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Environmental risk assessment of low molecule benzotriazoles in urban road rainwaters in Poland

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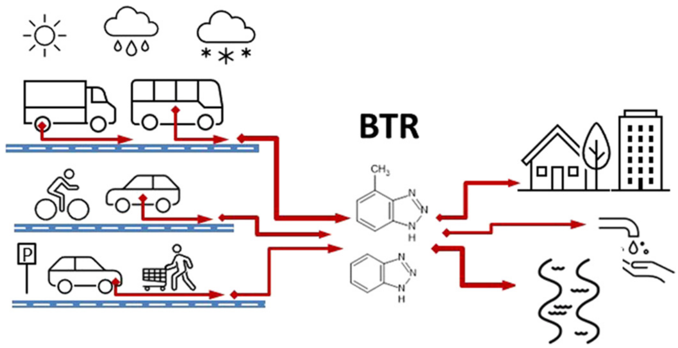
HIGHLIGHTS

- BTRs concentrations relate to the type of cover, traffic intensity, and vehicle type.
- ΣBTRs in rainwater ranged from 4.5 to 26.4 while in meltwater from 1.6 to 47.2 μg/L.
- 5Cl-BTR was dominant both in rainwater and in meltwater.
- 5Cl-BTR and 5Me-BTR present the highest risk quotients levels among tested compounds.
- BTRs concentrations in runoff are much higher than drinking water proposed limits.

GRAPHICAL ABSTRACT



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ABSTRACT

This study aimed to identify and quantify benzotriazoles (BTRs) emissions from road traffic and paved areas in an urban environment. Heterocyclic organic compounds BTRs are an emerging threat, under-recognized and under-analyzed in most environmental and water legislation. They are hazardous, potentially mutagenic, and carcinogenic micropollutants, not susceptible to effective biodegradation, and they move easily through the trophic chain, contaminating the environment and water resources. Traffic activities are a common source of BTR emissions in the urban environment, directly polluting human habitats through the different routes and numerous vehicles circulating in the cities. Using twelve heterogeneous locations scattered over a metropolitan area in Poland as a case study, this research analyzed the presence of BTRs in water samples from runoff produced from rainwater and snowmelt. 1H-BTR, 4Me-BTR, 5Me-BTR and 5Cl-BTR were detected in the tested runoff water. 5Cl-BTR was present in all samples and in the highest concentrations reaching 47,000 ng/L. Risk quotients calculated on the basis of the determined concentrations indicate that the highest environmental risk is associated with the presence of 5Cl-BTR and the sum of 4Me-BTR and 5Me-BTR, and the most sensitive organisms are bacteria and invertebrates. The results indicate that it is possible to associate the occurrence of these contaminants with the type of cover, traffic intensity, and vehicle type.

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1. Introduction

1.1. Benzotriazoles (BTRs)

Benzotriazoles (BTRs) are classified as Contaminants of Emerging Concern (CECs), meaning they might be candidates for future health regulations (Trček et al., 2018). These heterocyclic organic compounds are produced and widely used as additives of commonly applied chemicals worldwide in industry, aviation, transport, and households (Jia et al., 2019; Xu et al., 2015). The toxicity of benzotriazole and its derivatives has been deemed to induce cell cycle disruption, posing risks to human health (Wang et al., 2017), and causing acute and chronic effects in aquatic organisms (Minh et al., 2018). BTRs are proven mutagenic to bacterial cell systems (Salmonella, *Escherichia coli*). Due to its genotoxicity and carcinogenicity, BTR could act as a human carcinogen (Furumai et al., 2011; Xu et al., 2015; Wang et al., 2017). BTR can coexist with carcinogenic heavy metals such as Ni (II), Cr (VI), and As (III) (Minh et al., 2018; Xing et al., 2018). BTRs show the ability to bioaccumulate, i.e., accumulate in the tissues of living organisms, including humans (Furumai et al., 2011; Montesdeoca-Esponda et al., 2019; Verlicchi et al., 2017). Benzotriazoles have already been detected in human urine and adipose tissue (Jia et al., 2019; Liu et al., 2017; Wang et al., 2015; Shi et al., 2019).

