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Influence of microplastic decomposition conditions on the emission of substances harmful to the environment

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ABSTRACT

The work described the research on the possibility of the emission of plastic components under various environmental conditions. The research carried out aimed to estimate the amount of plasticizer emission from microplastics in the example of a used tire during its decomposition in an aqueous medium. The tests conducted confirmed that, depending on environmental conditions, tire particles are washed out, among others, of phthalic acid esters, benzenediamine, phenol, benzothiazole, and benzene. The analyzes conducted show that the pH value, temperature of the reaction medium, and incubation time have a significant influence on the elution mechanisms of the plasticizers from the polymer matrix. Sufficiently high temperatures can be a factor that causes partial decomposition of plasticizers. However, under natural conditions, the temperature in the aquatic ecosystem is too low to initiate the degradation process and, at the same time, sufficient to release the auxiliary components contained in the tires. An additional negative aspect of the distribution of tire particles in the aquatic environment is the emission of carbon dioxide and methane, which are greenhouse gases. There was also a significant increase in total organic carbon and fluctuations in pH values. The study also estimated the ecotoxicological risk of the plasticizers analyzed.

Keywords: Microplastics; Plasticizers; Phthalates; Decomposition; Greenhouse gases

1. Introduction

The exploitation of water resources and the neglect of issues related to their protection contributed to the progressive degradation of the environment [1,2]. In recent years, microplastics contamination has been a significant new environmental threat. When plastics enter the environment, they can be transported with wind and water flow. Precipitation, surface runoff and river transport can be the main routes for transporting plastics from land to water, or they can also be transported from water to land [3]. Its presence has been identified in all elements of the environment and the highest amount in the aquatic ecosystem. The elements of polymer materials present in natural water reservoirs decompose into smaller and smaller fragments, microplastics, under the influence of various conditions in the natural environment. Each plastic is a complex chemical structure made of atoms, the configuration of which determines the individual properties of a given material. The durability of plastics and their ability to degrade in the aquatic environment depend on them. The decomposition of microplastics in water reservoirs results in the release of toxic chemicals that are components of plastics, such as plasticizers, stabilizers, pigments, and flame retardants, into water. Most of these substances have a detrimental effect on the endocrine system and increase the risk of health disorders [4,5]. In the

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case of physical (external) plasticization, unfortunately, the polymer-plasticizer system is unstable over a longer period and plasticizer migration occurs because the plasticizer molecules are not chemically bound to the macromolecule chains of the polymeric material. Paluselli et al. [6], in their research, examined the migration of phthalates from the insulating layer of electric cables (polyvinyl chloride, PVC cables) and from plastic garbage bags (polyethylene, PE bags). For this purpose, the plastic was incubated in natural seawater under laboratory conditions. During the first month of incubation, both plastics significantly leached PAE into the aqueous solution. However, after three months of testing, more than 90% of the PAEs in the plastic still remain and eventually leach out over an extended period of time. Di-isobutyl phthalate (DiBP) and di-n-butyl phthalate (DBP) were the main PAEs released from PE bags, with the highest values of 83.4 ± 12.5 and 120.1 ± 18.0 ng/g, respectively. In addition, dimethyl phthalate (DMP) and diethyl phthalate (DEP) were the major PAEs released from PVC cables reaching 9.5 ± 1.4 and 68.9 ± 10.3 ng/g, respectively.

In addition to the migration of phthalates, previous leachability studies have also shown the release of additives such as brominated flame retardants (BFR) from plastics [7–10], bisphenol A (BPA) [11], additives fluorescent [12] and other organic pollutants [13]. However, the results of migration studies usually relate to seawater and food packaging. However, to the authors' knowledge, no studies have conducted comprehensive studies on this topic in surface water.

The microplastic particles contained in the aquatic environment are also harmful because they interfere with the ability of aquatic ecosystems to act as a natural carbon sink. It should be expected that during the decomposition of plastics, which are synthesized from natural gases, the emission of the same or other gases (mainly hydrocarbons), such as greenhouse gases (methane, carbon dioxide) and their precursors (e.g., ethylene), will be accompanied [2,4,5,14–16]. Research on greenhouse gas emissions from the decomposition of microplastics was conducted only by Royer et al. [17]. They have demonstrated that the production of trace gases from virgin low-density polyethylene increase with time, with rates at the end of a 212-day incubation of 5.8 nmol/(g·d) of methane, 14.5 nmol/(g·d) of ethylene, 3.9 nmol/(g·d) of ethane and 9.7 nmol/(g·d) of propylene.

