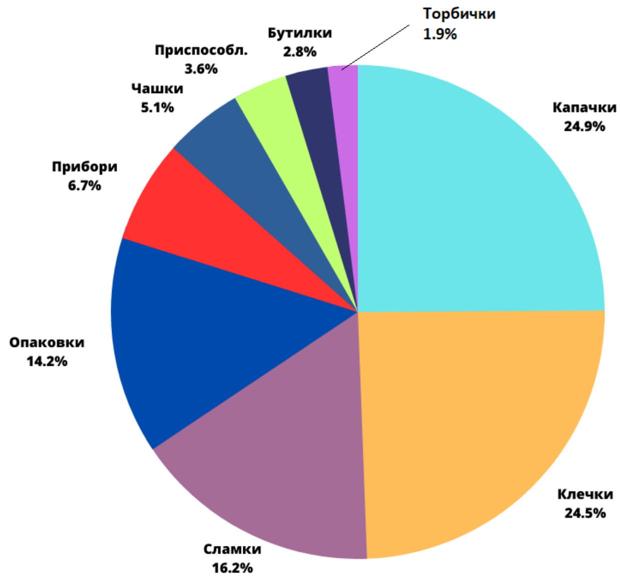


Fig. 7 Diagram reflecting the percentage of plastic waste allocated to the categories during the second crawl of the beach, excluding the "Other" category.

In addition, the Clean-Coast Index (CCI) was calculated, which is an objective method developed to assess the level of cleanliness of coastal areas (Alkalay, 2007). The calculation is made according to the following formula:

$$\text{Clean Coast Index (CCI)} = \frac{\text{number of items}}{\text{area}} \times K$$

where K is a coefficient equal to 20 (K=20). The amount of plastic waste is expressed in net number, and the area of the walked section of the beach is expressed in m^2.

The coastal cleanliness index can vary in 5 ranges:

- 0–2: very clean

- 2–5: clear

- 5–10: moderate

- 10–20: dirty

- 20 +: extremely dirty

Our calculated Clean-Coast Index during the first crawl is approximately equal to 0.38, which, relative to the ranges described, means that this stretch of beach is very clean. The average amount of waste/m^2 calculated for this section of the beach is of the order of 0.019 waste/m^2.

For the second beach crawl, we obtained results of CCI=0.4. The average amount of waste per square meter of the beach is 0.02 debris/m^2.

A total of 201 pieces of plastic debris were collected from the 61-meter long coastal section of the northern shore of Lake Varna, divided into five categories: bottles; caps; packaging; bags; others; In fig. 8 shows photos of some of the listed debris.

Fig. 8 Part of the debris found on the northern coast of Lake Varna.

Taking into account the almost entirely straight section of 61m and the collection of the samples up to 3 meters inland, the quadrangular section formed in this way has an approximate area of 146 m^2. Most of the debris was up to 1.5 m inland and only a small fraction was beyond that line.

The Clean Coast Index calculated by us in this section of the shore of Lake Varna is approximately equal to 31, which, compared to the described ranges, means that this section is extremely polluted. The average amount of waste/m^2 calculated for this section of the beach is of the order of 1.55 waste/m^2.

The total weight of all debris after washing and drying was 7.4 kg. The largest share of debris falls on those falling into the "Other" category - a total of 84 debris (42%). This is mostly unidentified waste, not belonging to any of the other categories. In second place in terms of frequency, there are bottles/tubes with a total of 58 pieces (29%), 11 of which are closed with a cap, and 6 of these 11 bottles are filled with liquid. In third place in terms of frequency were the caps, varying in 5 different colors: yellow, red, white, green, blue. They are a total of 29 in number (14%). Packaging is the 4th most frequent with a total of 18 items (9%), and bags were the least frequent: a total of 12 items (6%). Some of the packaging and the majority of the bags were fragmented to varying degrees, but this did not hinder their visual identification and, accordingly, they were assigned to the correct category. During the crawl, a further 34 pieces of plastic debris were collected floating freely in the lake, no more than half a meter into the water, but these were not included in the categorization. In fig. 9 graphically presents the percentage distribution of the detected categories of waste.

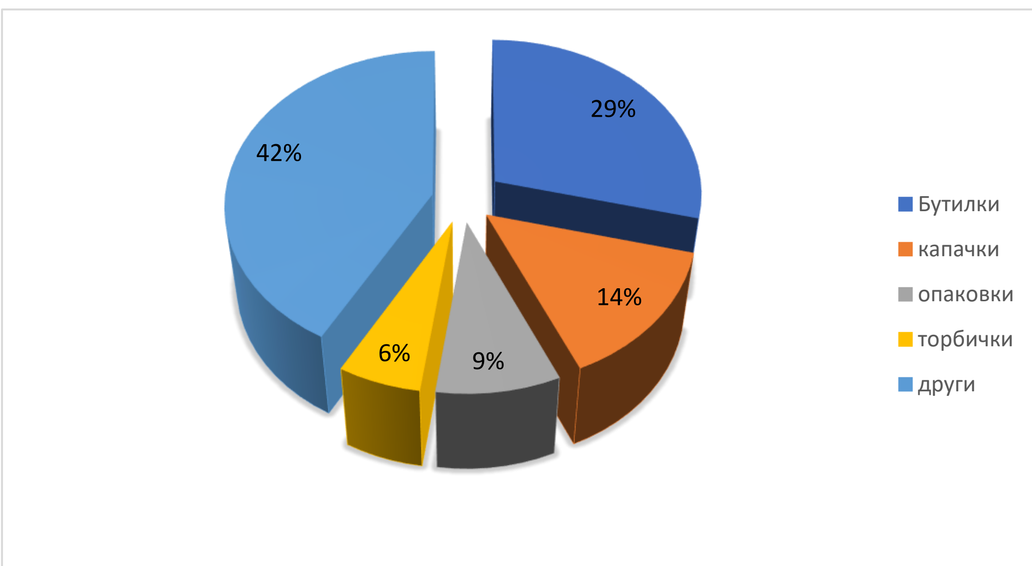


Fig. 9 Distribution of the categories of debris found and collected while traversing the northern coast of Lake Varna.

The majority of all plastic waste found falls into the macroplastic category (nearly 90%). These are items and debris measuring more than 2.5 cm along their longest axis, with several of the largest found here exceeding 40-50 cm. To the mesoplastics category (0.5-2.5 cm) belong nearly 8% of all debris, and to the category of microplastics (≤0.5 cm) – just over 3% of them (the majority of probable polystyrene origin). In fig. 10 shows the distribution of the size of the detected waste (micro-, meso- and macroplastic). Numerical values reflect the number of debris found, aggregated over the 3 expeditions.

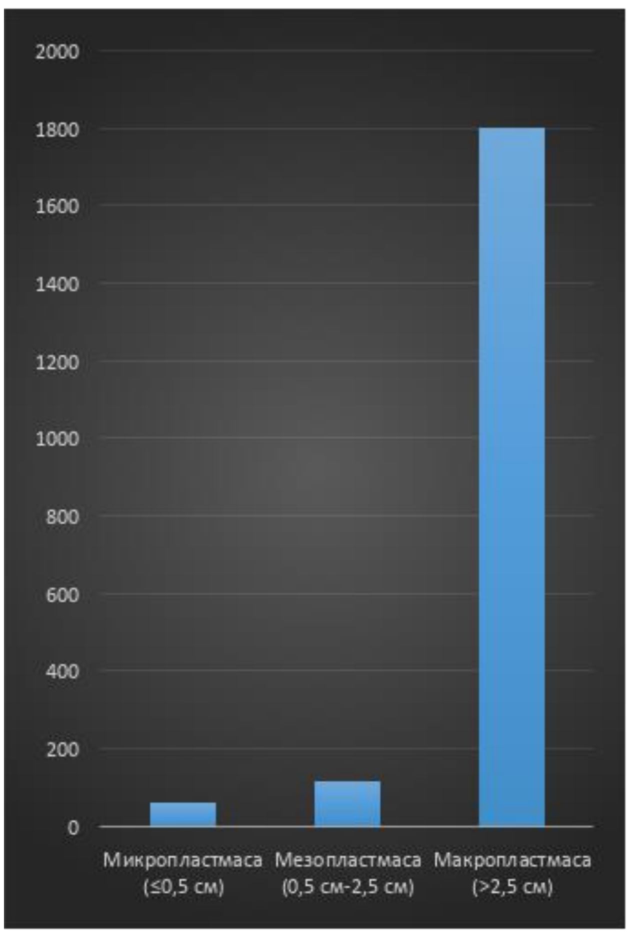


Fig. 10 Size distribution of waste found: micro-, meso- and macroplastic (summarized for the three expeditions).

The approximate percentage distribution in the color ranges of litter found on the central city beach (total from both crawls) is as follows: white and transparent/translucent ~ 31 (n=554); blue ~ 23 % (n=412); yellow/brown ~ 14 % (n=251); gray ~ 8 % (n=143); red ~ 5 % (n=89). All other colors, including black, green, pink, purple, and orange made up a total of about 19% of the samples (n=345). The percentage distribution of the colors of debris found is represented in Fig. 11. The percentage distribution of the colors of debris found along the northern coast of Lake Varna is almost the same: white and transparent/translucent ~ 36%, blue ~ 27%, yellow/brown ~ 18%, gray ~ 5%, red ~ 3%, other (black, green, pink, purple, orange) ~ 11% (Fig. 12).

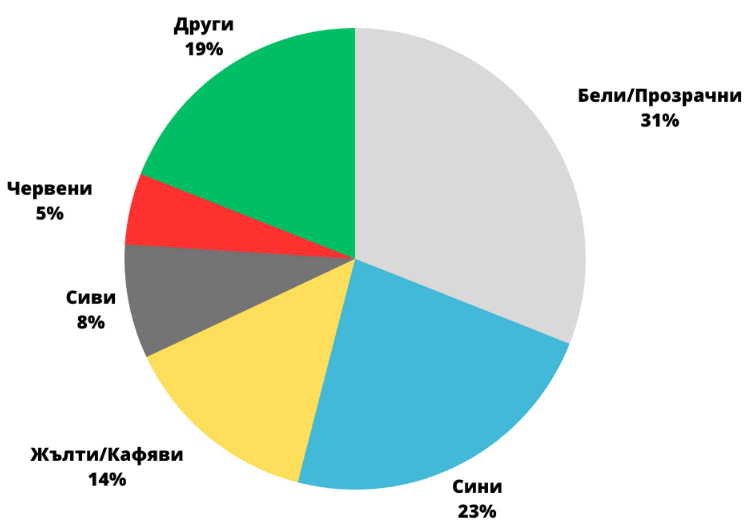


Fig. 11 Percentage distribution of debris colors found on a central city beach during both expeditions.