BTRs are high production volume chemicals (HPVC). Their annual production exceeds 9000 t worldwide. These chemical compounds are widely and frequently used. Micropollutants from the BTR group indicate various chemical conditions in subsurface, leading to a different set of degradative or transformative processes. The most important factors influencing the degradation of BTRs, including biodegradability are the chemical characterization of the surface (water, soil, sediment, dust, etc.) and its pollution history, it's anthropogenic characteristics, contact time and the vector for benzotriazole transport (Parajulee et al., 2017). According to the literature, the identified pathways of BTR degradation are biodegradation, biotransformation, bioaccumulation, bioadsorption, photochemical transformation, hydrolysis, hydroxylation, oxidation, chlorination, UV/chlorination, UV-A photolysis, AOPs, membrane processes, polymerization and methylation (Weiss et al., 2006; Reemtsma et al., 2010; Liu et al., 2011; Domínguez et al., 2012; Seeland et al., 2012; Asimakopoulos et al., 2013; Liu et al., 2013; Fent et al., 2014; Alotaibi et al., 2015; Cantwell et al., 2015; Mazioti et al., 2015; Molins-Delgado et al., 2015; Felis et al., 2016; Miksch et al., 2016; Lu et al., 2018; Martín-Rilo et al., 2018; Gatidou et al., 2019; Kowalska et al., 2019; Ahmad et al., 2020; Chen et al., 2020; Piekutin et al., 2021). The authors report different times and efficiencies related to the degradation pathways (physical, chemical and biological) and self-removal of BTR from the environment. Consequently, these BTR compounds persist in the environment so long that they reach and pollute surface waters and aquifers. For example an average half-life of BTR ranges from one month to at least one year (Giger et al., 2006; Matamoros et al., 2010; Durjava et al., 2013; Hu et al., 2018; Lee et al., 2019; Wagner et al., 2020; Golovko et al., 2021). A significant effect on the biodegradation of BTRs could have redox conditions changing from aerobic to anaerobic, including nitrate-reducing, sulphate-reducing and methanogenic conditions (Liu et al., 2013).

Several studies have been published on the occurrence of BTRs in tap water; however, guidelines regarding BTRs in drinking water are scarce. The Danish Environmental Protection Agency proposes a limit of 20,000 ng/L for BTRs in drinking water (Beltoft et al., 2013). Other authors suggest that the maximum allowable concentration should follow that of the Tolyltriazole, which for instance, in Australia is 7.0 ng/L (Janna et al., 2011). Relatively low concentrations of benzotriazoles ranging from 10 ng/L to 200 ng/L were found in drinking water samples collected from the Netherlands (van Leerdam et al., 2009). 1H-BTR and the sum of 4Me-BTR + 5Me-BTR were detected at concentrations ranging from 0.6 to 79.4 ng/L in tap water samples collected in the UK (Janna et al., 2011). Higher levels of 1H-BTR residues and the sum of 4Me-BTR + 5Me-BTR were reported in tap water samples collected from 51 major cities in China (Wang et al., 2016). A study that included 51 major cities in China found that the type of water source and the degree of industrial development were the main factors affecting the level of residual benzotriazoles in tap water (Wang et al., 2016). Its findings indicate that the mean total BTR concentration varied depending on the location: southern China (36.2 ng/L), northern China (7.2 ng/L), western China (10.9 ng/L), and eastern and central China (16.5 ng/L). The authors also found that chlorine disinfection is a contributing factor to the presence of BTRs, and that boiling water for up to 10 min is ineffective in removing these compounds.