The aim of this article was to check the impact of various environmental factors on the degradation of microplastics from car tires. As a result of the friction caused by the moving tires of the car, mechanical degradation occurs. Tire, road and brake wear occurs due to the mechanical forces exerted on the brake pads, tire threads and road surface, resulting in stress and fatigue. This paper aims to provide knowledge for the development of microplastic risk management strategies as well as to provide a deeper insight into the factors responsible for the degradation of microplastics once they enter the aquatic environment. The paper focuses on the following main elements: (a) factors affecting the degradation of microplastics when in contact with an aqueous solution; (b) an analysis of the possibility of plastic additives migrating into water; (c) ecotoxicological impact on aquatic fauna. The uniqueness of the research consisted in checking the emission of greenhouse gases during the decomposition of a used car tire.

2. Materials and methods

2.1. Reagents and materials

A mixture of 11 phthalic acid esters (EPA 8270) was purchased at a concentration of 2,000 µg/mL from Sigma-Aldrich (Darmstadt, Germany). Benzyl benzoate (1 g/mL) – internal standard was purchased from Sigma-Aldrich. The research material was a used car tire intended for disposal (styrene-butadiene rubber). Microplastics with a fraction of 1,000 to 4,000 µm were purchased from Orzeł S.A. (Poniatowa, Poland). Solvents for chromatographic analysis and other reagents were purchased from POCH (Gliwice, Poland).

2.2. Experimental procedure

Microplastics in the amount of 2 g were placed in 40 mL bottles, then 20 mL of distilled water were added and tightly closed with Teflon caps. Blank samples were also prepared without the addition of the analyzed microplastics. The prepared samples were incubated in the dark at various temperatures (20°C, 60°C, 90°C) and analyzed after 1, 3, 5, 7 and 14 d. The aim of the investigation was also to check the influence of the pH of the aquatic environment on the amount of emission of plastic components. For this purpose, appropriate amounts of HCl or NaOH were introduced into the samples. In turn, the flowing conditions reflecting the movement of water were achieved by placing the samples on a shaker at a speed of 100 rpm.

For the analysis of methane and carbon dioxide emissions, microplastics samples in the amount of 2 g were placed in glass bottles with a capacity of 100 mL, then 14 mL of degassed distilled water was added. The bottles were tightly closed with a cap. The samples were prepared in a helium atmosphere using a Glove Box from Plas Labs, INC. (Michigan, USA). The samples were then incubated at 20°C in the dark and in sunlight. Three independent repetitions were performed for each parameter.

2.3. Analytical methods

Analysis of the eluted substances from microplastics was performed using a gas chromatography coupled with a mass spectrometry (GC-MS) (Thermo Scientific, Waltham, USA). The operating parameters of the GC-MS are presented in Table 1.

Methane and dioxide analysis was performed using a gas chromatograph GC 2010 Plus (Shimadzu, Maryland, USA) equipped with a Barrier Discharge Ionization Detector (BID). The GC operating parameters are shown in Table 2.

In order to, determine the basic parameters of the analyzed microplastic particles, an automated direct infrared laser – LDIR (with a quantum cascade laser) Imaging (8700 LDIR, Agilent Technologies) was used. The parameters of the exemplary particles analyzed are presented in Table 3. Circularity is defined as the distance within which a given particle shape is within a perfect circle. Solidity is the ratio of the actual surface area of the object to the surface area of the thread stretched around the particle.

The dissolved organic carbon was also analyzed in the extracts obtained using a total organic carbon (TOC) analyzer (Shimadzu, TOC-VCPN, Maryland, USA). pH values and electrical conductivity (EC) were also checked using a portable single-channel HACH HQ30d multichannel meter (Loveland, USA).

2.4. Ecotoxicological risk assessment

The evaluation of environmental risk was evaluated using the risk ratio (RQ), which was estimated based on the guidance provided by EMA (2005) for the three trophic levels of the aquatic ecosystem. For this purpose, the following formula was used [18]:

$$RQ = \frac{MEC_{max}}{PNEC_{acute}} \tag{1}$$

The risk quotient values were estimated using the ratio between the highest MEC – measured environmental concentration and the $PNEC_{acute}$ – predicted no-effect concentration of acute toxicity. The $PNEC_{acute}$ value was obtained using the formula [18]:

$$PNEC_{acute} = \frac{EC_{50} or LD_{50}}{1000} \tag{2}$$

The necessary values for the calculation of this parameter are presented in Table 4. The denominator value (1,000) is an arbitrary safety factor in line with the recommendations of the European Parliament and the Council (2000) [19].

The obtained risk ratio values were taken to signify three risk levels [21]:

- low/negligible risk ($0.01 < RQ < 0.1$),
- medium risk ($0.1 \le RQ < 1$),
- high risk ($RQ \ge 1$).

