On some physical and dynamical properties of microplastic particles in marine environment

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ABSTRACT

Simplified physical models and geometrical considerations reveal general physical and dynamical properties of microplastic particles (0.5–5 mm) of different density, shape and size in marine environment. Windage of extremely light foamed particles, surface area and fouling rate of slightly positively buoyant microplastic spheres, films and fibres and settling velocities of negatively buoyant particles are analyzed. For the Baltic Sea dimensions and under the considered idealised external conditions, (i) only one day is required for a foamed polystyrene particle to cross the sea (ca. 250 km); (ii) polyethylene fibres should spend about 6–8 months in the euphotic zone before sinking due to bio-fouling, whilst spherical particles can be retained on the surface up to 10–15 years; (iii) for heavy microplastic particles, the time of settling through the water column in the central Gotland basin (ca. 250 m) is less than 18 h. Proper physical setting of the problem of microplastics transport and developing of physically-based parameterisations are seen as applications.

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1. Introduction

Problems related to increasing plastic pollution of our seas and oceans are of concern for a large number of ecological, biological, social, and economic studies (e.g., Kershaw (2015)). It is already shown that marine litter, beach debris, tourism-related and other macroplastic pollution causes ecological and aesthetic problems, whilst microplastic particles, on top of that, serve as effective collectors of various toxins and chemical pollutants and are able to climb up the food chain to our dishes (Andrady, 2011; Hidalgo-Ruz et al., 2012; Law and Thompson, 2014; Thompson, 2015). At the same time, the majority of studies on microplastics are concentrated on their abundance, biological and chemical consequences, whilst physical properties of the very microplastic particles are shadowed. It is, however, practically evident that the progress in this field is related to physical and mathematical analysis of the microplastic particles behaviour in stratified marine environment, their transport and fate. Such analyses definitely require numerical modelling, and, consequently, certain parameterizations of the particles' properties and their variations in time. This work aims to gather published information on physical and dynamical properties of marine microplastics particles, as well as to provide the results of simple geometric and kinematic considerations and some approaches, targeted at further parameterizations of their behaviour in hydrodynamic numerical models.

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concentrations to be 3 particles in m³ of water (Doyle et al., 2011) and 8 particles in a kg of sediment (Thompson et al., 2004). Taking the sand density for recalculation, this gives 21,200 particles in m³, i.e., again the same several orders of magnitude difference.

Such a high difference in concentrations might be explained by the difference in sampling methods — the density separation or analysis of the volume-reduced samples can be used; for the latter — the mesh size of the net used for sampling in water column is important. Along with the methodology, the site-specific features are obviously important — from recreation/industrial load to the kind of bottom sediments. Thus, the conclusion that bottom sediments have the highest concentrations of microplastics particles looks not yet properly substantiated; however, we will see in the following analysis that there are also certain physical reasons underpinning this distribution.

As it is pointed out on the base of field measurements (see, e.g., (Hidalgo-Ruz et al., 2012) for the review), the observed differences between types and amounts of microplastics in the main marine habitat compartments indicate that import, export, and residence times of microplastics vary depending on their characteristics, mostly size and specific density of the polymers.

### Size classes

Description of physical properties, addressed in this work, requires more strict definitions, at least for size classes. Arthur et al. (2009) gave the definition of microplastics as “fragments and primary-sourced plastics that are smaller than 5 mm”. There, however, is still ongoing debate on the minimum size limits for ‘microplastics’ (Thompson, 2015; Ryan, 2015), because it directly depends on the sampling and processing methods (Hidalgo-Ruz et al., 2012). For example, if sediment samples were sieved, the minimum sizes of collected particles ranged from 0.5 to 2 mm (Costa et al., 2010; Fujieda and Sasaki, 2005), whilst the minimum size of microplastics collected from seawater samples is determined by the mesh size of the net — typically from 53 μm to 3 mm (Thompson et al., 2004; Norén, 2007; Hidalgo-Ruz et al., 2012). Since it is common practice to use the neutron nets with the mesh size 333 μm (0.33 mm) to collect the samples (Arthur et al., 2009), this value can be taken as the lower limit for the size of microplastics particles as well. In (Hidalgo-Ruz et al., 2012) it is proposed to distinguish two main size categories of microplastics: (i) < 500 μm and (ii) 500 μm to 5 mm.

For the evaluations below, we assume the particle size in the range from 0.5 to 5 mm. The lower limit is chosen quite arbitrarily and is based on physical reasoning: we consider properties of particles at the scale much above the molecular one and their motion in transitional flows, i.e., at the Reynolds numbers much above the Stokes case Re ≈ 1.

### Kinds of polymers and their densities

The specific density of plastic particles can vary considerably depending on the type of polymer and the manufacturing process. Density values for plastics range from <0.05 g cm⁻³ for polystyrene foam to 2.1–2.3 g cm⁻³ for polytetrafluoroethylene (Teflon).