As in most countries, precipitation is Poland's primary source of water resources. This water cycle component introduces micropollutants into the trophic chain and spreads micropollutants in the environment. For further context, 70% of Poland's drinking water is from groundwater and 30% from surface waters. The required water quality tests for potabilization in Poland follow the most common physicochemical and microbiological parameters employed worldwide, based on the World Health Organization Guidelines (World Health Organization, 2017) and EU Directive (Directive (EU), 2020). Similarly, there is EU Directive for the quality of treated wastewater (Council Directive, 1991) but there is no limit value for micropollutants. It is noteworthy that Switzerland was a pioneer in adopting legislation requiring the monitoring of specific micropollutants (including BTR) in treated wastewater, but only in selected, most modern wastewater treatment plants (Eawag, 2019).

Many micropollutants, including the BTR group, are not analyzed in drinking water sources. Similarly, tests to determine the presence of BTRs in effluents from municipal and industrial wastewater treatment plants to surface waters are not a requirement. This lack of knowledge about the concentration and accumulation of BTR in water resources might threaten human populations and ecosystems.

1.2. Classification of BTR

The primary representative of compounds from the benzotriazole group is benzotriazole. Benzotriazole is a bicyclic nitrogen heterocycle formed by the fusion of the benzene ring with the 4,5-positions or the "d" site of 1H-1,2,3-triazole. In the literature, benzotriazole and its derivatives are designated by many (up to fourteen) different abbreviations. This multiplicity makes difficult the analysis of issues related to this topic and often misleads the reader. Supplementary material (Table I) provides the abbreviations used by various authors for defining the same compound, as well as the chemical structure of the studied compounds and their applications.

1.3. Primary sources of BTR pollution

Road transport is recognized as the largest emitter of micropollutants in urban areas (Asheim et al., 2019). It is a large, widespread, and uncontrolled linear emitter. It is hazardous because it emits micropollutants directly into human-inhabited environments. Pollutants accumulate on surfaces and around roads, and precipitation washes them away and puts them into the water cycle. Urban rainfall runoff is one of the major sources of micropollutants emitted from traffic to surface waters (Asheim et al., 2019; Parajulee et al., 2017; Han et al., 2020).

BTRs increase the performance and durability of products. In the road transport sector, BTRs are added as safeguards and enhancers which end up released to the environment through various routes during the operation, aging, or damage of vehicles and roads and their ancillary elements. The following paragraphs present some instances in this regard. Benzotriazoles are widely used as corrosion inhibitors and surface corrosion protection for metals, including copper and its alloys (Davis et al., 1977). The most commonly used compounds are those with hydrogen in the 1 position, as well as those with a methyl group: 1H-BTR, 4Me-BTR, 5Me-BTR, 5Cl-BTR (Allam et al., 2009; Antonijević et al., 2009; Luchkin et al., 2020; Miksch et al., 2016; Pilsits et al., 1999; Simonović et al., 2020). Road elements and vehicle components constructed, coated, or containing copper are a source of micropollutants when subject to abrasion. Benzotriazoles also serve as UV stabilizers and UV absorbers for making fabrics and plastics resistant to this type of radiation (Li et al., 2019;

Montesdeoca-Esponda et al., 2019; Xu et al., 2015). In road transport, any abrasion and degradation of vehicle components containing such protection (e.g., tarpaulins or veneers) is a source of BTR.

BTR compounds are also widely used as de-icing, anti-freezing, and anti-fogging agents in road transport and aviation. BTR derivatives are also used in detergents and cleaning agents commonly employed in car washing (Alotaibi et al., 2015; Janna et al., 2011). Once applied, rainfall washes them from roads, car parks, pavements, or airports, allowing their introduction into the environment by their accumulation in the road lanes (Cantwell et al., 2015; Fink, 2012; Książek et al., 2016; Wu et al., 1998).

Micropollutants from the benzotriazole group are found in the residue of windshield wipers and tire treads (Bye and Johnsen, 2015). The attrition caused by frequent braking and direction changes in the city roads intensify tire wear and increase the emission of micropollutants. Even if the BTR emission per vehicle is low, the cumulative effect is likely the highest source of BTRs from roads in urban environments. These contaminants commonly reach aquifers and water bodies through stormwater and combined sewers.