2.5. Statistical analysis

The MS Excel 2013 and Statistica 13 programs were used for the statistical analysis of the results obtained. Non-parametric statistical analyzes were used due to unequal variances and sample size. The homogeneity of the variance was checked using the Levene and Brown-Forsythe tests. Calculations were carried out to determine the value of the probability level (*p*). The criterion of significant differences was used at $\alpha \le 0.05$. For multiple and pairwise comparisons of these data, non-parametric Kruskal–Wallis ANOVA was used. The Kruskal–Wallis test was used to compare the differences between the concentrations of substances.

3. Results and discussion

3.1. Influence of temperature and time

The migration potential of additives in the three-dimensional porous structure of the polymer depends on

Table 1
Operating parameters of the gas chromatography coupled with a mass spectrometry

Parameters	
Type of column	DB-5MS coated with 5% phenyl-95% dimethylpolysiloxane (film thickness 0.25 mm)
Sample volume	1 μL
Injector temperature	300°C
Carrier gas	Helium
Carrier gas flow rate	1.0 mL/min
Temperature program	40°C hold for 1 min, 9°C/min to 300°C hold for 5 min

Table 2
Operating parameters of the gas chromatography

Parameters	
Type of column	Shin Carbon ST column (2 m, 1.00 mm ID)
Injector temperature	150°C
Detector temperature	100°C
Column temperature	60°C
Carrier gas	Helium
Carrier gas flow rate	50.0 mL/min

Table 4
EC50/LD50 (mg/L) of analyzed substances [16,18,20]

Analyte	First trophic level plants	Second trophic level invertebrates	Third trophic level vertebrates
DEHP	0.003	0.003	0.16
DBP	0.003	1.05	0.35
DOP	n.d.	0.00067	n.d.
DEP	21.0	86.0	12.0
DMP	24.6	33.0	29.0

Table 3
Parameters of exemplary analyzed particles

Width (μm)	Height (μm)	Diameter (μm)	Aspect ratio	Area (μm^2)	Perimeter (μm)	Eccentricity	Circularity	Solidity
1,336	2,359	1,568.9	0.57	1,933,188	8,473	0.86	0.34	0.84
1,334	1,192	1,202.0	1.12	1,134,738	5,119	0.68	0.54	0.92
2,285	2,605	2,753.0	0.88	5,952,425	9,780	0.60	0.78	1
1,174	1,364	1,253.0	0.86	1,233,138	5,054	0.59	0.61	0.92
1,613	2,284	1,792.8	0.71	2,524,338	8,408	0.70	0.45	0.91

several parameters. Substances of lower molecular weight, such as esters of phthalic acid (300–600 g/mol) pass more easily through the polymer having a larger pore size. The influence of temperature and time on the emission of plasticizers from microplastics is presented in Figs. 1–3. The leaching of 5 phthalic acid esters from the analyzed tire was observed. These substances act as plasticizers in plastics. At a temperature of 20°C, the leaching of four plasticizers such as DEHP (bis(2-ethylhexyl) phthalate), DBP (di-*n*-butyl phthalate), DOP (di-*n*-octyl phthalate), DMP (dimethyl phthalate) was observed (Fig. 1a and b). Differences in the elution of phthalic acid esters were observed. The DBP concentration was highest after 3 d, while DEHP, DOP, and DMP after 5 d. The amount of migration increases rapidly at the outset, before tending to a limit value known as the migration maximum (E_m). The time required to achieve E_m depends on the nature of the system, the thickness of the plastic and the diffusion coefficient. In general, work on the migration of solvent additives shows that amounts are directly proportional to $t_{1/2}$ [22]. Li and Tang [23] studied the effect of time on leaching of DBP from polyethylene (PE), poly(vinyl chloride) (PVC) and poly(ethylene terephthalate) (PET) in pseudo-marine water. The concentrations of DBP leached from PE, PVC and PET from $t = 4$ to 16 d were in the ranges of 0.558–0.711 mg/L, 0.518–0.760 mg/L and 0.540–0.791 mg/L, respectively.

Dissolved organic carbon (DOC) and EC values increased with time, which was confirmed by the elution of components from the polymer matrix (Fig. 1c). The eluted components caused a change in the pH value of the water. The initial pH value at $t = 0$ was 7.05. After 1 d of incubation, this value increased to pH = 7.27. In the following days, the pH value decreased to the value of 6.56 for $t = 5$ d. On the other hand, after 7 and 14 d, higher values of 6.88 and 7.62 were observed, respectively.