Specific densities of some plastic polymers are collected in Table 1 (Supplement Material). The values listed in the second column of the Table 1 are taken from the sources which report investigations in marine environment only; however, depending on the source (shown in the last column of the Table 1), they refer either to the very collected particles or to virgin resins, without taking into account the effect on density of various additives that might be added during product manufacturing. In order to stress on the physical sense of the values, the typical water density in the Baltic Proper (surface/bottom), the dry density of microbial biomass (Bratbak and Dugdale, 1984), and the material density of sand are included in the Table 1, as well as the Baltic amber density, shortly touched in the discussion.

The measured densities (obtained from environmental samples) may also differ from those listed in the Table 1 because of stuck sediment particles or algae, bacterial or microbial overgrowth on particle surfaces and inside their cracks, or because of weighting them during the processing in wet or in dry state (Andrady et al., 1998; EN ISO 4611, 1999; Morét-Ferguson et al., 2010; Hidalgo-Ruz et al., 2012). Plastic density may also change due to residence at sea condition. For example, the specific density of pellets decreased during prolonged exposure to the marine environment, from 0.85 to 0.81 g cm⁻³ for high density polyethylene (HDPE) and from 1.41 to 1.24 g cm⁻³ for polyethylene (PS) (Morét-Ferguson et al., 2010). Thus, it is in fact not surprising that specific densities of many pelagic microplastics do not coincide with those of primary polymers.

The particular distribution of polymer types in marine waters and sediment samples is, obviously, site specific and to a certain extent dependent on the sampling and processing methods used. For example, (Woodall et al., 2014) reported that, in deep-water sediment samples, 56.9% of the total number of synthetic fibres were made of rayon (viscose), a man-made non-plastic polymer (density 1.5–1.52 g cm⁻³), whilst among the plastic fibres polyester was the most prevalent (53.4%; typical polyester density is 1.2–1.5 g cm⁻³), followed by polyamides (1.02–1.05 g cm⁻³) and acetate (34.1%, 1.32 g cm⁻³), and then acrylic (12.4%, 1.14–1.18 g cm⁻³). Typically, at the surface of an open ocean, the buoyant microplastics are most abundant — the high-and low-density polyethylene (0.89–0.97 g cm⁻³) and polypropylene (0.83–0.85 g cm⁻³), however, the particles denser than water are also reported — those from polystyrene (1.04–1.1 g cm⁻³), polyvinyl chloride (1.16–1.58 g cm⁻³) and polyethylene terephthalate (1.29–1.45 g cm⁻³) (Hidalgo-Ruz et al., 2012). An opposite situation — the low-density microplastics in bottom sediments — has not yet been reported, however (van Cauwenbergh et al., 2013) suggested this possibility. At the same time, (Holmström, 1975) reported that plastic sheets from low-density polyethylene were found by Swedish fishermen in great abundance at the bottom of Skagerrak, being encrusted with a calcareous bryozoan and brown algae. The presence of many plastic bags on the bottom of the Gotland deep in the Baltic Sea was confirmed by oceanographers who did trawling at the bottom in order to find the equipment lost at sea (A. Podufalov, V. Paka, personal communication). Thus, fouling of microplastics is highly probable as well, and is considered and discussed below from its physical side.

**Common shapes** of microplastics particles are fibres, pellets and fragments of various geometries, from irregular to spherical ones. At the surface and on the beaches, fragments from plastic products were often numerically dominant, followed by plastic pellets (e.g., Ryan, 1988; Browne et al., 2010; Moore et al., 2001) and styrofoam as the second most abundant material (Yamashita and Tanimura, 2007). Most fragments found in subtidal and estuarine sediments were fibres (Thompson et al., 2004; Browne et al., 2010; Browne et al., 2011). It is suggested (Hidalgo-Ruz et al., 2012) that the shape of plastic fragments depends on the fragmentation process as well as residence time in the environment: sharp edges might indicate either recent introduction into the sea or the recent break-up of larger pieces, whilst smooth edges are often associated with older fragments that have been continuously polished by other particles or sediment (see also Carpenter and Smith, 1972; Doyle et al., 2011). Gillifan et al. (2009) noted that larger particles had more elongate shapes and/or irregular surfaces, whilst progressively smaller particles were consistently more circular (cited after Hidalgo-Ruz et al., 2012). In deep-water bottom sediments, (Woodall et al., 2014) reported that microplastics were all fibrous in shape, commonly 2–3 mm in length and less than 0.1 mm in diameter. Plastic films are reported in abundance on the beaches, at the water and bottom surfaces in their macro-size form: shopping and package bags, or various greenhouse, construction, insolation, package films. Among microplastics, they are almost never reported, most probable reason being they break up mainly into threads and filaments (Fig. 1), and thus are considered as fibres.
The information collected above allows for estimation of some physical and dynamical properties of microplastic particles, as well as of time scales of certain periods of their existence in marine environment. For lighter microplastics (like foamed polystyrene), the windage when floating at the sea surface is most important for their transport; for slightly buoyant particles — the celerity of their fouling up to sinking is crucial; and for the heavy microplastics, the sinking velocity is informative to provide the scale for their travel time within the water body. These features are important, on the one hand, for the general understanding of microplastics behaviour and fate in marine environment, and, on the other hand, they may provide various kinds of possible parameterisations vital for further numerical modelling.