The authors indicate the spatial and seasonal variability of the actual BTR concentrations in road runoffs, determined by the local anthropogenic characteristics and climatic conditions. The road network density, traffic volume, pattern of dry and wet periods, chemical de-icing events, snow retention and melting, surface type and deposited historical pollutants are considered to be significant vectors of BTR emission and transport vectors for BTR (Awonaike et al., 2021, Han et al., 2020, Parajulee et al., 2017). Poland is located in a Central European climate with a long winter with sub-zero temperatures and snow events. BTR-containing chemicals and de-icing salts are commonly used. According to the literature data, urban traffic provides the sustainable base emission of BTR. There is a lack of information about the load, rate and paths of transport of BTR micropollutants from roads to the aquatic environment in Poland. Snow winter is considered the period of the highest BTR emissions from roads as roadside snow piles accumulate pollutants from both vehicles and road de-icing. During snow melting, the accumulated BTR causes high or even maximum annual pollution loads (Parajulee et al., 2017).

Identification of the sources and deposition of BTR in the urban environment will allow for the assessment of environmental risk and will become the basis for pollution models. An interesting example is the integrated statistical and deterministic model for analyzing contaminants in high-density residential stormwater runoff. The model allows to simulate the presence, maximum loads and mitigate loads of contaminants in runoff for implementation of best practices in urban wastewater management (Brown et al., 2019).

1.4. Environmental risk of BTRs

Risk assessment provides technical support for decision-making in the face of uncertainty. In practice, this assessment aims to determine the probable impact of a chemical compound or mixture of chemical compounds contaminating a specific environment (place, region) on the life processes of organisms living there. The results of toxicological analyses on a laboratory scale are used for this purpose. Similarly, risk estimation evaluates the threat to human life and health. Literature often distinguishes between environmental risk assessment or ecological risk, assuming that the former is more concerned with the danger that environmental pollution poses to humans and the latter with the hazard that contamination poses to other organisms, their populations, and entire ecosystems (Suter, 2006).

Studies about the chronic effect of BTR and its derivatives on living organisms and ecosystems are scarce, and this is a relatively new research topic. Additionally, this lack of complete knowledge regarding the BTRs toxicological data, coupled with the widespread use and low toxicity indices of many of these compounds (considered in classical terms), might lead to unknown chronic effects at the sublethal level and environmental contamination (Janna et al., 2011; Beltoft et al., 2013).

The meaning of risk quotients (RQ) has a critical significance in interpreting toxicological and analytical data. For instance, in line with US regulations (US-EPA), the obtained RQ values are compared with Levels of Concern (LOC) to consider the potential risk to non-target organisms and subsequent management efforts. If the RQ exceeds the values 1.0 for chronic test data, 0.5 for the acute test data, or even 0.05 in the case of endangered species – such risk is unacceptable. According to the EU, all values below the one are acceptable (Thomaidi et al., 2017).

1.5. The aim of the study

Based on the literature review, observations, and preliminary tests conducted by the Authors, this study aims to identify, quantitatively, and qualitatively analyze and assess the environmental risk resulting from benzotriazoles in runoff from roads and paved areas in an urban environment. For this research, two periods were selected based on an expected high concentration of pollutants: rainfall after a long period without precipitation (pollutants flushed from paved surfaces) and the beginning of snowmelt after winter (pollutants accumulated in snow). This type of evaluation has not yet been conducted to the best of our knowledge. This study is particularly relevant from the point of view of quality and protection of water resources and human health.

2. Materials and methods

2.1. Materials

The research was carried out in the city of Białystok with 300,000 residents and an area of 102 km^2, located in central Europe, in the north-eastern part of Poland. The average annual precipitation in the city of Białystok is 715 mm.

The research material was rainwater (1st cycle) and meltwater (2nd cycle) sampled in 2020 and 2021 from 12 points (street inlets) situated on the main communication routes of the city (Fig. 1).