The temperature increase from 20°C to 60°C resulted in a higher degree of DBP and DMP emission and a lower degree of DEHP and DOP emission (Fig. 2a and b). Bis(2-ethylhexyl) phthalate and di-*n*-octyl phthalate were likely to be degraded or adsorbed. A statistically significant difference was found in the content of substances that migrate from microplastics over time. The following values were obtained for DBP ($p < \alpha$, $p = 0.0090$), DEHP ($p < \alpha$, $p = 0.0119$), DOP ($p < \alpha$, $p = 0.0091$). The DOC value increased more than five times at each analyzed time compared to incubation at 20°C. In turn, the obtained EC values confirm the elution of inorganic components from the polymer matrix to a greater extent (Fig. 2c). Keresztes et al. [24] reported a more pronounced leaching of phthalates, including DBP and DEHP, from PET bottles into mineral water at a storage temperature of 60°C compared to 22°C after 44 d.

Research on plasticizers emission at 90°C showed significantly higher concentrations of phthalates analyzed on the first and third day of the decomposition process compared to the temperature of 20°C and 60°C. In the following analyzed incubation times, comparable values of phthalates were observed up to T = 20°C were observed. This phenomenon may indicate a faster decomposition of these substances at higher temperatures. There were statistically significant differences in tire component emission over

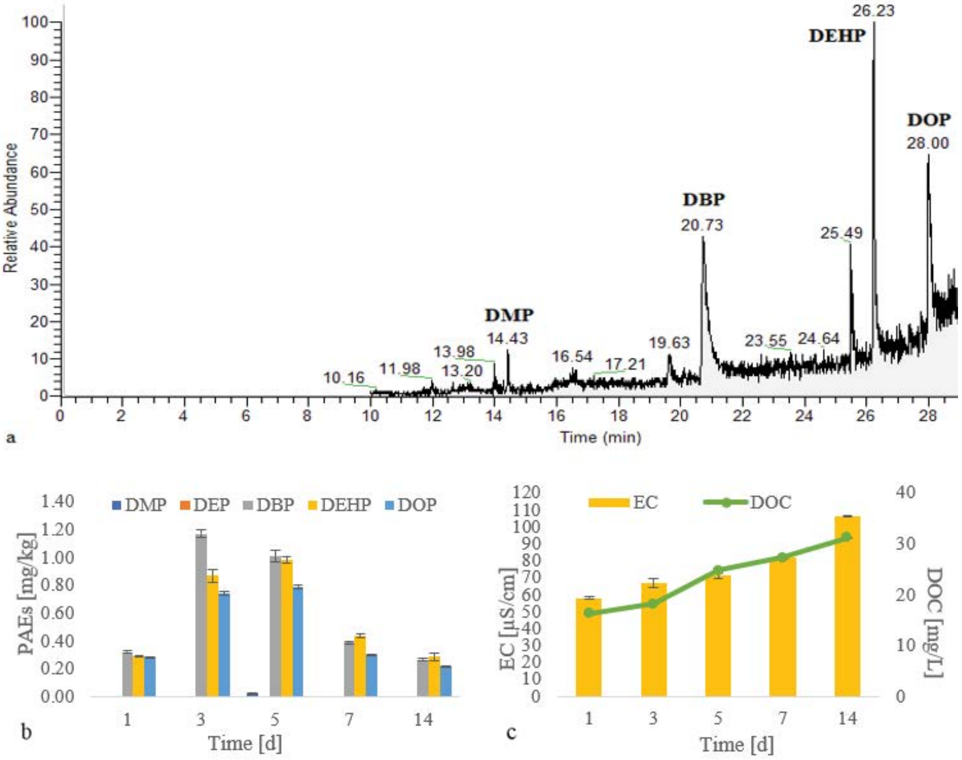

Fig. 1. Effect of the temperature of 20°C on the amount and type of substances leached of microplastics (a) chromatogram (t = 5 d, m/z = 149), (b) plasticizers, (c) electrical conductivity and dissolved organic carbon.