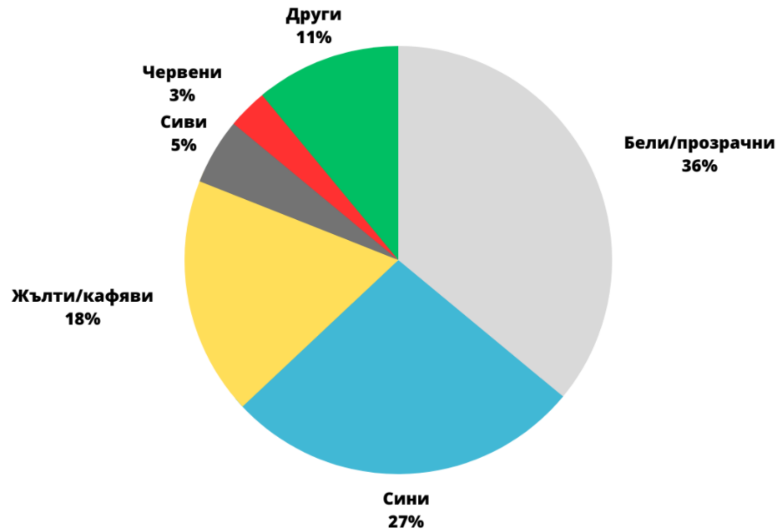


Fig. 12 Percentage distribution of colored debris found along the northern coast of Lake Varna.

15 visibly worn fragments belonging to the "Other" category were selected for microscopic analysis. Those of the debris that show visible lesions of a different nature - scratches, cracking, microcracks, peeling, as well as loss or change of color distribution on their visible surface - are considered as worn. Basically, these are small fragments between 1 and 2 cm in size (Fig. 13)

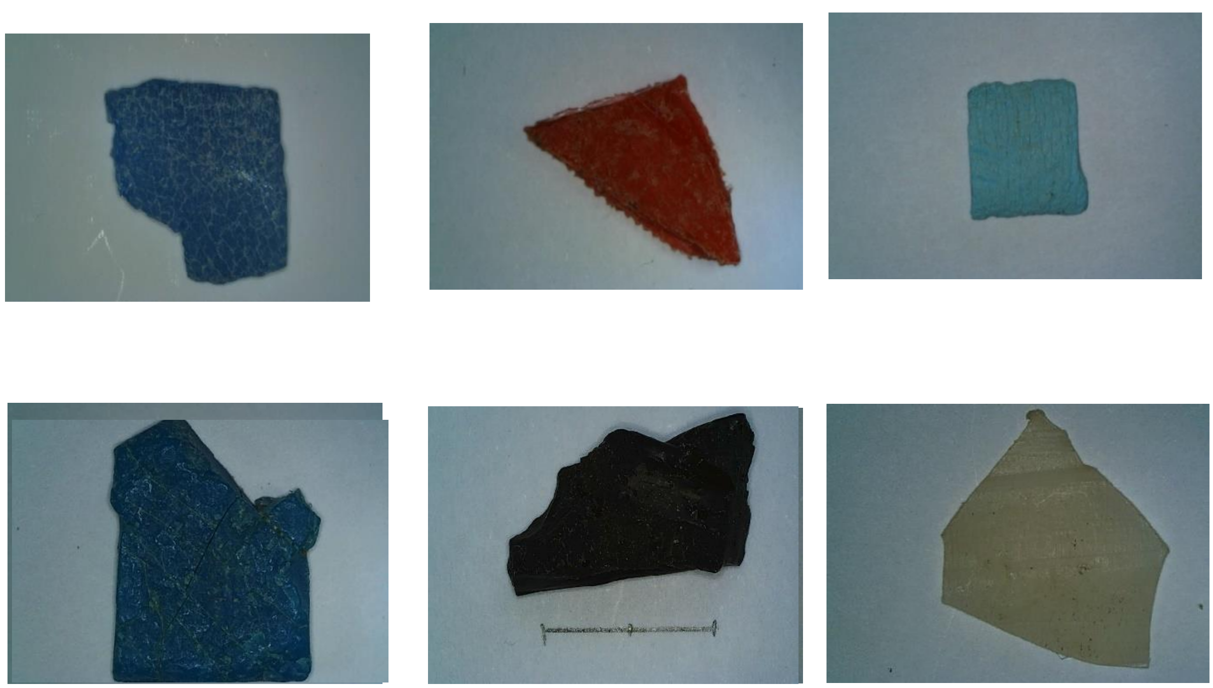
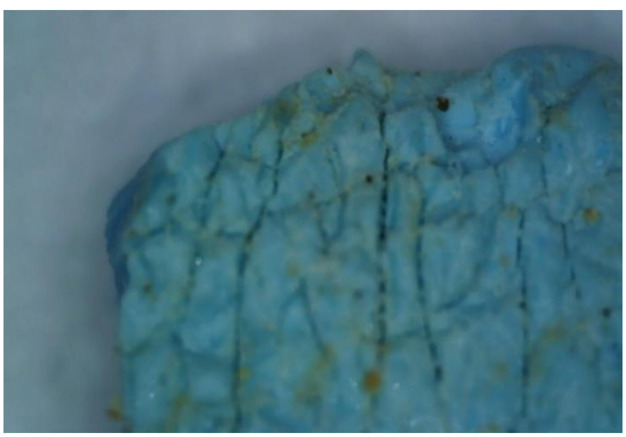
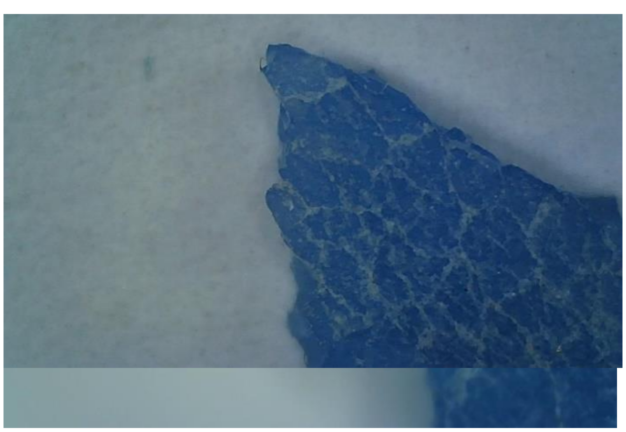


Fig. 13 Some of the fragments separated for microscopic analysis. All of them were found on the central beach of the city of Varna during the two crawls of the beach.

All 15 pieces of debris are unidentified fragments, in view of the fact that they could not be attributed to any of the other categories of waste described. With a large microscopic approximation, it becomes clear that the surface of the examined fragments is strongly split, with the presence of microcracks (Fig. 14). In other fragments, only peeling of the surface is observed (Fig. 15). The scales that form do not come off easily when you try to remove them with metal tweezers.





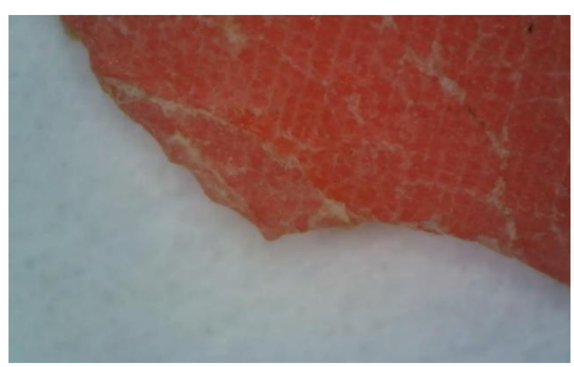


Fig. 14 Presence of microcracks on the surface of some of the fragments examined with a microscope.

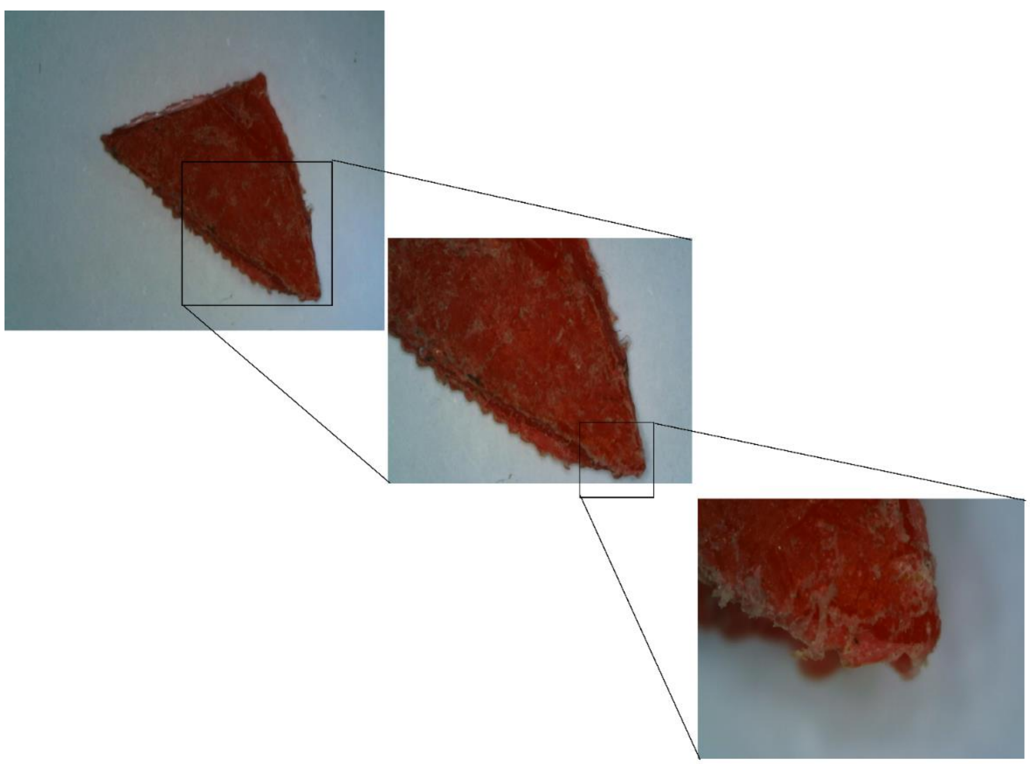


Fig. 15 At higher microscopic magnification, exfoliation of the surface layer of some of the examined fragments was observed. Exfoliation also occurs when metal tweezers are passed over the surface of the fragment without applying particularly high pressure.