Supplementary material (Table II) presents a short description of the sample collection site, including the type of land development, the characteristics of the catchment area, and the intensity of car traffic.

The first collection of samples was carried out on 12 December 2020, after the first light snowfall with rain, and the second collection of samples was carried out on 25 February 2021, at the beginning of the thaw. The water sampling followed the applicable methodology (Baird et al., 2017). These samples were collected in the winter season when the highest expected amount of pollutants (drivers use soft tires, salt is spread onto the roads, traffic is less smooth due to poor road conditions, consumables wear at a higher rate, December sees the largest numbers of cars parked next to shopping centers, among other factors).

The sample collection at each measurement point consisted of the gathering of ten consecutive samples gathered at regular 1-h intervals. Runoff from rainwater and meltwater samples were collected into glass bottles and filtered. The samples intended for the quantitative and qualitative analysis of benzotriazoles were stored at −20 °C until testing.

There was practically no rainfall during the two weeks preceding the first collection of samples, and the temperatures fluctuated between −8.2 °C to 7.2 °C (Fig. 2). The snow fell on 10 December, and on 12 December, it melted due to rainfall, causing surface runoff. A significant period of accumulation of micropollutants in the area of the road lane preceded the collection of samples.

Rainfall was absent during the two weeks preceding the second collection of samples, and the temperatures were mostly below zero (as low as −17.7 °C). There was a considerable snow cover with a 30–40 cm depth over this period (Fig. 3). Starting on 20 February 2021, temperatures began to reach positive values, causing the melting of the snow cover to be particularly intense on 25 February, when the second series of samples was collected.

2.2. Methods

2.2.1. Physico-chemical analyses

Analyses of micropollutants from the benzotriazole group were carried out in the Laboratory of the Department of Environmental Chemistry of the University of Białystok.