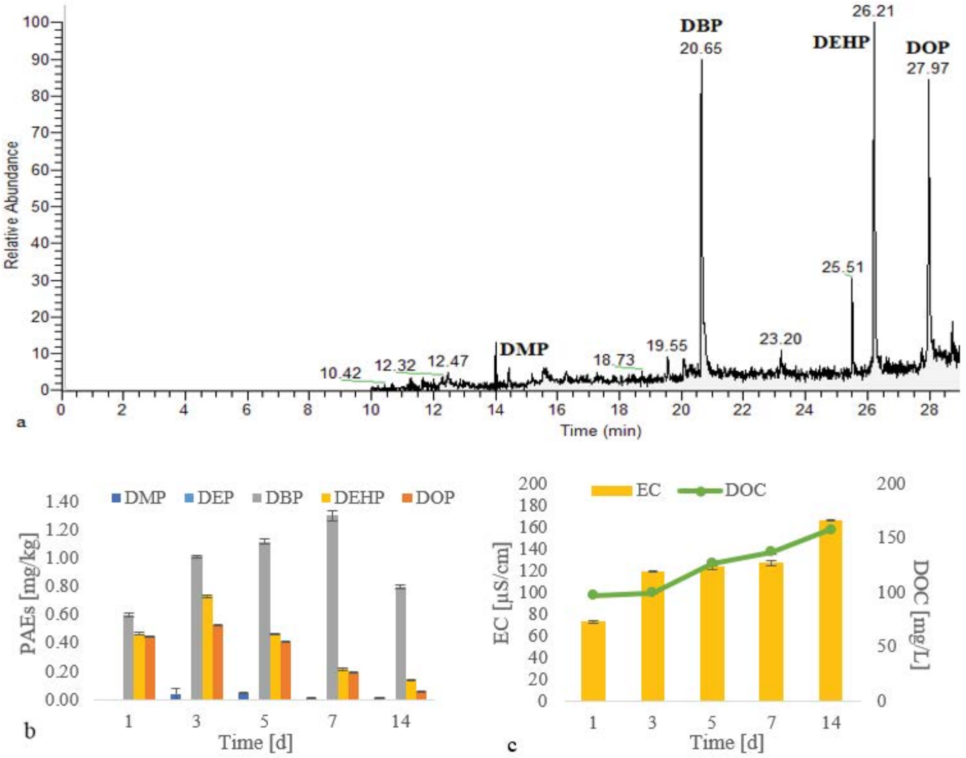

Fig. 2. Effect of temperature of 60°C on the amount and type of substances leached of microplastics (a) chromatogram (t = 5 d, m/z = 149), (b) plasticizers, (c) electrical conductivity and dissolved organic carbon.

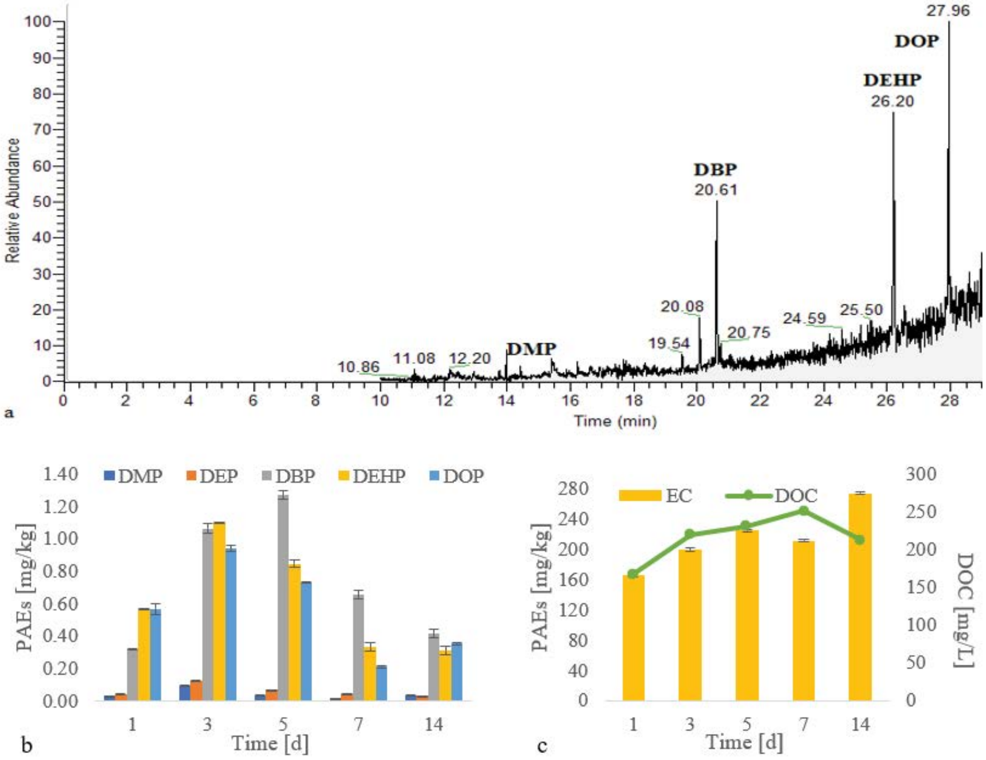

Fig. 3. Effect of temperature of 90°C on the amount and type of substances leached of microplastics (a) chromatogram (t = 5d, m/z = 149), (b) plasticizers, (c) electrical conductivity and dissolved organic carbon.

time for DBP ($p < \alpha$, $p = 0.0090$), DEHP ($p < \alpha$, $p = 0.0111$), DOP ($p < \alpha$, $p = 0.0091$), DEP ($p < \alpha$, $p = 0.0090$) and DMP ($p < \alpha$, $p = 0.0111$). Only under these conditions was an elution of DEP from microplastics analyzed. The recorded DOC and EC values at 90°C also indicate that the degradation of microplastics is most efficient under these conditions (Fig. 3c). Li and Tang [23] studied the effect of temperature on the leaching of bis(2-ethylhexyl) and di-*n*-butyl phthalate from microplastics in pseudo-marine water. The authors did not observe DBP and DEHP at 25°C, and a small amount of DBP was detected at 45°C. Higher temperatures favored leaching of DBP. Liu et al. [25] reported a greater release of harmful substances from disposable plastic materials into the water at elevated temperatures (100°C). The result showed that organic chemicals with maximum concentrations of 2.1 ± 0.85 mg/L were detected in the leachate from plastic packing and cups, indicating the potential risk of these materials while holding hot food or drink.