Our results are laid down below in accordance with the following logic.

General motion of a microplastic particle in marine environment is driven by physical forces — the gravity force, the Archimedean buoyancy force, the drag force — which depend on the particle's characteristics, most important ones being size, shape, and density. Microplastics of low density are positively buoyant and thus are likely to spend a long time at the sea surface, where they are transported over long distances and found in remote places, e.g. on sandy beaches, distant from their sources (e.g., Gregory, 1977, 1978, 1983). Exploring this question, we consider first the windage of a floating spherical polystyrene foam particle and evaluate the corresponding speed and time of travel at the scale of the Baltic Sea (Section 2.1).

However, particles with low specific density have also been found in subtidal sediments (Thompson et al., 2004; Browne et al., 2011; Claessens et al., 2011, cited after Hidalgo-Ruz et al., 2012). The CHN elemental analysis revealed relatively high contents of nitrogen (N) on microplastics, which suggested abundant epibiont overgrowth, because N is not a component of synthetic polymers (Morét-Ferguson et al., 2010). Overgrowth by micro- and macro-organisms causes an increase in specific density and thus contributes to a loss in buoyancy and sinking of microplastics (Holmström, 1975; Harrison et al., 2011; Hidalgo-Ruz et al., 2012). This aspect is geometrically considered for particles of different shapes in Section 2.2.

Section 2.3 is devoted to estimations of the sinking velocity of microplastic particles. Two important points require special caution when applying common dependencies to the motion of microplastic particles: (i) due to their small size, corresponding Reynolds numbers indicate the transitional regime of motions, where neither Stokes, nor developed-turbulence relationships are applicable, and (ii) the majority of investigations on suspended matter transport in marine environment deals with sand, clay and other bottom sediments, however, the densities of microplastics are much less, so that the applicability of the developed formulae must be controlled. We offer just the first attempt in handling this complicated problem, based on application of previously published research of other authors.

### 2. Some geometrical considerations of physical and dynamical properties

#### 2.1. Windage of buoyant particles

Microplastic particles of very low density (e.g., foamed polystyrene (<0.05 g cm$^{-3}$) or polyurethane (0.08–0.75 g cm$^{-3}$)) float at the surface and are highly exposed to winds, waves and currents. Drift due to wind forces is commonly referred to as leeway drift, also called the windage (Hackett et al., 2006). The exact solution of the drift problem is very complicated because both external conditions and the drifting body's properties are important. However, some rough estimates for a particular case and typical (but idealised) conditions are possible and practically useful.

Consider a spherical foam particle of a diameter $d$ and density $ho_0$ (e.g., 5 mm and 0.05 g cm$^{-3}$ for further evaluations), floating at the water surface ($\rho_{\text{water}} \approx 1.007$ g cm$^{-3}$ — the Baltic Proper). It is pushed by wind on its upper side, thus moves relative to water - and is subject to the drag force applied to its lower (underwater) part. If water were inviscid, the resulting motion would be rolling over the water surface. Formally (ignoring phenomena introduced by viscous forces), the wind pressure force acting on the upper part of the particle is opposed by the water drag force applied to the lower (underwater) part (see Fig. 2), implying the balance

$$\frac{1}{2} C_1 \cdot S_{\text{above}} \cdot \rho_{\text{air}} \cdot (V_{\text{wind}} - V_{\text{drift}})^2 = \frac{1}{2} C_2 \cdot S_{\text{below}} \cdot \rho_{\text{water}} \cdot (V_{\text{drift}} - u)^2,$$

(1)

typically accomplished on a relatively short timescale (Anderson et al., 1998; Isobe et al., 2011).

Here

$S_{\text{above}}, S_{\text{below}}$ — represent dry and wetted cross-section areas of the particle,

$V_{\text{wind}}, u, V_{\text{drift}}$ — are the wind speed, current speed and the drifting speed of the particle, all relative to inertial frame of reference,

$\rho_{\text{air}}, \rho_{\text{water}}$ — are air and water density,

$C_1, C_2$ — are dimensionless drag coefficients in air and in water dependent on the shape and the flow parameters.

The main challenging question of this classical problem is the definition of the drag coefficients. It is well known that drag coefficients

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**Fig. 1.** Plastic bags typically break up into threads and filaments, which is the most probable reason why they are reported among microplastics not as films but as fibres.

**Fig. 2.** Notations and forces acting on a light sphere rolling over the water surface.
suddenly decrease when Reynolds numbers around flow-past objects exceed their critical values (e.g., $Re \approx 3.38 \times 10^5$ for rigid spheres (Isobe et al., 2011)). Generally, the ratio is set to be unity (e.g., Richardson, 1997; Anderson et al., 1998) assuming that the Reynolds numbers above the sea surface are close to those in seawater. In the considered case and for typical environmental conditions ($T_{w0} \approx 15^\circ$C, wind speed $V_w \approx 10$ m s$^{-1}$, current speed $u \approx 10$ cm s$^{-1}$), the Reynolds numbers $Re = \frac{V}{\nu}$, are about $7 \times 10^3$ (in air) and $10^3$ (in water), indicating both the laminar regime of the flows around the particle and the applicability of the ratio $C_1/C_2 = 1$ (see also Isobe et al., 2011).