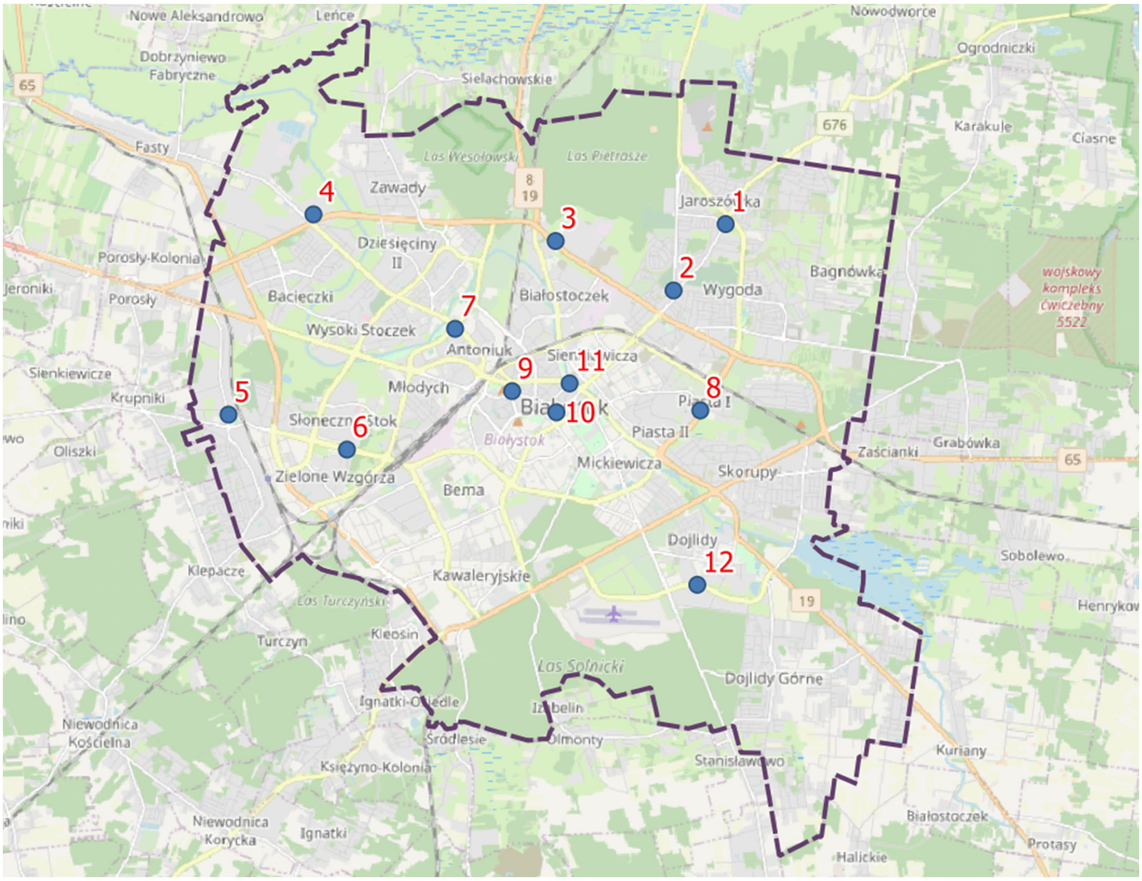

Fig. 1. Sample collection points in Białystok.

2.2.1.1. Chemicals and materials. Standards of 1H-BTR (≥98%), 4Me-BTR (4 methyl 1H benzotriazole isomer; ≥90%), BTR COOH (99%), 5Cl-BTR (99%), 5 ABTR (Aldrich CPR grade), 2 S-BTH (97%), 2 OH BTH (98%), 2 ABTH (97%), 2 Me S BTH (97%), 2 M BTH (CPR), 1 OH BTR (≥97%) and BTR2d4 (10 μg/mL in ace-tone) were purchased from Sigma-Aldrich (Steinheim, Germany). Methanol (MeOH) and acetonitrile (I) of LC-MS grade and dichloromethane (DCM) of analytical grade were obtained from Merck (Darmstadt, Germany). Formic acid (98% v/v), hydrochloric acid (HCl), and ammonium hydroxide were acquired from Sigma-Aldrich (Steinheim, Germany). Concentrated nitric acid (UltraPure grade) was obtained by distillation with Milestone SubPur (Sorisole, BG, Italy). Water was purified with a Milli-Q grade water purification system (Q-option, Elga Labwater, Veolia Water Systems LTD, U.K.).

2.2.1.2. Benzotriazoles. The study included the identification of four low molecule benzotriazoles and two benzotriazole UV stabilizers in rainwater

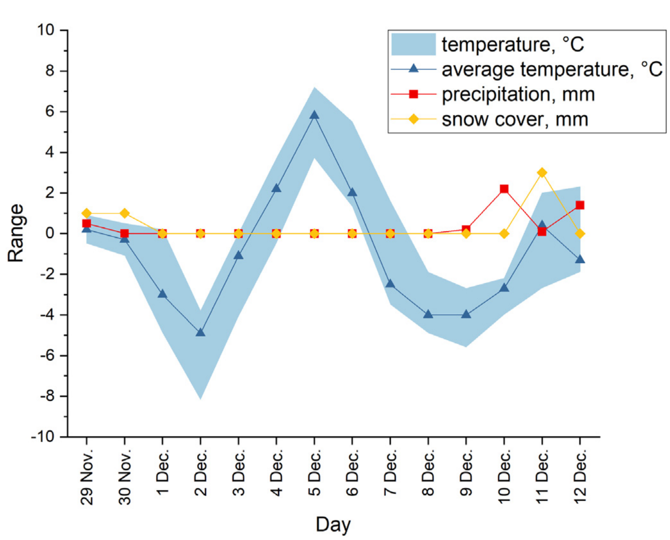

Fig. 2. Daily temperature, precipitation, and snow depth during the two weeks preceding the collection of samples on 12 December 2020.