It is estimated that there are 1 billion end-of-life tires generated globally each year. The plastics exposed to sunlight on land can experience "heat build-up", reaching temperatures higher than the surrounding air and experiencing accelerated degradation. Temperatures in some landfills and industrial composters have been reported to reach 80°C–100°C, accelerating degradation rates provided sufficient oxygen and/or moisture are present for the thermal-oxidative degradation and hydrolysis pathways, respectively [26].

The maximum rate of migration of the additives occurs under conditions that result in maximum swelling without dissolving it. Above the glass transition temperature (T_g) and below the melt temperature of the polymer (T_m) is the softening point. This is the temperature at which the polymer loses its stiffness. As a result of the block structure of styrene-butadiene rubber, there are two ranges of glass transition temperatures. This range for the polybutadiene block is –85°C, and for the styrene block it is 75°C. As the styrene content increases, the glass transition temperature increases [21,27].

The analysis of the results obtained also showed the emission of other components of the plastic to the aquatic environment. Fig. 4 shows an exemplary chromatogram obtained from the tire analysis in the full scan option ($t = 5$ d and $T = 60°C$). The presence of benzene as a basic component in the plastic was detected. Substances such as benzothiazole and 2(3H)-benzothiazolone were the functions of the corrosion inhibitor in the analyzed tire [28–30]. The presence of stabilizers (benzenediamine, neodecanoic acid), a modifying agent (pentadecanoic acid, 9-hexadecanoic acid) and a rubber antioxidant (cyclohexamine) was also observed. Studies on the leaching of 4-tert-octylphenol (OP) and 4-nonylphenol (NP) from car tires into seawater were conducted by Staniszewska et al. [31]. During the first 3 d of the experiment, the concentration of 4-tert-octylphenol and 4-nonylphenol increased. The highest concentration observed for OP and NP was approximately 2.70 μg/L. Halsband et al. [14] also analyzed the emissions of components from granulate from tires. The organic compound with the highest concentration in all leachates was benzothiazole.

In addition, the degree of risk of the presence of washed phthalates in aquatic organisms was calculated for the use of used tires. This is especially important in terms of the use of used tires for construction purposes. So far, the negative effects of tire particle degradation on the soil and water environment have not been taken into account. The RQ results are presented in Table 5.

All the values obtained significantly exceed the value of 1, which indicates a high ecotoxicological risk in the case of introducing such a amount of microplastics into the water ecosystem. The highest risk value was recorded for the DOP for invertebrates. The least risk is DBP for invertebrates.

Table 5
RQ of analyzed phthalates

Analyte	First trophic level plants	Second trophic level invertebrates	Third trophic level vertebrates
DEHP	97,472.1	97,472.1	1,827.6
DBP	107,921.3	308.3	925.0
DOP	n.d.	418,665.6	n.d.

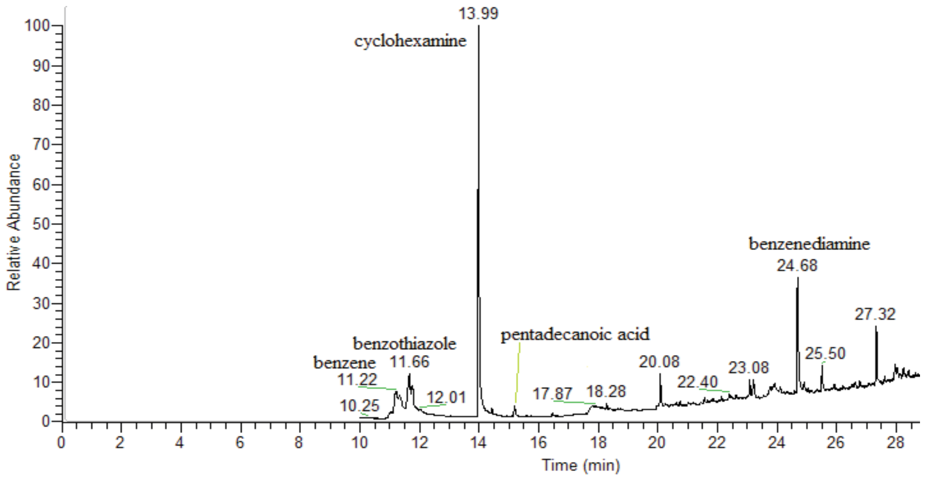

Fig. 4. Chromatogram obtained from rubber analysis ($t = 5$ d, $T = 60°C$) – full scan.