Thus, from Eq. (1) we have:

$$\frac{(V_{drift} - u)}{V_w} = \frac{\rho_{air}}{\rho_{water}} \frac{S_{above}}{S_{below}}$$

(2)

The value of $S_{above}/S_{below}$ depends on the particle density. Balancing the gravity force acting on the spherical particle of the density $\rho_0$ and the Archimedean force due to current pressure on the underwater spherical segment of the height $h$ (see Fig. 2), one obtains an equation for the height of the submerged part $h$:

$$\left(\frac{h}{R}\right)^2 \left(3 - \frac{h}{R}\right) = \frac{4}{\rho_0} \frac{S_{segm}}{S_{sect}} \rho_{water}$$

While solving it numerically, the ratio $h/R$ (where $R = D/2$) can be determined (see Fig. 3a) as the first step. Using the formula for the area of a segment

$$S_{segm} = \frac{\pi}{2} R^2 (\alpha - \sin \alpha),$$

we arrive at the equation for $S_{above}/S_{below}$:

$$\frac{S_{above}}{S_{below}} = \frac{S - S_{sect}}{S_{sect}} = \frac{2\pi}{(\alpha - \sin \alpha)} - 1.$$

The dependence of the ratio $S_{above}/S_{below}$ on $\rho_0/\rho_{water}$ is presented in Fig. 3b. The arrows show, for example, the relative densities of foamed polystyrene ($0.05$ g cm$^{-3}$) and polyethylene ($0.95$ g cm$^{-3}$) particles: the first one has underwater height of 0.27 R only and the ratio of dry to wet cross-sectional areas as large as 11.4, and the second one $-1.73$ R and 0.09 R, correspondingly.

The obtained results allow for some quantitative conclusions. Assuming for estimative purposes that the wind blows in the same direction as the current moves and the particle drifts, taking typical conditions and scales of $\rho_{air} = 1.2 \times 10^{-3}$ g cm$^{-3}$, $\rho_{water} = 1.007$ g cm$^{-3}$, $V_w = 10$ m s$^{-1}$, $u = 3\% \ V_w = 0.3$ m s$^{-1}$ (Oceanography Course Team, 1989), obtaining $S_{above}/S_{below} = 11.4$ from Fig. 3a for the foamed polystyrene particle and using the relation (2), we arrive at the drift speed of a scale of $V_{drift} = 1.2$ m s$^{-1}$. This is four times larger than the current speed. For the polyethylene particle ($\rho_0 = 0.95$ g cm$^{-3}$), the drift speed is about 0.4 m s$^{-1}$, or 25% larger than the current speed. The speed does not depend on the particle size ($R$) since $S_{above}/S_{below}$ is the same for any spherical particle of the given density $\rho_0$.

The values are obtained for idealised external conditions and certainly give the maximum estimates, since effects of water viscosity are ignored, which could be quite significant at such a small scale. On the other hand, if the particle is rolling over the surface (which is highly probable in the case of foamed plastics), then the drag force acting on its underwater part is smaller, somehow compensating additional water mass entrained into the rolling motion by the particle’ surface. Influence of small to moderate surface waves (without breaking) cannot cardinally change the rolling motion, since the wave length is much larger than the particle size. Floating particle motion in the field of breaking waves is definitely much more complicated; however, the Stokes wave drift implies that wave crests move faster and water foam from their tops flies ahead of them; this evidence is in full agreement with the faster motion of the floating microplastics. Overall conclusion is that the foamed microplastics particles, under the real open-sea conditions, move obviously faster than the water does. At the scale of the Baltic Sea (for the considered highly idealised conditions), it takes about 2–3 days only for the foamed plastic particle to cover the distance equivalent to the Baltic Proper from one coast to another (ca. 250 km) under quite moderate winds of 10 m s$^{-1}$ of constant direction. By comparison with transport of Lagrangian tracers in the Baltic, the observed mean speed of underwater drifters (12–18 m depth) in the Baltic Proper is only about 3–4 cm/s; they pass about 30 km during 10 days (Kjellsson and Döös, 2012; Soomere et al., 2014). Drift of oil spills over the water surface is typically estimated as the sum of the current speed and 3% of the wind speed (e.g., see Seatrack Web model at https://stw-helcom.smhi.se/). This way, high-floating and especially rolling light microplastic particles might be the fastest in their spreading among all the marine pollutants.

2.2. Surface area and its link to the fouling of particles of different shapes

The surface area of a microplastic particle and its texture are practically important parameters, since they may affect the concentrations of sorbed chemicals. It is shown (e.g., Mato et al., 2001) that the pollutant adsorption on the plastic pellets increases with the surface area and as a
result of weathering. Let us consider the dependence of the surface area on the particle size and shape, applying simple geometrical rules to the particles of different sizes, shapes and qualities of the surface.