After applying pressure with metal tweezers in different directions, detachment of smaller particles from the main fragment was observed from the surface of other fragments (Fig. 16; Fig. 17; Fig. 18 and Fig. 19). In other fragments, after applying pressure or passing tweezers over the surface, only flaking/delamination was observed (Fig. 15).

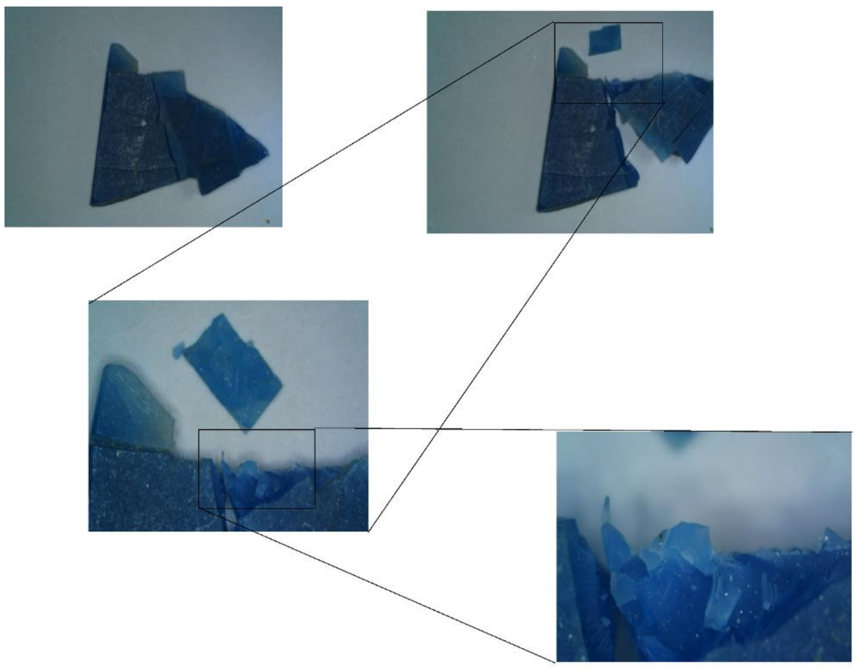


Fig. 16 Breaking off smaller fragments after applying light pressure to a fragment, using metal tweezers. The images represent increasing microscopic magnification in sequence.

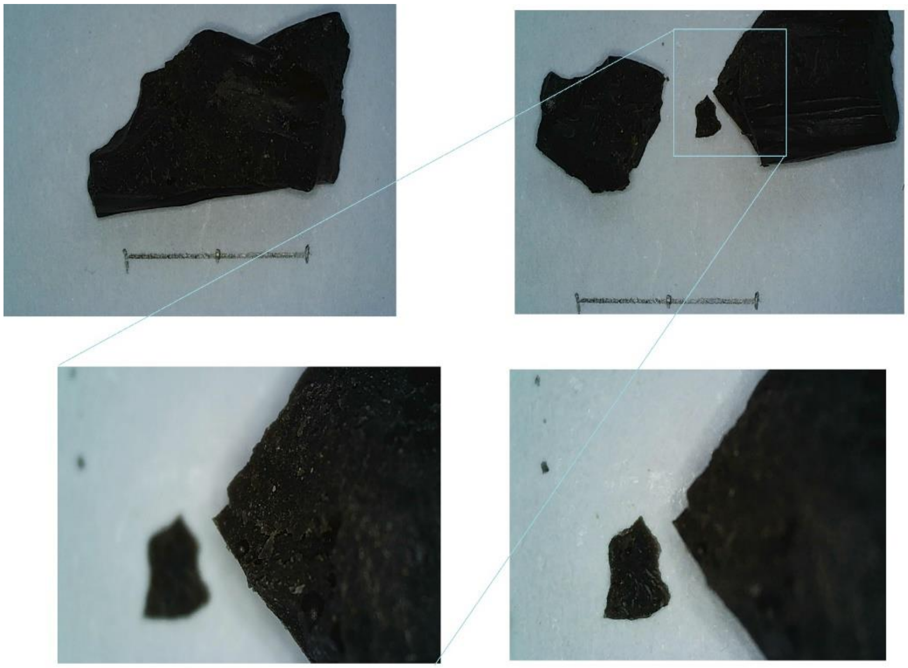


Fig. 17 Breaking off smaller fragments after applying light pressure to a fragment, using metal tweezers.

The observed fragmentations and exfoliations occur under different application of pressure i.e. some plastic debris fragmented much more easily with very little pressure or scraping, while others required greater force to observe fragmentation. In a third, only slight deformation was observed without breaking off (even after application of greater force) or breaking off of a smaller particle which, however, remained attached to the larger fragment and was difficult to separate from it using tweezers (Fig .18 and 19). 2 of the fragments showed extremely high fragmentation, even with very light tweezer pressure. From all of them, a large number of microfragments with dimensions of the order of fractions of a millimeter broke off (Figs. 20 and 21).

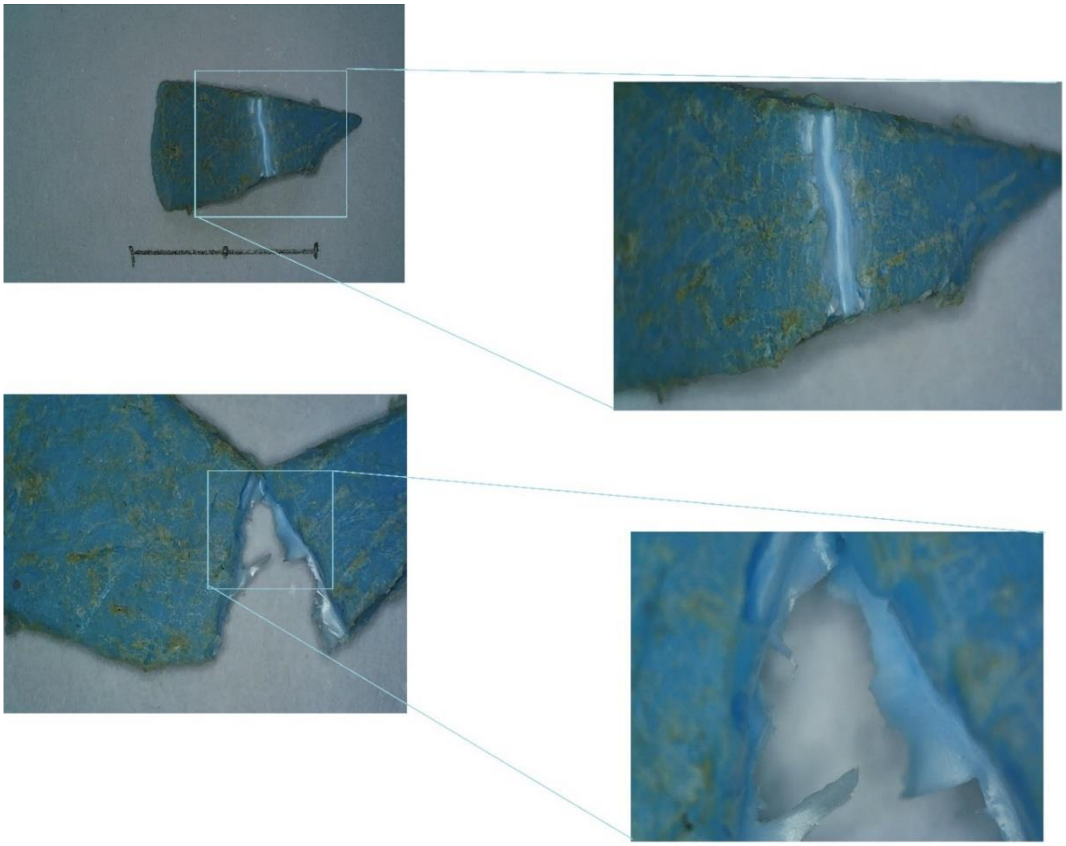


Fig. 18 Break-off of a smaller particle that remains attached to the larger fragment and is difficult to separate from it using tweezers.

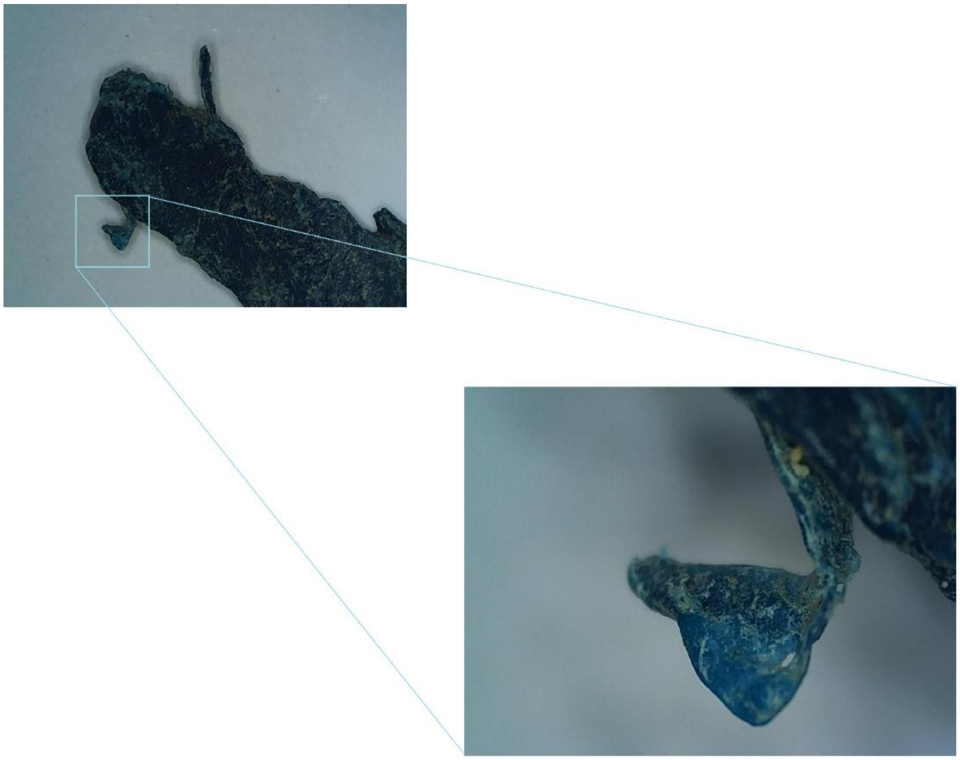


Fig. 19 Break-off of a smaller particle that remains attached to the larger fragment and is difficult to separate from it using tweezers.