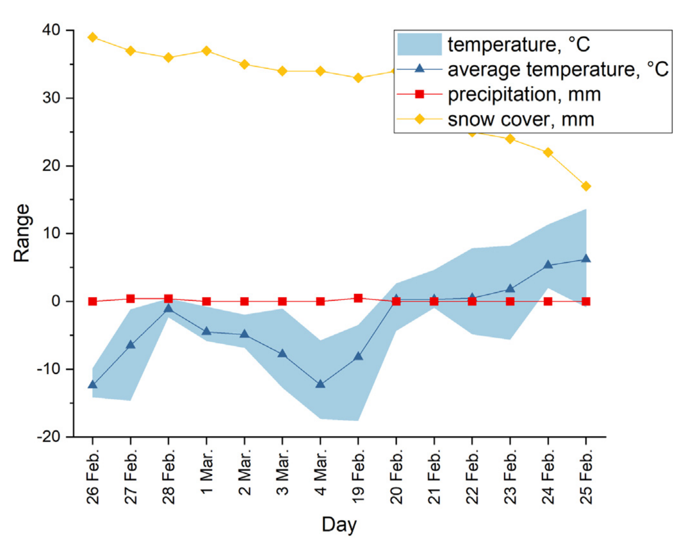

Fig. 3. Daily temperature, precipitation, and snow depth during the two weeks preceding the collection of samples on 25 February 2021.

and snowmelt. The selection of these compounds was based on their carcinogenic or mutagenic properties to living organisms and because they can move through the trophic chain. Table 1 presents the physicochemical properties of these compounds.

The method employed for benzotriazoles' quantitative and qualitative analysis based on microextraction by ultrasound-assisted emulsification (USAEME) with in-situ acetylation and gas chromatography–mass spectrometry (GC–MS). This method was described in detail by the authors of this paper in Kotowska et al. (2021).

2.2.1.3. The procedure of benzotriazole extraction and determination. This analysis was performed with an HP 6890 gas chromatograph with a mass spectrometric detector MSD5973 and HP 7673 autosampler (Agilent Technologies, USA). Aliquots of 5-mL of the samples were placed in 10-mL glass centrifuge test-tubes containing 0.1 g sodium hydrogen phosphate for the simultaneous extraction and derivatization of 1H- benzotriazole (1H-BTR), 4-methyl-1H-benzotriazole (4Me-BTR), 5-methyl-1H-benzotriazole (5Me-BTR), 5-chloro-benzotriazole (5Cl-BTR), 2-tert-Butyl-6-(5-chloro-2H-benzotriazol-2-yl)-4-methylphenol (UV-326), and 2-(2H-Benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol (UV-329). The extraction solvent (chlorobenzene, 100 μL) and the derivatization reagent (acetic anhydride, 120 μL) were added to such prepared samples and mixed. Then, tubes were immersed in an ultrasonic bath (Polsonic, Sonic-3, Poland). Extractions were performed at 42 kHz of ultrasound frequency and 230 W of power for 5 min at room temperature. Emulsions were disrupted by centrifugation at 6000 rpm for 6 min in an MPW-250 Med. Instruments (Poland) laboratory centrifuge. The organic phase settled at the bottom of the conical tube and was removed using a 100 μL Hamilton syringe (USA) and transferred into a 150 μL insert of chromatographic vial. 1 μL of the extract was then analyzed using the HP 6890 gas chromatograph with a mass spectrometric detector MSD5973 and HP 7673 autosampler (Agilent Technologies, USA). Determination of BTRs concentrations in rainwater was carried out using the standard curve method. Calibration plots were obtained by spiking the rainwater (taken from the area outside the city and not containing BTRs) with six concentration levels in the range 50–50,000 ng/L and performing the extraction and GC–MS analysis. The procedure was repeated four times for each concentration. The obtained validation parameters are summarized in Supplementary materials (Table III). Good linearity was registered for all studied compounds with determination coefficients (r^2) higher than 0.99. The limits of detection (LoDs) were estimated as concentrations giving a signal-to-noise ratio of 3 and its values were between 5 and 15 ng/L. To determine the precision, the value of the coefficient of variation (CV) calculated as a ratio of the root mean squared error to the mean of the concentration was used. The CV values ranging from 5.1 to 9.4 were obtained for analyzed BTRs. Recoveries were calculated comparing nominal concentration with the value determined on the basis of calibration plot and they were between 102 and 118%.