Consider a sphere of radius \( R_0 \) and density \( \rho_0 \); its mass is \( m_0 = \rho_0 \cdot \frac{4}{3} \pi R_0^3 \) and the surface area is \( S_0 = 4\pi R_0^2 \). If this initial mass \( m_0 \) is divided into smaller spherical pieces of radii, say, \( R_0/2 \) and \( R_0/3 \), there will be 8 and 27 smaller spheres, respectively, and their total surface area will be \( 2S_0 \) and \( 3S_0 \), correspondingly.

Let us consider now the particle of radius \( R_0 \) which is fouling with a surface film from biological or mineral matter. If the density of the particle is smaller than the water density, \( \rho_0 < \rho_{\text{water}} \), it will float at the surface and undergo biofouling, which physically means that the surface becomes covered by a thin film of growing thickness, \( d \) (\( d \ll R_0 \)), that has a larger density, \( \rho_f \) (by definition, \( \rho_f > \rho_{\text{water}} \)). See Table 2, first line.

With time, the film thickness increases, causing an increase in the particle size, \( R = R_0 + d \), as well as in the mean particle density, \( \bar{\rho} \):

\[
\bar{\rho} = \frac{m_0 + m_f}{V_{R,d}} = \frac{\rho_0 \cdot \frac{4}{3} \pi R_0^3 + \rho_f \cdot 4\pi (R_0 + d)^3 - R_0^3)}{4\pi (R_0 + d)^3} \approx \rho_0 + \rho_f \frac{3d}{R_0} \tag{3}
\]

(in the last step it is assumed that \( d \ll R_0 \)). This expression shows explicitly that, in the beginning (\( d = 0 \)), the particle had a (mean) density \( \rho_0 \), which increased with time (i.e., with the thickness of biofilm). When (in time interval \( \tau_{\text{sink}} \)) the mean density of the particle becomes equal to the water density, the particle begins to sink.

Fig. 4 shows principal behaviour of the function (3) for the particles of different radii \( R_1 \) and \( R_2 \) (\( R_1 < R_2 \)): the larger the initial radius is, the thicker film \( d_{\text{fou}} \) is required in order to increase the mean particle density up to the water density, \( \bar{\rho} = \rho_{\text{water}} \). From Eq. (3) we yield \( d_{\text{fou}} = \frac{\Delta R}{3} \frac{(\rho_{\text{water}} - \rho_0)}{\rho_f} \). Assuming that the rate of fouling is constant in time, the value of \( d \) can be directly treated as time, bringing an important conclusion: time of fouling up to the water density is directly proportional to the radius (diameter) of a sphere; i.e., the smaller the particle is, the faster it begins to biofoul and begins to sink. The dependence of \( \tau_{\text{sink}} \) on radius is quite strong:

\[
\tau_{\text{sink}} \sim \frac{R_0}{3n}, \text{ where } n = R_0/R. \tag{4}
\]

If \( \tau_0 \) is the time of fouling up to the mean density \( \bar{\rho} = \rho_{\text{water}} \) of a sphere of radius \( R_0 \), then for spheres of radii \( R_0/2 \) and \( R_0/3 \) the fouling time is \( \tau_0/6 \) and \( \tau_0/9 \), correspondingly.

Probably, this dependency may shed some light onto the question of why smaller fractions are reported more often in bottom sediments than in water column and at the surface.

Spherical shape has (for the given mass \( m_0 \)) the minimum surface area among all other possible shapes in 3-d space. For plastic pieces and microplastic particles, most common alternative shapes are films and fibres. Taking a low-density polyethylene pellet (density 0.92 g cm\(^{-3}\)) as an example, we obtain its volume \( V_0 = 0.065 \text{ cm}^3 \), mass \( m_0 = 0.065 \text{ g} \) and surface area \( S_0 = 0.8 \text{ cm}^2 \). A T-shirt bag from the same material typically has a thickness of 15–30 \( \mu \text{m} \), whereas the surface area of the two sides of the film of the same volume/mass is about 80–40 \text{ cm}^2 \), or 100–50 \( S_0 \) (see Table 2). For a fibre in deep-water sediments, 100 \( \mu \text{m} \) is reported as a maximum diameter value (Woodall et al., 2014). Taking its shape as a cylinder of a diameter of 30–100 \( \mu \text{m} \) (Claessens et al., 2011) with a smooth surface,

### Table 2

<table>
<thead>
<tr>
<th>Shape</th>
<th>Surface area (for a smooth surface) and time of fouling up to the mean density ( \rho_{\text{water}} )</th>
<th>Mean density ( \bar{\rho} ) of the fouled particle</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_0 )</td>
<td>64 ( \tau_{\text{sink}} )</td>
<td>( \bar{\rho}_{\text{sphere}} = \rho_0 \left( \frac{R_0}{(R_0 + d)^3} + \rho_f \right) \left( 1 - \frac{R_0}{(R_0 + d)^3} \right) )</td>
</tr>
<tr>
<td></td>
<td>50–100 ( S_0 ) ( \tau_{\text{sink}} )</td>
<td>( \bar{\rho}_{\text{film}} = \rho_0 \left( \frac{R_0}{(R_0 + d)^3} + \rho_f \right) \left( 1 - \frac{R_0}{(R_0 + d)^3} \right) )</td>
</tr>
<tr>
<td>30–110 ( S_0 )</td>
<td>2 ( \tau_{\text{sink}} )</td>
<td>( \bar{\rho}_{\text{film}} = \rho_0 \left( \frac{R_0}{(R_0 + d)^3} + \rho_f \right) \left( 1 - \frac{R_0}{(R_0 + d)^3} \right) )</td>
</tr>
</tbody>
</table>
we obtain (for the same volume/mass) its length of about 93–8.3 m and the minimum surface area of about 110–26 m². The surface of fibres from sediment and marine environment is not perfectly smooth, thus this estimate gives a minimum value, and fibres appear to have the largest surface area for the given mass.