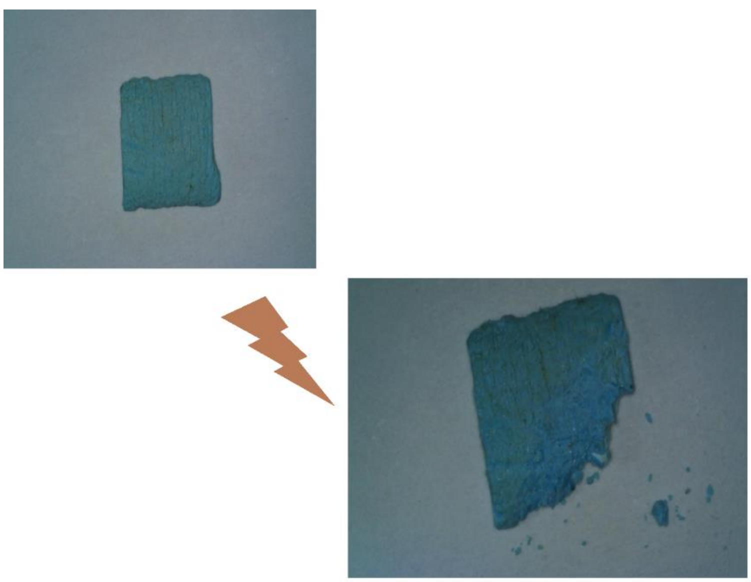


Fig. 20 Breaking off a large number of microfragments from a debris, after applying light pressure using metal tweezers. Most of the broken off small particles are on the order of fractions of a millimeter.

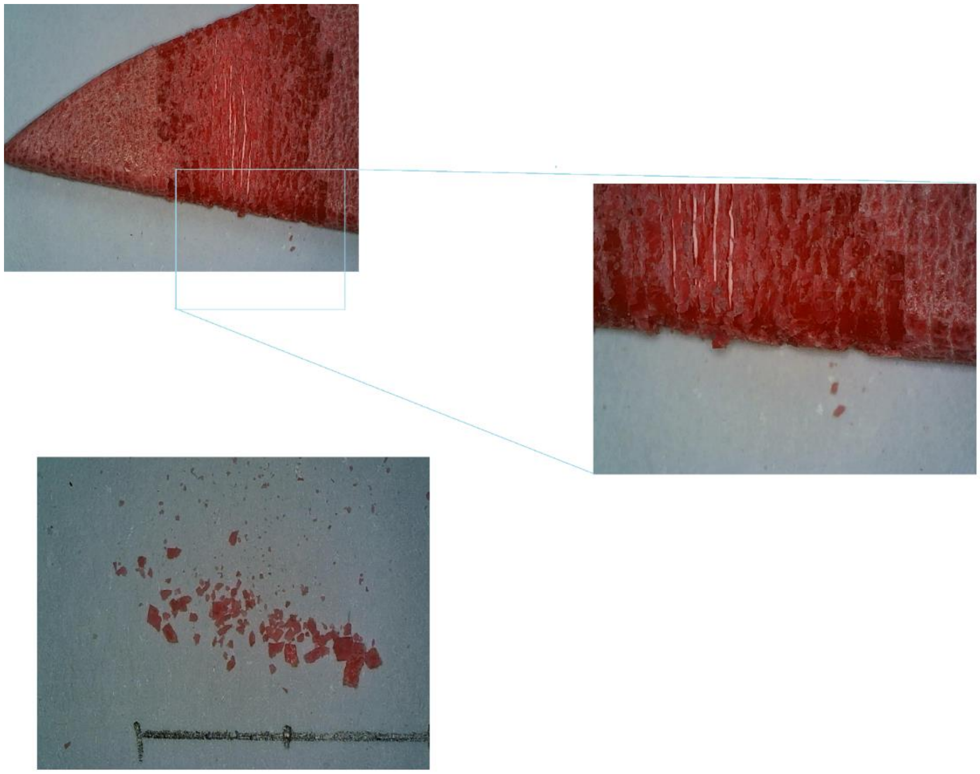


Fig. 21 Breaking off a large number (over 60) of microfragments from a larger fragment, after applying light pressure using metal tweezers. The smaller particles broken off are on the order of a millimeter and fractions of a millimeter.

Using the "Beat the Microbead" smartphone application, a total of 65 products available for sale in a single retail store located in an outer district of the city of Varna were scanned for the presence of microbeads. In this way, the most common primary potential microplastic components contained in some commercially available personal care products were identified. In order to avoid a conflict of interest, the names of the studied products should not be described verbatim. The complete list of their names can be provided upon inquiry and contact the author of the present scientific work. The majority of them are hair (shampoos, conditioners) and body (shower gels) products. After scanning the label of each product, information and a description of some of the ingredients categorized in the app as proven MP-ingredients is obtained. For another part of the constituents, apparently there is still not enough empirical material to be assigned to this category with great certainty, which is why they are labeled as unconfirmed/uncertain MPs constituents. In

31 products only unconfirmed particles were present, with no proven polymer ingredients present, while in 3 of the products only proven polymer ingredients were present. In 15 products, no traces of microbeads were found, neither with a proven polymer composition, nor those with an unconfirmed composition, and in the application these products are labeled as "plastic free". In 16 products, both proven polymer ingredients and ingredients with suspected or unconfirmed polymer composition were present. For the analysis and evaluation of the most common proven polymer microbeads, only the products in which, after scanning, exactly the proven polymer microbeads were present (19 in total) were included. In 13 of them, the presence of the so-called Dimethicone. The second most common type of proven polymer is labeled "Carbomer". Its presence was found in 8 of the personal care products. The remaining polymer-based ingredients found after the scan were labeled as "Polyquaternium-7" found in 2 products and "Polyquaternium-6" found in a single product. In summary, the most common polymer-based ingredients are Dimethicone, Carbomer, Polyquaternium-7 and Polyquaternium-6. In 31 out of a total of 65 scanned products, the presence of ingredients with an unknown but suspicious polymer composition was found.

Discussion

The results obtained in the present scientific work provide initial baseline data for future studies of plastic pollution in the Varna region, concerning not only macro- and mesoplastic waste, but also microplastic ones. In addition, we provide some preliminary data on the aging behavior of plastics in the marine and coastal environment in the Varna city area, as well as data on the presence of potential polymeric constituents in commercially available personal hygiene products. The application of the main methodologies in the scientific work does not require approval from the Commission on Ethics of Scientific Research (KENI), since no invasive methods and interventions were used, as well as identifying data for the survey respondents.

The results of our short survey indicate that the respondents consider bags, cups and bottles to be the most common representatives of waste of plastic origin on the beach of the city of Varna. This contrasts with the results for the actual pollution of much of the beach, where it was found that the most common categories of plastic litter were actually unidentified fragments (fragments broken off from a larger object or debris of established origin that did not fall into any from the other categories described). After the unidentified debris, the next most common debris we found during the expeditions were caps, various types of packaging, straws, etc., while bags, cups, and bottles were the least common along the crawled stretch of beach. These results bring us closer to the conclusion that the respondents lack an objective assessment of the actual pollution of the beach, which is in line with other studies on the subject, showing that there are still some gaps in people's awareness of some aspects of this specific environmental problem (Heidbreder, 2019). Conducting extensive information campaigns is one way to make citizens aware of the actuality of the problem of plastic pollution and to influence their preferences and attitudes regarding the use, substitution and recycling of plastic products. Sometimes, citizens clearly realize that combating plastic pollution is of paramount importance, along with the fight against other environmental crises on a global scale. But because of the pervasiveness of this problem and its prevalence in certain remote areas of the planet, it is very likely that they are not considered directly responsible for it. In this line of thought, it is essential to implement other strategies among the general public to increase individual responsibility and motivation to fight this environmental problem on the part of individual citizens and end users. One such strategy is, for example, citizen science projects, the so-called citizen science or science for citizens (Adler, 2020; Fraisl, 2022). Involving people in various campaigns, field studies and environmental initiatives seem to be promising approaches to increase both their awareness and responsibility, as well as their motivation to change thinking and behavior in a positive environmental direction (https://eu-citizen.science/).

The summary assessment after analyzing the results of our expedition studies shows the presence of plastic pollution in a part of the coastal areas around the city of Varna. It is important to note that the results present us with a snapshot of pollution, at a precise point in time, in precisely defined locations. As far as we know, our findings regarding the quantity and composition of the waste, are the first ones published for the specific visited locations in the region of the city of Varna. To date, there are only 2 other published studies describing plastic pollution in other coastal areas within the city (Simeonova, 2017; Panayotova, 2020). For this reason, the possibilities of comparing the results are very limited, but nevertheless, adding data from studies in other coastal locations of the Black Sea basin, we could make some initial correlations. The results after the counting and categorization of the samples taken by us show a great heterogeneity of the waste. The most common waste is unidentified debris belonging to the "Other" category (with an average share of all expeditions - 52%). Depending on the location and season, the distribution of the most common waste is followed by the categories "Packages", "Bottles/tubes", "Caps", "Sticks" and others. Allowing for some differences, these results are very similar to the results of studies in other coastal areas of the Black Sea, in particular in the Istanbul city area, where the most common plastic waste belongs to the categories "beverage packaging" (19%). "foam/sponge particles" (9%), "ropes (5%)" and "plastic packaging" (4%) - bags, food packaging, etc. (Topçu, 2013). In contrast to the debris found there, classified as "ropes", no similar type of waste was found in our expeditions. On the other hand, it is interesting to note that the percentage of "Other" debris found in our study is absolutely identical to the percentage of unidentified debris found near the Istanbul city area - in both studies, exactly 52 % of all waste found. Despite the differences in the designs of the individual studies and the impossibility of exact correlations and comparisons of their results, the striking similarity found in the percentage of waste in the "Other/unidentified debris" categories raises many questions about the unclear origin of more than half of the items found. What are the primary articles/products from which these wastes originate, how long they have been in the environment, and what potential toxicological risks they pose to the environment and humans are questions that remain to be answered in future studies.

The most common plastic waste found during our expedition along the northern shore of Lake Varna - the bottles - is also found most often on the opposite side - along a section of the southern coast. This can be established by comparing the results of ours and one of the two available studies on the topic, specifically concerning a location within the city (Simeonova, 2017). Some of the other waste types described in our study are also found there in similar quantitative ratios. In the table 2 presents the 4 most common plastic wastes found during our expedition along the northern shore of Lake Varna (the "Other" category was removed). For comparison, the last column of the table presents the amounts of the same types of waste found and described in the survey conducted between 2015 and 2016 (Simeonova, 2017). The only difference is that in our study, the second most common item was plastic caps, while in the other study, the second most common item was packaging, which in our study was ranked 3rd. Plastic bags were the least common in both surveys.