3.2. Influence of pH and hydrological conditions

The effect of the pH of the aqueous solution on the degree of elution of the plasticizers of the tire is shown in Fig. 5. No statistically significant differences were observed in the leaching of the components of the tire for different pH values. No elution of DOP was observed in the alkaline reaction medium. Li and Tang [23] studied the effect of pH on leaching of DEHP and DBP from microplastics in pseudo-marine water. The effect of pH on the amount of DBP leached could not be concluded with different polymers having different optimal pH of leaching. According to Yan et al. [32] the pH of the solution (3–9) also has little effect on the release of phthalates from microplastics.

A four-fold higher degree of leaching of inorganic components, expressed by the EC index, was recorded in the acidic environment compared to the neutral reaction (Fig. 5b). In the case of organic ingredients expressed by the DOC index, the values recorded under acidic conditions were three times lower compared to those recorded in a neutral environment. Phthalates are non-ionic compounds; therefore, the interaction between phthalate and plastic is less affected by pH [32]. Furthermore, the components eluted from the microplastics neutralized the aqueous solution. The initial pH values of 3, 7 and 10 after 1 d were 4.11, 7.27, and 9.21, respectively.

The research investigated the influence of water movement on the elution of plastic components (Fig. 6). Under flowing conditions, a higher emission of microplastic components was observed compared to that understanding conditions. This is confirmed by the concentrations of plasticizers obtained, as well as the DOC and EC values. The particles that are set in motion are additionally subject to mechanical degradation, which contributes to the destruction of the surface of the material.

The DEHP concentration was almost three times higher under flowing conditions. On the other hand, the DBP concentration was twice as high under these conditions. Halsband et al. [14] analyzed the leaching of DEHP and other phthalates from car tires. A DEHP concentration of 17.7 mg/kg was detected in the highest amount, followed by DiNP (diisononyl phthalate) and DBP (10.1 and 2.60 mg/kg). DBP and DEHP are classified by ECHA as toxic to reproduction in category 1B. In contrast, DBP has also been classified as toxic to the aquatic environment. Furthermore, the ECHA Member State Committee (MSC) confirmed that these phthalates are endocrine disruptors related to human health and that DEHP is an endocrine disruptor in the environment [33]. Approximately 57.8–16,100 kg/y of PAEs were estimated to be released into oceans from microplastics [34].

3.3. Greenhouse gas emissions

During the decomposition of microplastics, methane and carbon dioxide are formed. The results of these studies are presented in Fig. 7. The concentration of methane ranged from 0.95 to 30.78 ppm in the analyzed time period (at dark conditions). Higher concentrations for carbon dioxide were recorded. After 360 d, this value was 11,260.26 ppm and was more than 9 times higher compared to *t* = 30 d in dark

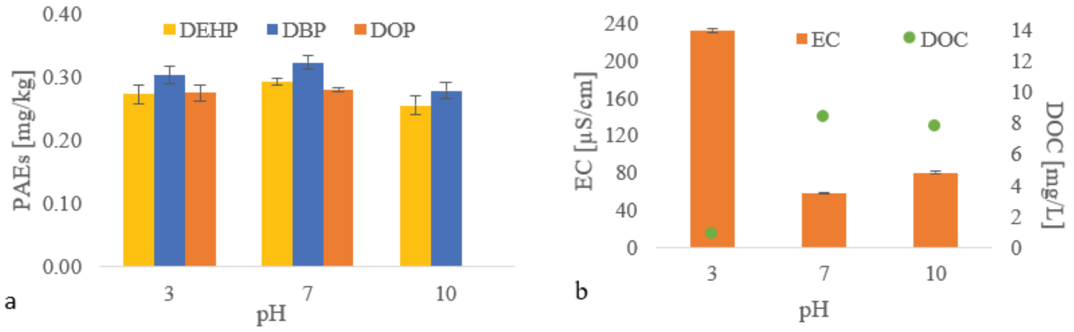

Fig. 5. Effect of pH on the amount and type of leached substances of microplastics (t = 1 d, T = 20°C) (a) plasticizers and (b) electrical conductivity and dissolved organic carbon.