These simple geometrical considerations make it possible to analyse the mean density of the fouled particles of the listed shapes and to evaluate which one of them will reach water density \( \rho_{\text{water}} \) faster with growing \( d \), see Table 2. In order to find out which one of these particles grows faster at small \( d \), one should analyse their derivatives with respect to \( d \):

\[
\begin{align*}
\left( \bar{\rho}_{\text{sphere}} \right)_{d} &= \left( \rho_{f} - \rho_{0} \right) \left( \frac{3R_{0}}{(R_{0} + d)} \right)^{2} \frac{3}{R_{0}} \text{ as } d \to 0, \\
\left( \bar{\rho}_{\text{film}} \right)_{d} &= \left( \rho_{f} - \rho_{0} \right) \left( \frac{2h}{(h + 2d)} \right)^{2} \frac{2}{h} \text{ as } d \to 0, \\
\left( \bar{\rho}_{\text{fibre}} \right)_{d} &= \left( \rho_{f} - \rho_{0} \right) \left( \frac{2r}{(r + d)^{3}} \right)^{2} \frac{2}{r} \text{ as } d \to 0.
\end{align*}
\]

The formulae indicate that the smaller the characteristic scale (the radius of a sphere and a fibre, or the thickness of a film) of a particle is, the faster its mean density increases with progressive fouling. Since for microplastics particles \( R_{0} > h - r \), the time rate of change of fibres’ and films’ mean density is the largest, whilst that of spheres — the smallest. Among different spheres, again, the largest particles have the smallest time rate of change of their mean density.

As before, the thickness of fouling can be considered as a characteristic of time of the bio-fouling process. Then, the formulae from the third column of Table 2 can be used for comparative analysis: which one of the growing mean densities \( \bar{\rho}_{\text{sphere}}, \bar{\rho}_{\text{film}}, \) or \( \bar{\rho}_{\text{fibre}} \) will be the first to reach the water density, \( \rho_{\text{water}} \). In other words, for the same material \( \rho_{0} \), a particle of which shape is first to begin sinking?

From the equality \( \bar{\rho}_{f} = \bar{\rho}_{\text{water}} \), one obtains the following parameterized “times until sinking”, \( t_{\text{sink}} \), i.e., the thicknesses of the fouling film which are exactly enough to make the mean particle density equal to that of surrounding water:

\[
\begin{align*}
\text{for the sphere} : d_{\text{sphere}} &= R_{0} \left[ \left( \frac{\rho_{f} - \rho_{0}}{\rho_{f} - \rho_{w}} \right)^{1/3} - 1 \right], \\
\text{for the film} : d_{\text{film}} &= \frac{h}{2} \frac{\rho_{w} - \rho_{0}}{\rho_{f} - \rho_{w}}, \\
\text{for the fibre} : d_{\text{fibre}} &= r \left[ \left( \frac{\rho_{f} - \rho_{0}}{\rho_{f} - \rho_{w}} \right)^{1/2} - 1 \right].
\end{align*}
\]

Straightforward formal conclusion is: time of fouling is linearly dependent on the characteristic length scale of a particle (radius of sphere, thickness of the film, or radius of a fibre), i.e., the smaller the scale of the particle is, the faster it is fouled up to the water density. This is in full agreement with the conclusion of the previous paragraph and Fig. 4, as well as with field experience showing that microplastics size in open-sea sediments is smaller than that in water column and at the water surface (Hidalgo-Ruz et al., 2012).

As for the comparison of the time of bio-fouling until sinking for particles of different shapes, the conclusion is dependent on numerical values. For more or less realistic spatial scales of \( R_{0} = 2.5 \times 10^{-3} \text{ m}, h = 25 \times 10^{-6} \text{ m}, r = 50 \times 10^{-6} \text{ m} \) (i.e., \( \rho_{f}/h r = 100/1/2 \)) and densities of the microbial biomass \( \rho_{f} = 1.5 \text{ g cm}^{-3} \) (Brattbakk and Dudas, 1984) and of the low-density polyethylene \( \rho_{0} = 0.9 \text{ g cm}^{-3} \) (see Table 1), the ratio of “times until sinking” in fresh water is about

\[d_{\text{sphere}}/d_{\text{film}}/d_{\text{fibre}} \sim 63/1/2.\]