Categories	Our data	Simeonova, 2017
Bottles	58	55 (292)
Caps	29	19 (146)
Packaging	18	32 (283)
Bags	12	5 (101)

Table 2 Quantities (expressed in number of items) of 4 of the most common plastic waste found during our expedition along the northern shore of Lake Varna. For comparison, the last column of the table shows the amounts of the same types of waste found during the survey of the opposite shore (southern shore of Lake Varna) during the winter season. In parentheses is the total number of litters found in all samplings of the 4 seasons.

Despite the impossibility of direct comparisons due to differences in methodologies, timing of expeditions and other variables, some similarity in results is noticeable, at least for some of the matched waste categories for both studies (bottles, caps, packaging, bags) . We can assume that the section from the northern shore of Lake Varna studied by us is much more polluted than the opposite shore, because the distance traveled by us is only 61 meters, while the traveled section from the southern coast is about 1 km long, with almost the same net quantities of waste found. These differences are most likely due to geographic, landscape, economic, infrastructural and other reasons that should be further explored.

In the other study of plastic pollution in the territory of the city of Varna, published in 2019. (Panayotova, 2020), some of the most common categories of plastic waste found on the beach in the municipality Asparuhovo, are very similar to the categories found and described in our expeditions. Plastic fragments, cigarette filters, plastic packaging, etc. are most often found on "Asparuhovo" beach. Although there is no clearly defined explanation as to whether the fragments found in this study are unidentified, we could assume that this category corresponds to the most common category of our expeditions - "Others", which morphologically are predominantly plastic fragments of various shapes and sizes. This is also the greatest similarity in results between the two studies, in case we stick to the assumption in question. On the other hand, there is a large discrepancy in the number of plastic bottles found and described in the two studies. In our expeditions, bottles were one of the most common types of litter, while in the other study they were not described as part of the litter categories found.

Our calculated Clean Coast Indexes (CCIs) for the first two central city beach crawls were CCI=0.38 and CCI=0.4, respectively. According to the ranges described in the "Results" section, we can conclude that this section of the beach is "Very Clean". The average amount of litter/m^2 calculated for this stretch of beach is in the order of 0.019 litter/m^2. For the second beach crawl, we obtained results of CCI=0.4. The average amount of waste per square meter of the beach is

0.02 debris/m^2. These results are similar to those obtained in other studies of plastic pollution along different coastal zones (Nachite, 2019; Loizia, 2021).

Our calculated Clean Coast Indexe (CCI) at the northern shore of Lake Varna is approximately 31, which, according to the ranges described in the "Results" section, means that this section is "extremely polluted". The average amount of waste/m^2 calculated for this section of the beach is of the order of 1.55 waste/m^2. These results are very similar to the results of other studies where the calculated coastal cleanliness indices are also in the CCI range corresponding to "extremely polluted" (Akarsu, 2022; Mugilarasan, 2021). According to these results, we can conclude that the section of the sandy shore of Lake Varna is much more polluted than the central city beach, despite the differences in the terrain, the area covered and some other parameters.

The Clean Coast Indexes for the beach in „Asparuhovo" varies between 3.32 and 8.19 depending on the season. In other words, the beach in Asparuhovo is "moderately polluted" in spring and "Clean" in autumn. These results are closer to the calculated CCIs for our first two expeditions (CCI=0.38 and CCI=0.4, respectively) than to our results for the northern shore of Lake Varna (CCI=22.0). The reasons for this have yet to be elucidated.

We could summarize that, with some exceptions, the most common categories of plastic waste calculated for other coastal areas in the Varna city area share a similar species/categorical distribution with our results regarding these parameters. On the other hand, there are large variations in the Clean Coast Index (CCI). We must emphasize that it is impossible to make direct comparisons between the results of our study and those of the other two studies for the city of Varna, due to methodological, geographical and meteorological differences. However, initial calculations show that the cleanest of the three locations is the central city beach, followed by the beach in the city center. Asparuhovo (varying between "Clean" and "Moderately polluted", depending on the season), and lastly, classified as "extremely polluted", is the section of the northern shore of Lake Varna. Furthermore, it is important to note that our findings present only a snapshot of pollution in a specific geographic location. Apart from the meteorological and geographical parameters, many factors of anthropogenic nature are also important for the results obtained by us. For example, it would be good to take into account the activities of various environmental and other organizations conducting their own field studies or other initiatives in the areas we explore. Their activities could influence the representativeness of the results obtained.

The activities of individual stakeholders and employees can also be added here, which would also have an impact on the reliability of the results. During our expeditions on a central city beach, we noticed individuals who, independently of us, were carrying out cleaning activities. This could underestimate our estimates of the current state of the beach, in terms of the amounts and types of litter in that particular section. For still unclear reasons, comparing the results of the first 2 sweeps, no noticeable difference was found in the species distribution of the most common types of waste. The temporal and spatial dynamics in the type and quantity distribution of waste along the coastal areas in and around the city of Varna are aspects that have yet to be clarified. In addition, more in-depth studies are needed to establish the mechanisms of transport and accumulation of this type of pollutants in the environment, as well as their potential to create ecological and health risks, with serious consequences for aquatic ecosystems and humans.

Due to the relatively preserved integrity, in just under 2% of the total sample taken in the two crawls of a central city beach, it became possible to identify the type of polymers symbolically/literally indicated on the surface. Among them, varieties of PE (HDPE, PET) and PP were found. Despite the lack of other direct evidence for the types of polymers and additives of which the debris found here is composed, based on its itemization (indirect evidence), it can be assumed that much of it is composed primarily of PE. This is indicated by the large presence of packages, bottles and other containers, which are most often produced from different subtypes and variations of PE. Due to the uncertainties regarding the types of plastics that make up the waste of the "Other" category, we can assume that among them there could also be items that are also made of PE and other representatives of the polyethylene family. All this supports the assumptions that one of the main types of polymers found in our expeditions is precisely PE and its derivatives. These assumptions are also in line with the scientific literature on plastic pollution in different parts of the planet, in the majority of which, the most common type of polymer is precisely PE and its varieties (Issac, 2021; Tiago, 2023). This is no accident, given the fact that PE is also currently the most produced type of polymer (Plastic - The Facts, 2022). For even more accurate identification of the specific type of polymer and various other additives found in the environment in the form of pollutants, the use of precise laboratory technique with specific complementary software is necessary.

The majority (nearly 90%) of the waste found during our expeditions are of macroplastic size (over 2.5 cm along their longest axis). About 8% belong to the category of mesoplastics (0.5-2.5 cm). Only about 3% of all waste found is of the order of millimeters (microplastics, ≤0.5 cm). These results are somewhat expected, given the fact that they are based on visual identification, where larger debris on the surface is mostly noticed, while smaller ones may be missed. On the other hand, the different sizes of waste found in the environment could give us a rough idea of their residence time there. In other words, the more fragmented an item is, the more likely it has had a longer stay in the environment. This marker is quite conditional because the duration of the life cycle for any plastic waste is a function of many other internal and external factors, including the type of polymer and additives to it, action of various meteorological parameters, transport and transfer mechanisms, influence of microorganisms, etc.

The degradation of plastics can be caused by heat (thermal degradation), light (photodegradation), ionizing radiation (radiodegradation), mechanical action or by fungi, bacteria, yeasts, algae and their enzymes (biodegradation) (Wypych, 2018). All these factors are present to varying degrees in nature, but due to the different combinations and proportions of them, sometimes different degrees of degradation of synthetic polymers are observed between seemingly identical places and locations.

From the microscopic analysis here, it can be assumed that a portion of the unidentified fragments belonging to the "Other" category have undergone varying degrees of fragmentation. At a close microscopic magnification, it becomes clear that the surface of the examined fragments is highly cracked, with the presence of microcracks. Other fragments show only surface exfoliation. After applying pressure with metal tweezers in different directions, detachment of smaller particles from the main fragment was observed from the surface of some fragments. In other fragments, after applying not too much pressure or passing tweezers over the surface, only peeling/delamination is observed. These differences are most likely due to different types of polymers from which the individual samples are made, the substances added to them and the residence time in the environment. The observed fragmentations and exfoliations occur under different application of pressure i.e. some plastic debris fragmented much more easily with very little pressure or scraping, while others required greater force to observe fragmentation. In a third, only slight deformation was observed without breakage (even after application of greater force) or breakage of a smaller particle, which, however, remained attached to the larger fragment and was difficult to separate from it with tweezers. 3 of the fragments showed extremely high fragmentation, even with very light pressure. From all of them, a large number of microfragments with dimensions of the order of fractions of a millimeter broke off. All these results speak in favor of the assumption that a large part of the samples have probably been in the environment for some time and already undergo a different degree of fragmentation, which, in addition to the environmental conditions and exposure time, also depends on the type of polymer and the presence of additives. Due to the lack of hardware identification, at this stage it remains unclear what the polymer composition and additive content of the unidentified debris found, assigned to the "Other" category, is. This, in turn, raises new concerns of an ecotoxicological nature, due to the unknown number of potentially ecosystem-risky substances released from plastic waste.

The first visual effects of polymer degradation are color changes and surface cracking (Vasile, 2000). As it has already become clear, the main responsible and initiator of these processes is UV radiation. Surface cracking makes the interior of the plastic material accessible for photon absorption and further degradation. The migration and desorption of substances through the polymer matrix further destabilizes it, ultimately leading to brittleness and disintegration of the material.

Coloring substances added to plastics can be various pigments and dyes (Christie, 1998; Mohamed, 2017). Pigments can be both inorganic and organic. For the production of thin-walled products such as films and fibers, organic pigments are more preferred (Pfaff, 2021). In addition, they are also used for multi-color printing on films, as they achieve a higher color intensity than inorganic pigments. If high weather resistance of plastic products is required, inorganic pigments are the colorants of choice. Pigments are generally used more in the production of plastics from the polyolefin family (PE, PP, PB, etc.). The choice of pigment is determined by the type of polymer, the compatibility with it, the toxic potential of the pigment and other factors. For example, due to the specificity of the production process of PET (high temperatures for a long period of time), only inorganic pigments and very few organic pigments with a polycyclic structure (quinacridone, copper phthalocyanine, naphthalene tetracarboxylic acid and perylene tetracarboxylic acids) are suitable for this type of polymer). The other large group of colorants added in the production of plastics, the dyes, dissolve in the polymer medium and are usually retained as a result of the affinity between the individual molecules of the dye and the polymer molecules. Therefore, in case of possible fragmentation of plastic debris as a result of the influence of environmental factors, migration/transfer of dyes through the polymer substrate, with subsequent desorption to the environment, can be expected. Dyes are added more frequently in the production of plastics from the polycarbonate, PS, acrylic and other polymer groups (Patel, 2006).