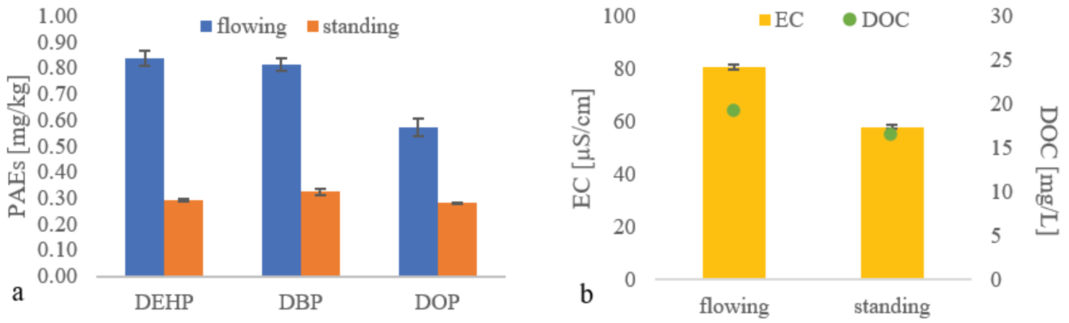

Fig. 6. Effect of hydrological conditions on the amount and type of substances leached from microplastics (a) plasticizers and (b) electrical conductivity and dissolved organic carbon.

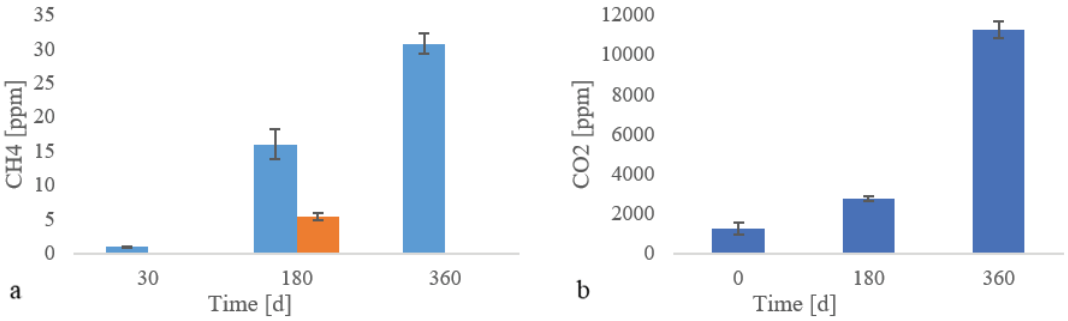

Fig. 7. Greenhouse gas emissions from the decomposition of microplastics (a) CH_4 and (b) CO_2.

conditions. However, in the presence of sunlight, the carbon dioxide concentration was negligible (*t* = 180 d). Research by Royer et al. [17] confirms greenhouse gas emissions from plastics. As plastics are decomposed into microplastics and even nanoplastics, the rate of greenhouse gas production is gradually increasing. Methane and ethylene were reported to be emitted upon exposure to ultraviolet light. These results are not consistent with those obtained in this study. Consequently, research in this area should take into account a greater number of factors.

The degradation of the analyzed microplastics leads to a reduction in the mass of the material and conversion to carbon dioxide and methane. Loss of mass from microplastics may result from the mineralization of plastics and leaching of components of the polymeric material. The weight of the rubber is 85.0% of the total weight of the tire. A report by the Environment Agency [35] suggests that tires lose 12.0% of the weight of rubber over their lifetime. The average new tire weighs 10 kg, which would mean a loss of about 1 kg of rubber over its lifetime.

4. Conclusions

The results obtained constitute a significant contribution to the shaping of environmental protection due to the provision of new information on the possibility of removing microplastics using natural processes. Information on another negative environmental impact of microplastics, which unfortunately constitute an increasing environmental pollution, and spread among the society, may be an important factor contributing to the strengthening of appropriate ecological attitudes in the field of waste avoidance, including plastic waste. Waste in the form of used shredded tires should not be underestimated due to the risk associated with the migration of plasticizers and other components and degradation products of this material. In addition, methane and carbon dioxide during tire decomposition has been shown to be released in a relatively short time, resulting in increased greenhouse gas emissions. Greenhouse gas emissions from the decomposition of microplastics have not yet been taken into account in the development of models showing the probable climate change in the future. However, much remains to be done to elucidate the exact mechanisms of tire decomposition in the wild.

Research confirms that the emission of plasticizers and polymer degradation is a complex process, whose course is determined both by environmental factors and by the physicochemical properties of individual additives:

- The temperature of the medium has a significant impact on the emission of the analyzed plastic plasticizers. The temperature increase from 20°C to 90°C resulted in a higher emission of the plasticizers analyzed.
- The pH of the reaction medium had no significant effect on the amount of plasticizers eluted from the microplastics, except for DOP, which was not found in an alkaline environment.
- In flowing water ecosystems, the emission of the microplastic component is higher than in stagnant water ecosystems.
- The decomposition of microplastics results in the emission of methane and carbon dioxide.

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