In the open sea, the formulae (6)–(7) do not contain the film area or the length of the fibre. This makes it possible to use these relationships for the following estimates of the residence time of a particle at the water surface. As it was shown in (Holmström, 1975), plastic bags found on the bottom of the Kattegat area should have spent about 3–4 months in eutrophic zone before the biofouling thickness became large enough to force them to sink. Hence, the polyethylene fibres of the same density should spend 6–8 months within the upper layers, and spherical particles and plastic pieces — up to 10–15 years. At the same time, order-of-magnitude estimates for idealised conditions (Section 2.1) indicate that only one week may be required for the polyethylene particle floating at the surface to cross the entire Baltic Sea. Thus, mechanical destruction of macroplastics and large particles to smaller pieces at the sea shores is of utmost importance for the fate of microplastics. Even though these estimates are very approximate (and consider the only mechanism of the mean density increase), they may shed some light onto the question why pellets and pieces are persistently abundant at the sea surface and on the beaches, whilst tiny fibres and plastic bags are reported on the bottom and in bottom sediments. The fact that plastic pellets have also been found on urban beaches distant from potential sources, implying long-distance marine transport (Costa et al., 2010, Gregory, 1977, 1978, 1983), also supports the obtained conclusions.

The performed calculations are based on the assumption that the particle surfaces are smooth. Field evidence, however, proves that microplastic particles found in marine environment have quite rough, mechanically damaged, cracked surfaces (Shaw and Day, 1994; Corcoran et al., 2009). Films are shown to have fractal ends after mechanical ruptures (Sharon et al., 2002); plastic fibres, however, are reported to be smooth (Norén, 2007). This suggests that in some cases for estimations of the particle surface areas the fractal description might be more suitable. An increase in the surface area due to its fractal structure seems to have limited influence on the particle bio-fouling rate: on the one hand, the corrupted surface begins fouling easier, but, on the other hand, too small fractures will soon be covered by relatively large algae/bacteria cells.

### 2.3. Settling velocity of negatively buoyant microplastic particles

Transport and fate of negatively buoyant microplastics particles in the sea crucially depend on their settling velocity: in the case when the velocity is large, a particle settles in the close vicinity of its release point (most probably — in subtidal zone); if it is small — a particle travels with currents as long as the settling lasts. The Reynolds numbers \( Re = \frac{\nu}{v_{l}} \) for settling microplastics particles (maximum size 5 mm) can be up to \( 10^{-2} \times 5 \times 10^{-3} \times 10^{-5} \), which indicates laminar regime (conventionally, \( Re < 200 \)), but the Stokes formula (applicable in the regime with \( Re \ll 1 \)) is definitely not the best choice even for estimative purposes. At the same time, the settling velocity is one of the key variables in investigation of suspended matter and sediment transport, deposition, exchange processes. As a consequence, quite a large number of quasi-theoretical or semi-empirical approaches offered a set of formulae applicable to a wide range of Reynolds numbers — from Stokes flow to turbulent regime (see, e.g., (Zhiyao et al., 2008) for the review and discussion).

The key question in such problems is proper definition of the drag coefficient \( C_{d} \) of a particle. In turbulent regime with \( Re > 10^{3} \), this coefficient is shown to approach a constant (Dallavalle, 1948; Schlichting, 1979), but again this is not the case with microplastics. Zhiyao et al. (2008) suggested an expression for the drag coefficient for the flow in-between these poles — the Stokes and the turbulent flows — with the \( Re \) numbers less than 2 \( \times 10^{3} \). Via comparison with laboratory measurements they demonstrated its higher prediction accuracy than other
published formulae. The proposed in (Zhiyao et al., 2008) formula for the drag coefficient is

$$C_d = \left[ \frac{3A}{2d^2} \right]^{1/3} + B^{1/n},$$  \hspace{1cm} (9)

where $A = 32.2$, $B = 1.17$ and $n = 1.75$ are constants, obtained from comparison with laboratory measurement data, and $d$ is the dimensionless particle diameter

$$d = \left( \frac{\rho_w - \rho_v}{\rho_v} \right)^{1/3} \cdot D.$$

The settling velocity, $W_s$, is then expressed as (Zhiyao et al., 2008)

$$W_s = \frac{V}{d} \left[ \frac{3A}{4} + \left( \frac{2B}{4} d^2 \right)^{1/3} \right]^{-n/2} \cdot \left( 38.1 + 0.93 d^{3/7} \right)^{-3/7}. \hspace{1cm} (10)$$

The behaviour of the functions $W_s(d)$ for different density excess (in the range characteristic to that of plastics) are shown in Fig. 5. Taking the polystyrene particle (1.05 g cm$^{-3}$, the relative density excess in fresh water $\Delta \rho/\rho_v = 0.05$, the diameter $D = 0.5$ mm) and the polyoximethylene particle (1.6 g cm$^{-3}$, $\Delta \rho/\rho_v = 0.6$, $D = 5$ mm, see Table 1) as contrasting numerical examples, we obtain the settling velocities $4$ mm s$^{-1}$, and $18$ cm s$^{-1}$, correspondingly. Thus, assuming that the idealised laboratory conditions can be applied in the turbulent sea environment as well, the time of travel of the example 5-mm-polyoximethylene particle from the surface to the bottom of, say, the Gotland deep of the Baltic Sea (~250 m) will take less than half an hour, whilst the 0.5-mm-polystyrene particle will need about 18 h to make the same way down.