The most common colors of plastic debris found in water bodies are white and transparent/translucent (47%), yellow and brown (26%) and those in the blue range (9%) (Martí, 2020). The remaining 18% of waste has colors in almost all other color ranges. The frequency of white color was found to increase among the smallest pieces (<5 mm), in most cases away from coastal areas (>500 km). A precise assessment of the color distribution of the debris found in our expeditions is difficult due to a combination of subjective factors and the presence of multiple debris containing more than one color. However, we do find some similarities with the results of worldwide assessments of the most common litter colors and the color range of debris found during our expeditions. The approximate percentage distribution in color ranges of litter found on a central city beach is as follows: white and transparent/translucent ~ 31%, blue ~ 23%, yellow/brown ~ 14%, gray ~ 8%, red ~ 5% (Fig .7). All other colors, including black, green, pink, purple and orange, made up a total of about 19% of the samples. As a result of the presence of this rich range, including all possible shades of all primary colors, we can assume that under certain circumstances, the colorants contained in the debris found could be released from the polymer matrix and enter the environment. Some of the debris found here show differences in the color shading of individual sections of their surface. This may indicate the presence of existing migration processes, in which the dyes move into the plastic matrix and at some point are separated from it, falling into the environment.

From the presented data on plastic pollution in the water basins of the planet, it became clear that the most common types of plastics in them are from the group of polyolefins - polyethylene and polypropylene. The results of our studies in some sense support these findings, even without performing a precise instrumental identification of the types of plastics from which the waste found here is made up. A rough estimate of the types of polymers can be made based on the item belonging and the presumed commercial and other functions that the found debris performed, i.e. it can be assumed that the majority of bags, packages and bottles are made of various types of PE, PET and their additives. It can be assumed that PP and other plastics made up a portion of the unidentified debris reported here under the "Other" category. This is a hypothesis that deserves to be tested. The samples from our studies were almost devoid of polystyrene-based particles and granules. Since most of the samples found in our expeditions show signs of different degrees of degradation, we can assume that they also had different stays in nature. Although indications of degradation processes can be observed as early as about the second month after a given debris enters the environment, due to the presence of a large number of confounding factors, it is still impossible to calculate the exact residence time in the environment only on the basis of visual wear markers. In subtropical salt marshes, degradation of 3 common plastic polymers (high-density polyethylene, PP, and extruded polystyrene) has been reported to begin relatively rapidly, with evidence of surface erosion leading to delamination and production of microplastic particles within a period of only 8 weeks (Weinstein, 2016). The SEM images suggest that the microplastic particles have detached as a result of surface delamination. Numerous microcracks, chipped edges and grooves are observed on the surface of the debris, similar to those found in some of our samples. On the other hand, it is suggested that the delamination processes may be delayed to some extent due to the blocking of UV light caused by the growth of biofilms on the surface of the debris. And yet, due to the degradation processes described in the literature, occurring in plastic waste after it enters the environment and based on our microscopic findings, we can assume that in the Black Sea water area and the adjacent coastal areas of the Varna region, over time smaller and smaller microparticles separated from larger fragments/debris under the influence of environmental factors will accumulate. Their quantities and behavior at this stage remain largely unknown.

PP-based plastics containing BPA have been shown to release it faster into surface waters than PLA-based plastics, which also contain BPA as an additive (Rosa, 2018). Considering the potentially large amounts of polypropylene-based debris found during our expeditions, we can assume that certain amounts of BPA could be released in the coastal areas of the city of Varna. Since at this stage the fate and cycles of waste from terrestrial to aquatic environments and vice versa are insufficiently understood, these quantities cannot yet be precisely measured.

There are reasons to assume that sediments in different biotopes of the terrestrial environment represent a kind of reservoir of BPA, since it bioconcentrates and accumulates through the trophic networks between individual micro-organisms and other ecosystems (Torres-García, 2022). Therefore, based on these assumptions, in addition to the findings from our expeditions, we can assume that certain amounts of BPA could also be deposited deep below the surface of coastal areas. This hypothesis calls for further research to assess the quantities and possible modes of transfer of this substance and its derivatives between the individual segments in the different coastal biotopes on and below the surface.

For the polymers PE, PP, PS and PVC, abiotic degradation probably precedes biodegradation (Berit, 2015; Chamas, 2020). Photoinitiated oxidative degradation of PE, PP and PS leads to a decrease in molecular weight and formation of carboxyl end groups, and UV light is able to initiate dechlorination of PVC. When the polymer chain is cleaved after UV-initiation, lower molecular weight polymer fragments are formed that can be biologically degraded. In the marine environment, several degradation pathways can occur simultaneously, as different factors initiate degradation. Therefore, the degradation products may be more diverse than expected for each individual degradation pathway.

It has been shown that smaller polymer fragments formed by abiotic degradation can cross cell membranes and be further biodegraded within microbial cells by cellular enzymes, but some microbes also secrete extracellular enzymes that can act on certain plastic polymers (Shah, 2008). As with abiotic degradation, in the biodegradation of most plastics, they degrade first at the surface of the polymer, which is exposed and accessible to chemical or enzymatic attack. Therefore, microplastics degrade faster than meso- and macroplastics because microplastics have a higher surface-to-volume ratio.

Despite the vast amount of scientific literature on the subject, at this stage the question of the potential impact of synthetic polymers on living beings and the risks they pose when entering their organisms remains insufficiently clarified. While some studies show visible morphological or biochemical damage to organisms as a result of passing or accumulating plastic particles in them, other studies show no apparent toxic or lethal effects, even at high particle concentrations. So far, it appears that the greater risks are not the polymers themselves, but the various additives that are used in their production, or other substances that can sorb on the surface or in the depth of the polymers, during a longer stay in the environment (Rios , 2010).

Plastic waste has long been known to have the potential to sorb and transport persistent organic pollutants, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) or even heavy metals (cadmium, lead, zinc, copper, chromium, etc.) by invertebrates to other higher trophic levels (Holmes, 2012; Lee, 2014; Crawford and Quinn, 2017). In the tissues of several Black Sea fish of commercial importance, some PCB congeners were found in different concentrations (Stancheva M, 2017). After the analysis, it becomes clear that the levels of PCBs in marine fish from the Bulgarian Black Sea are lower than those reported in other marine regions around the world. Estimated dietary intake of PCBs through consumption of marine species does not appear to pose a risk to human health. Sometimes the levels of heavy metals can rise dramatically in the marine environment, mainly due to anthropogenic pollution. Studies by Bulgarian scientific teams have analyzed the levels of heavy metals in the tissues of various fish from the Bulgarian Black Sea, including sprats, saffron, mullet, etc. (Makedonski, 2017; Stancheva, 2013; Peycheva K, 2022). In the majority of studies, slightly elevated concentrations of Cd, As, Hg, Pb, Zn and Cu were found, which nevertheless remained within acceptable levels for human consumption without risk to human health. The results of these studies show that in the gills of the studied fish, a higher concentration of the described metals is observed, while in their muscle and other tissues, it is lower.

In the light of these findings, knowing that some plastic waste can act as a source or vector for the transport of adsorbed heavy metals and other persistent organic pollutants, it is necessary to further investigate the various aspects of the transport of these substances in the marines and coastal environments. It would be useful to look for relationships between the detected categories and amounts of plastic waste in our and future studies, and the possibility that they may play a role in the transport and distribution of the described chemicals. Tracing their pathway to different trophic levels will reveal the mechanisms of potential dietary exposure in humans, which is implied in the second stage of our proposed conceptual framework, described below. This would contribute to a comprehensive assessment of the toxicological risk that the substances in question carry, not only in relation to marine ecosystems, but also in relation to human health, which in turn is part of the third level of the conceptual framework – biomonitoring studies.

In addition to the described substances proven to be harmful to ecosystems and humans, there are already data on the adsorption of various antibiotics from the environment on plastic waste (Li, 2018). It turns out that polyamide has the strongest adsorption capacity for antibiotics. Antibiotics identified were sulfadiazine, amoxicillin, tetracycline, ciprofloxacin, and trimethoprim. These results are extremely concerning, against the background of increasing worldwide antibiotic resistance, and suggest new additional pathways and prerequisites for its potential increase.

The COVID-19 pandemic has caused unprecedented upheavals on a global scale that have profoundly affected countries around the world, not only in terms of health and demographics, but also affecting people's economic, socio-cultural, political, media, and even spiritual lives. From the perspective of time, it turned out that this global pandemic catastrophe also played an inevitable ecological role in some climate processes. Although significant declines in some air pollutants have been reported in many regions of the world during the worst of the epidemic (mainly due to mass travel bans and transport restrictions), there is evidence of an increase in plastic pollution associated with the mass overproduction of personal protective equipment, medical and other commercial supplies (Aragaw, 2020; Parashar, 2021; Hu, 2022; Klemeš, 2020; Fadare, 2020). The results of the studies show that the overproduction and excessive consumption of face masks, combined with inadequate waste management, have contributed to a significant increase in plastic pollution in water bodies, as these products are mostly made from PP, PU, PE , PC, polyester and other polymers. Already in the first months after the start of the pandemic, medical waste of all categories generated in some provinces in China has reached an increase of more than 370%, and in just 3 months (from January to March), the total amount of medical waste in the whole China has reached over 207 kilotons, with a high proportion of plastic products and consumables. Due to the rapid onset of the pandemic, the lack of logistics and the lack of incineration systems, this waste has been mismanaged, which in turn has led not only to an increased carbon footprint for the environment, but also to an increase in transportation risks of viral and bacterial pathogens found on the surface of discarded masks for example. Wet wipes and polymer-based food containers also increased their production levels during the pandemic, which subsequently made them no less significant environmental pollutants.