It is important to have in mind that the laboratory experiments of many authors, used by (Zhiyao et al., 2008) to deduce their formulae, were mainly carried out with natural sediments (natural and crushed sand, gravel, smooth cobbles, silt particles, including cohesive sediment aggregates), but they also included “spherical particles”, “long cylinders”, “organic and inorganic flocks”, “artificial particles”. Thus, the authors conclude that their formula (10) takes into account “various sizes, shapes, roundnesses, and densities” and “may be used for all kind of material of any shape”. However, the very densities are not reported, and the applicability of formula (10) to plastic particles still requires verification by both laboratory experiments and field observations. Our own laboratory tests with microplastic particles (Isachenko et al., 2016) have demonstrated that dependence (10) works well for spherical particles and more or less round plastic pieces, however, for fibres and flakes it fails. This implies that, whilst the density range, characteristic of plastics, is described well by classical relationships, it is the particular shape of a microplastic particle that is of primary importance for its settling velocity.

3. Discussion and conclusions

Physical properties of marine microplastics particles – their density, size and shape – define their behaviour and fate in the sea, i.e., their motion in stratified and turbulent marine environment, the residence time in different marine habitats, and bio-fouling celerity. We have made an attempt, for the first time in microparticles publications, to quantify – on the base of just geometrical considerations – some properties of particles of different shapes, to compare their fouling rates, sinking velocities, and finally provide some rough estimates for the main spatial and temporal scales, describing the behaviour of the particles of different densities and shapes in the Baltic Sea.

For extremely light microplastics floating at the surface (e.g., foamed polystyrene particles, 0.05 g cm$^{-3}$), the key factor is their windage. Analysis of forces indicates that light spherical particles should roll over the water surface, and their drift speed may be up to four times larger than the current speed. The obtained drift velocities are the maximum estimates, since effects of water viscosity, influence of surface waves and other factors are ignored. Anyhow, a very light floating and rolling microplastics particles should move obviously faster than the water does, and it might take only about 2–3 days for the foamed plastic particle to cross the Baltic Proper from one coast to another (ca. 250 km) under quite moderate winds of 10 m s$^{-1}$. These results correspond very well to the observed facts that positively buoyant microplastics are widely dispersed across the world’s oceans (Hidalgo-Ruz et al., 2012), easily transported over unbelievably large distances (Gregory, 1977, 1978), washed ashore (Thompson et al., 2009; Andrady, 2011; Engler, 2012), and accumulated on shorelines (Ryan et al., 2009) even on most distant beaches.

For slightly buoyant (e.g., polyethylene, polypropylene) particles, the bio-fouling was considered, which leads to an increase of the mean particle density and its sinking. Assuming that the rate of increase in the total mass is directly proportional to the particle’s surface area, it is demonstrated that, for the same mass of plastic material, many small particles have larger surface area than one single large particle, and — macroplastics stay at the water surface longer than microplastics. For spherical particles and constant fouling rate, proportional to the surface area, the time of fouling up to the water density is directly proportional to the radius of a sphere. Spherical shape has (for the given mass $m_0$) the minimum surface area among all other possible shapes in 3-d space; the fibres appear to have the largest surface area for the given mass, immediately followed by films. Correspondingly, time of fouling up to the water density is shown to be of the same order of magnitude for films and fibres, and almost two orders of magnitude higher for spherical particles (of the same mass $m_0$). More generally speaking, time of fouling is linearly dependent on the characteristic length scale of a particle (radius of sphere, thickness of the film, or radius of a fibre): the smaller the scale of the particle is — the faster it is fouled up to the water density.

Using information reported in (Holmström, 1975) concerning the residence time of polyethylene films in the euphotic zone of the Baltic Sea (3–4 months), we estimate the euphotic-zone residence time for polyethylene fibres as 6–8 months, and that for a spherical particles and plastic pieces (if they are not destroyed to smaller fractions) — up
to 10−15 years. This is consistent with the results of (Brandon and Goldstein, 2015), who used plastic's chemical structure changes due to weathering to estimate the age of oceanic particles collected at the surface: the polyethylene particles showed the age >9 months, with some particles of age >30 months, and the polypropylene samples showed the ages >18 months.

For the microplastics particles of rounded shapes with the density (1.05 + 1.6)·ρwater, the settling velocity is estimated to be 0.4–18 cm s−1, so settling through the water column of the scale of the depth of the central Gotland basin (ca. 250 m) should last from about half an hour to 18 h. This is the shortest time scale among all the cases estimated above.

The presented considerations rely on simple geometric calculations and very simplified physical models. They are, nonetheless, quite important as the first steps on the way towards physical understanding and numerical modelling of microplastics particles transport in marine environment, since they provide temporal and spatial scales of the problem and assist in developing of a certain “physical feeling” of it. All the complexity of the microplastics particles transport under real problem and assist in developing of a certain and numerical modelling of microplastics particles transport in marine environment: critical review. Environ. Sci. Technol. 46 (22), 12302–12315. http://dx.doi.org/10.1021/acs.est.2016027105.