For the purposes of the present scientific work, a short pilot study was carried out for an initial assessment of potential microplastic particles in personal hygiene products commercially available in the city of Varna. The dominant type of particles found in personal care products described in the scientific literature are primarily PE-based (Gouin, 2015; Sun Q, 2020). When scanning the products from our pilot study, the particles described on the package with a proven polymer composition were Dimethicone, Carbomer, Polyquaternium-7 and Polyquaternium-6. These are the most common ingredients found in personal care products and in other studies (Nawalage, 2022). Dimethicone and its derivatives are cast siloxane polymers, which are themselves a variety of silicones. Although their chemical backbone is not carbon-based, but silicon-based, they are also considered polymers. Added to personal care products, they perform a variety of functions in them - absorbents, bulking agents, film formers, skin softening agents, etc. (Nair; 2003; Becker, 2014). Carbomers are actually a group of polymers made primarily from acrylic acid (https://www.cosmeticsinfo.org/ingredients/carbomer/), i.e. the term "Carbomer" can be said to denote the trade name of various derivatives of polyacrylic acid. Because they represent an extremely heterogeneous group, studies are still insufficiently definitive regarding the potential environmental risks these substances pose. The potential risks to humans are also yet to be elucidated. The term “Polyquaternium” is a neologism used in the International Nomenclature of Cosmetic Ingredients (https://www.cirs-reach.com/Cosmetic_Inventory/International_Nomenclature_of_Cosmetic_Ingredients_INCI.html) to denote a group of polycationic polymers containing quaternary ammonium centers in their molecule. They are used in various shampoos, conditioners, hair sprays, hair dyes and other products. Being positively charged, polycationic polymers neutralize the negative charges occurring in the various ingredients of commercial products. Despite the available evidence of toxic effects in some marine organisms (especially for Polyquaternium-6), studies on the potential harm to aquatic ecosystems and humans are still at a very early stage (Rawlings, 2022). In our pilot study, 31 out of a total of 65 scanned products were found to contain ingredients of unknown but suspect polymer composition. This necessitates conducting additional in-depth analyzes of these suspect ingredients, establishing their morphology, transport mechanisms in the environment, as well as their toxicological parameters.

Limitations of the study

The current research work contains certain design limitations and weaknesses caused by multiple factors of a geographic and resource nature. First of all, it can be noted that a limited number of areas in the Varna region have been studied, and future studies should further expand the area of investigations and survey additional unexplored locations. Difficult traversability in some areas may hinder safe crawling, which is why it is necessary to take into account the landscape characteristics of the surveyed areas. In addition, it is necessary to investigate plastic waste not only on the surface of coastal areas, but also those located in depth. Future studies should reveal what the concentration gradient of plastic particles is at different depths below the sand/soil surface, as well as in different geographical locations.

As a limitation of the study, we could point out the small number of participants in the samplings, as well as the lack of seasonal monitoring of the pollution dynamics. In addition, it would be good to study the characteristics of plastic pollution also in the territories inside the city of Varna, including for future surveys not only water basins (city canals, smaller rivers and reservoirs), but also separate sections of land . In this way, a more complete and objective picture of the quantities and types of plastic waste thrown into the urban and non-urban environment will be achieved.

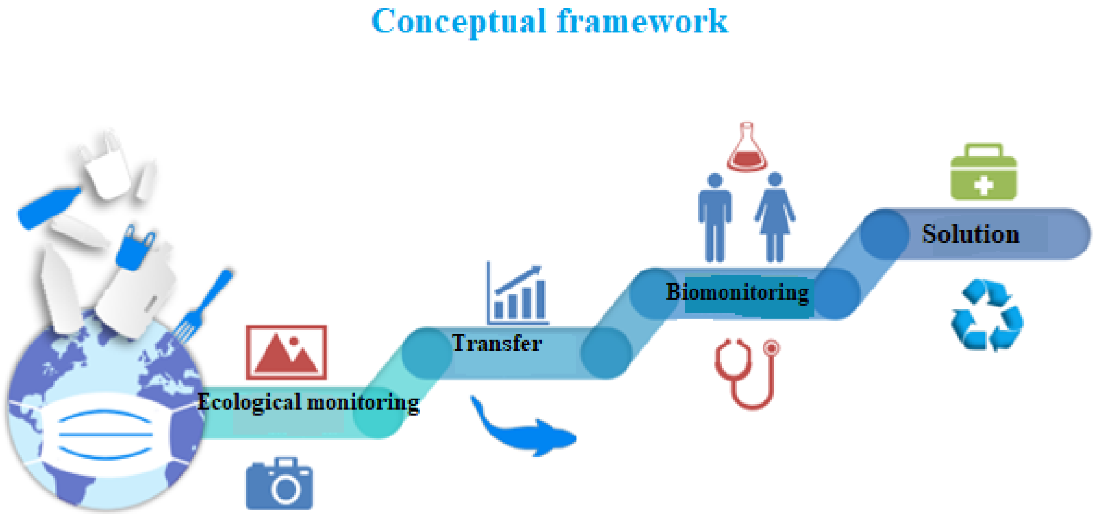
Another limitation of the study is the non-representative sample of survey respondents. It is necessary to make a more comprehensive selection of respondents of different age, gender, social status, etc., in order to reach a higher level of objectivity and representativeness.

When applying microscopic methods, even more powerful professional equipment should be used, including stereomicroscope, scanning electron microscope (SEM), etc. In addition, for accurate qualitative analyzes of the types of polymers and various additives to them, the application of powerful spectroscopic or chromatographic equipment is necessary. Currently, some of the most effective methods used to identify polymer types are Raman spectroscopy and Fourier-transform infrared spectroscopy (FTIR). Another limitation of the study is the non-representative sample of survey respondents. It is necessary to make a more comprehensive selection of respondents of different age, gender, social status, etc., in order to reach a higher level of objectivity and representativeness.

Another limitation of the present study is that it scanned the packaging of a small number of commercial products for the presence of potential plastic additives in their contents. The objective here was to do a small-scale pilot study to test the feasibility of the mobile application "Beat the microbead app". In future studies, it is necessary to expand the scope of product scanning in a larger number of commercial establishments for food and cosmetic goods in the region of the city of Varna and beyond. In addition, other types of items including oral hygiene products need to be scanned, e.g. toothpastes that have also been shown to contain polymer-based microparticles. By collecting additional data on the sales of these products over certain periods of time, examining the exact amounts of microplastic fragments contained in them, as well as other variables, a calculation could be made of the approximate amounts of these particles entering the environment. environment through the sewage system in populated areas. In this way, it will help to carry out a more complex assessment of the risk of ecological catastrophes threatening aquatic ecosystems, as well as an assessment of the risk of health consequences for the population.

Recommendations and future directions

Based on the results of our expeditions, in addition to the physicochemical and ecotoxicological parameters of plastic products and their widespread environmental pollution discussed in the literature review, we propose a model of a conceptual framework for a phased and segmented study of this problem in the Varna region . The conceptual framework is a set of 4 different groups of methodologies, applied in a certain sequence, with the aim of in-depth study of different aspects of plastic pollution in the environment, as well as aspects of its harmful impact on ecosystems and human population (Scheme 2). In the following lines, we will focus on some of the aspects of the first segment of the proposed conceptual framework, namely ecological monitoring. Our main goal is to summarize and give additional new guidelines and recommendations for its optimization in future studies, in view of the individual landscape features of the coastal areas in and around the city of Varna.



Scheme 2. Conceptual framework for a phased and segmented study of the different aspects of the problem of plastic pollution in the environment and the potential risks to ecosystems and humans.

In the first segment of the proposed conceptual framework, as already mentioned, environmental/ecological monitoring is presented, including its various aspects (identification of "hot spots", visual inspection, sampling, documentation, laboratory analyses).

A starting point before starting an expedition is the identification of "hot spots" of pollution. This can be done by preliminary visual survey/site crawl (field crawl) or by identifying contaminated areas from satellite/satellite images. Due to the ever-advancing technology of satellite systems in orbit around the Earth, improved resolution and quality of images will facilitate the identification of pollution hotspots. The use of more affordable drone-type aircraft would also contribute to the easy detection of polluted areas, not only on land, but also on the surface of large water bodies. In addition to aerial drones, underwater drones can also be used to take samples from different depths.

The second segment of the proposed conceptual framework examines aspects of the possible transfer of plastic pollutants from the environment to living organisms, as well as their potential transfer between different organisms, including humans. The implementation of different methodologies facilitating the detection of plastic pollutants in the tissues of a large number of organisms and their possible transfer to different segments of the environment, as well as interspecies transfer, are considered. Because humans are part of nature's global food web, it is assumed that they will ingest a portion of plastic particles and related substances, primarily by consuming aquatic organisms that have already ingested the pollutants in question. This peculiar transfer of particles from one trophic level to another is a prerequisite for their reaching humans, in their role as final consumers, and exhibiting potential harmful effects for their health. In about 50 years, global per capita consumption of seafood (fish, crustaceans, molluscs and other aquatic organisms, excluding mammals) has doubled from 9.0 kg in 1961 to 20.2 kg in 2015. (FAO. The State of World Fisheries and Aquaculture, 2018). Considering this growth in consumption, we can assume that the amount of ingested plastic particles has also increased in the last few decades. All this necessitates the improvement and unification of the protocols for the accurate implementation of the methodologies in the study of these aspects, which is laid down precisely in the second segment of the conceptual framework proposed here.

The third segment of the conceptual framework involves the implementation of biomonitoring studies to study the content and behavior of plastic particles and other substances in the human body. It would be possible to establish and analyze the interrelationships between the microparticles found in marine organisms and their finding in unchanged or metabolized form in the human body. The study of the content, toxicodynamics and toxicokinetics of given particles and substances would be of great benefit. Furthermore, it is important to study their potential for bioaccumulation and possible interactions with other ecopollutants.

The last fourth segment of the conceptual framework contains the possible solutions to the problem of plastic pollution of the environment, based to some extent on the accumulated empirical data of the previous 3 segments. One of the most important prerequisites for an effective fight against plastic pollution and the protection of natural resources is the development and implementation of directives and other strategies of a legislative nature. One of the key objectives of such legislative measures is to reduce single use, as well as to reduce the use of single-use plastic products. In addition, directives and regulations may introduce different standards for sustainability and biodegradability of plastic products. This would stimulate industry to use greener alternatives and develop new biodegradable materials.

One of the main prerequisites for the protection of the environment by man is the awareness of society about environmental problems in nature, and in particular those that are directly related to anthropogenic pollution in all its aspects. In this line of thought, a proper understanding of human civilization's contribution to the ubiquitous plastic pollution of water bodies and its consequences for the planet is critical to maintaining ecosystems at an optimal level of well-being. In recent years, public interest and awareness about plastic pollution of water bodies has grown significantly. However, there are still some gaps in people's awareness of some aspects of this specific environmental problem (Heidbreder, 2019). For example, knowledge about biodegradable plastics and other alternative substitutes for traditional plastic products is still weak, especially in developing countries. There is a tendency for a large part of the media to share false information and some misconceptions about plastic pollution, which plays a role in the general public's misunderstanding and objective understanding of this problem (Hahladakis, 2020). On the one hand, this is mostly due to the inadequate interpretation of the results of serious scientific publications on the subject. In addition, mainstream media tend to distort data or speculate on some facts for purely subjective reasons, which can further distort people's understanding of the various aspects of plastic pollution in nature. Therefore, conducting information campaigns related to plastic pollution could provide the necessary knowledge to citizens, including to change preferences and consumption behavior, which in turn is a good first step towards addressing this environmental problem (Latinopoulos, 2018). However, the change in environmental behavior and attitudes does not follow instantly, mainly due to already formed habits, practicality and convenience in the context of consumption. In this line of thought, the formation of individual attitudes, preferences and ecological thinking should be encouraged and implemented at an early age.

A major role in the formation of environmental awareness among adolescents is mainly played by their parents, teachers and mentors. It has been proven that the provision of additional knowledge in environmental sciences improves the attitudes of students towards the environment, which in turn is a prerequisite for building a sustainable value system in them (Bradley, 1999). Although the awareness and knowledge of primary and secondary school students in developed countries about the problems of plastic pollution is constantly increasing, the results of some studies show that students in other countries still have low levels of environmental literacy (Hammami, 2017). After educational environmental interventions, children up to the age of 8 show greater concern and awareness regarding marine litter (Hartley, 2015). Moreover, they even develop a responsibility to engage their parents, relatives and friends about these environmental issues, thus influencing in a positive direction the attitudes of adults towards environmental protection. The direct participation of high school students in beach clean-up field activities proves to be a useful tool to increase specific knowledge and stimulate their interest in the problem of plastic pollution (Locritani M, 2019).

It is necessary wherever it would be profitable to implement marketing mechanisms for environmental protection, which could stimulate the market to adopt more ecological behavior (Marinova, 2013). These methods include, for example, economic incentives, pollution quotas and compensation payments, a pollution payment system, etc. In essence, they are regulatory mechanisms that are used to persuade different companies to adopt greener behavior such as protecting the environment without harming their operations and making profits.

In view of the presence of microplastics in personal care products, it would be good consumer practice when choosing personal care products to check the label and manufacturer's information to ensure that the product does not contain plastic particles and is recognized as "Plastic free". The list of ingredients on the label must be drawn up in descending order depending on the amount of added mass at the time they are added to the cosmetic product (Regulation - EC - No. 1223/2009 of the European Parliament and of the Council of 2009). Ingredients with a concentration of less than 1% must also be listed, but may be listed in any order after those with concentrations greater than 1%. This means that regardless of the concentration of an ingredient, it must still be clearly stated in the product's ingredients list. These regulatory rules aim to provide transparency and consumer awareness about the ingredients in personal care products, and to ensure that manufacturers comply with safety and environmental standards. For maximum information, in addition to reading product labels, consumers should also look to various online resources to learn more about the ingredients in personal care products and the practices of manufacturers. Meanwhile, various organizations and institutions continue to work on regulations and standards to promote a sustainable cosmetics industry and environmental protection (Boots, M. G., and E. J. W. van Sambeek. European congeneration certificate trading-ECOCERT; https://www.ewg.org ; https://www.safecosmetics.org).

Conclusions

1. Plastic pollution in the Black Sea and its coastal areas shares many similarities, but also some differences, with plastic pollution observed in other parts of the world, including some Black Sea coastal areas.

2. Visible contamination with several different categories of plastic waste is observed in the Varna region, observed on the majority of pre-marked coastal locations.

3. The most common category of plastic waste is unidentified debris. They are fragmented pieces of larger plastic items that have broken down and dispersed into the coastal environment.

4. The most common categories of plastic waste with identified origin and use are packaging materials, plastic bottles, straws, caps and various other debris.

5. There are relative seasonal differences in the types and distribution of waste found on the central beach.

6. There is direct and indirect evidence of the presence of certain types of polymers, which are most likely made up of the waste found during our expeditions. Direct evidence is significantly less than indirect evidence and is based solely on a clearly distinguishable indication of polymer composition on the surface of the waste itself.

7. There is a varying degree of fragmentation and degradation of a portion of the debris found in coastal areas.

8. On the basis of the assumed polymer composition, according to the observed categorical affiliation of the debris, a part of them can be expected to pose risks of a toxic and epidemiological nature for the aquatic ecosystems, and indirectly for the human population.

9. In some of the commercially available personal hygiene products, the presence of polymeric ingredients and other substances of unconfirmed but suspected polymeric origin was found.

10. Despite the knowledge of the residents of the city of Varna regarding the existence of an environmental problem with plastic pollution, they do not have a realistic idea of the most common categories of plastic waste on the beaches.

11. Studies of plastic pollution in the freshwater basins of Bulgaria, the Black Sea water area and the adjacent coasts, are still at a very early stage and urgent measures are needed to increase the empirical power on the topic.

Final remarks

Although environmental pollution has been a part of human history for thousands of years, its scale and impact have increased significantly in recent centuries with the widespread use of industrial processes and modern technology (Mohajan, 2019). Along with air pollution, plastic pollution in water basins, in just a period of half a century, has acquired scales that put the well-being of not only aquatic ecosystems, but also the human population on the agenda.

The presence of large amounts of plastic waste in the water bodies on our planet contributes to the potential introduction of various chemicals, including additives, unreacted monomers and degradation products. Some of these substances have been identified as potentially hazardous to marine organisms and humans, but further studies are required for a precise and comprehensive risk assessment.

Although the development of unified protocols for monitoring plastic debris in the marine and coastal environment is already underway, the precise study of MP is still extremely hindered by various technical challenges and the large fluctuations in the concentrations of these pollutants in nature. Therefore, the actual exposure to MP-particles and their additive components remains difficult for a possible risk assessment for marine ecosystems, and therefore for humans.

Despite the large differences in the applied methodologies, we can conclude that depending on the location, type of coastal zone, as well as the area studied, the density and types of plastic waste show a high heterogeneity in the individual studies. For these reasons, direct comparisons between the results described in the various publications on the subject are still largely irrelevant, if not impossible. Still, if a conservative estimate is to be made when comparing the results between the global studies and those obtained in the Black Sea studies, it can be concluded that the plastic pollution of the Black Sea coast is very similar to much of the pollution of other coastal areas, at least in terms of the quantities and types of pollutants.

Based on the results of our studies, we can conclude that plastic pollution in the Black Sea and its coastal areas shares many similarities with plastic pollution observed elsewhere in the world. In the Varna region, there is visible pollution with different categories of plastic waste, with the most common categories being unidentified debris, which is broken pieces of larger plastic objects scattered in the coastal environment. In addition, identified waste such as packaging materials, plastic bottles, straws, caps and other debris is also found. A varying degree of fragmentation and degradation of some debris is observed, which may have a potentially hazardous impact on the environment. These results highlight the need for further comprehensive monitoring studies, and at the same time taking serious preventive measures to reduce plastic pollution and protect the marine and coastal environment.

From the above, it is clear that the issue of plastic pollution in water bodies is a wide-ranging and multi-layered problem, the solution of which will require not only the intervention of interdisciplinary scientific teams, but also the direct involvement of society, including the youngest age groups. While educators and organizers of various environmental activities and events are in a position to raise awareness and encourage alternative patterns of behaviour, stakeholders from the commercial and industrial sectors as well as politicians have a responsibility to promote appropriate policies, change attitudes and legislation regarding of consumption and waste management. Governments must cooperate not only regionally but also globally to regulate and improve practices in the production and trade of plastic products, as well as adequate waste management in the light of the circular economy. In addition, they need to encourage and finance further research and implementation of innovative modern technologies in the production of alternative, environmentally friendly substitutes for plastics.

On the agenda for current and future researchers is the question of supplementing and improving the set of methodologies helping to accurately detect and calculate the amounts of plastic pollutants in the environment, and in particular water basins and their adjacent coastal areas. The issue of identifying their species is also of vital importance, in view of the ever-increasing number of reports on emerging types of pollutants and the various potential harms they bring to ecosystems and humans. In addition, further studies are needed to establish the possible transfer pathways of the pollutants in question from and to the environment, as well as the resulting potential entry and multi-vector transfer of plastic particles and their derivatives at different levels of the trophic webs.

in which man also occupies a place. In this way, the implementation of the individual steps of ecological and biological monitoring will become a fundamental unit in the implementation of adequate primary prevention of potential harm to ecosystems and humans arising as a result of plastic pollution in water basins.

Despite the hypothetical risks, at this stage it appears that aquatic ecosystems and humans are still at low risk of a plastic ecological catastrophe capable of debalancing and destroying to a critical threshold various biological species, as well as having clinically significant manifestations in humans. But if our civilizational development continues at the same pace and the individual does not acquire a higher degree of individual ecological awareness, which then transforms into a collective one, one could expect that anthropogenic environmental pollution will be a problem of increasing importance, questioning the survival not only of natural ecosystems but also of man as a living being.

Contributions

Contributions of original character

1. The fundamental steps have been taken to implement ecological monitoring regarding the detailed morphology of plastic pollution in the coastal areas of the Varna region.

2. The first detailed categorization of the quantities, sizes and types of plastic waste in some coastal areas of the city of Varna was made.

3. An initial assessment was made of some of the most common types of microparticles of potential plastic nature added to commercially available personal care products.

4. For the first time, a microscopic analysis of waste from plastic pollution in the Varna region was made, with the aim of tentatively determining the degree of fragmentation and degradation of plastic waste left in the environment.

5. A visual conceptual framework has been created for a step-by-step and segmental study of plastic pollution and its various aspects in the Varna region.

Contributions of a confirmatory and applied character

1. A narrative theoretical review of the scientific literature addressing plastic pollution in water basins and coastal zones and the resulting potential risks to ecosystems and human health, was made.

2. The data from the present study could contribute to conducting future trainings, practical and informational campaigns, through which the problem of plastic pollution in the Varna region can be brought into the public discourse, including by engaging citizen science networks.

3. Recommendations are given for a step-by-step and segmental study of the problem of plastic pollution in the Varna Region, by optimizing and implementing the various aspects of environmental monitoring.

4. The data from the present study are a starting point for supplementing and expanding the teaching material on hygiene and ecology, as well as other areas of knowledge.

Appendices

This section presents voluminous data from photographic evidence presenting the categories of plastic waste found during all searches of the coastal areas of the Black Sea, in the area of the city of Varna. Due to the large volume of data, the images are reduced in size in order to fit within the current scientific work all possible samples taken from the coastal areas during the field crawls. Several of the photos also feature non-plastic items, such as metal jar lids or paper packaging, as only plastic waste has not yet been separated and sorted when the photos were taken.


ПИРИНСКО