2.2.2. Evaluation of the ecotoxicological risk

The ecotoxicological risk to the environment of benzotriazoles in water runoff from traffic routes has been assessed using the risk quotient (RQ) method and calculated based on the European Medicines Agency (EMA, 2006) guidelines for several water ecosystem trophic levels: producers - algae or plants, consumers divided into invertebrates (Crustacea; Branchiopoda) and vertebrates (Actinopterygii), and decomposers (Bacteria). The RQx values were estimated using the ratio between the highest environmental concentration (MEC) measured for each compound under study and the short-term Predicted No-Effect Concentration (PNEC).

$$RQ_x = \frac{MEC_x}{PNEC_x} = \frac{MEC_x}{\left(\frac{EC_{x,y[\%]}}{AF}\right)}$$

where: MEC_x – the highest measured concentration of the individual pollutant in the environmental sample; $PNEC_x$ – predicted no-effect-concentration [mg/L] of the pollutant x towards the given trophic level in the environmental conditions; AF – the assessment factor selected in such a way as to include the differences between laboratory data and natural conditions, taking into account of interspecies and intraspecies differences; $EC_{x,y[\%]}$ – the measure of toxicity (also IC for inhibition or LC for lethality) is the calculated concentration [mg/L] of compound x in which given percent of a laboratory population of model organism y (representing a given trophic level) shows the observed effect, or the percentile of this effect that is attained (e.g., usually 50 (median) for acute toxicity, or 10 for chronic exposition, if there is no data for acute toxicity). This research used literature data to set these reference values.

The criteria for high, medium, and low risk are based on the Hazard Quotient (HQ), which is the ratio between the MEC and the PNEC: HQ $\geq$ 1 (high), 0.1 $\leq$ HQ $<$ 1 (medium), and HQ $<$ 0.1 (low risk) (Zhang et al., 2018; Kotowska et al., 2020).

This study considers $RQ_x < 0.1$ as within an acceptable level of risk, 0.1 $\leq RQ_x < 1$ as medium risk, and $RQ_x \geq 1$ as an unacceptable level of ecological risk for the aquatic ecosystem, based on the guidelines of ECB (2003) and Perrodin et al. (2011) and following the ranking categories described in Table 2 based on available literature.

PNEC was calculated by taking the acute time exposition (15 min for bacteria to 96 h for some fishes) median lethal/inhibition/effect concentration EC/IC/LC_{50} or data based on chronic toxicity and EC_{10} and dividing it by a safety factor (AF). The AF of this study follows the recommendations of the European Parliament and the Council (2000a,b), usually 1000, and for chronic 100. These values could be adapted for other regions depending on local legislation.

In the case when more than one value of toxicity factor tested on a representative trophic level was found for a given compound, its lowest concentration value (highest toxicity) was adopted. The selected values of toxicity factors used in the calculations were defined based on available literature data (Table 2).

The experimental design for the laboratory analyses follows standard procedures, and the testing should be performed separately for each indicator species. In addition, they shall be conducted under strictly controlled conditions such that environmental factors do not influence the results. Consequently, in a risk assessment, an assessment factor (AF) is applied to reflect the actual safety level of a substance on an ecosystem organism by taking a divisor value for a given toxicity indicator (e.g., EC_{50}, EC_{10}, or LOEC) and a test model organism representing one of each trophic level. Based on these two variables, the AF usually ranges from 10 to 1000. Knowing the potential impact on indicator organisms expressed by the concentration of a compound causing a measurable toxic effect under laboratory conditions, reduced by the AF factor, allows assessing the predicted environment concentration (PEC) or evaluating the empirical data from environmental samples (MEC). In this paper, the concentrations of selected BTRs were

Table 1
Characteristics of benzotriazoles selected for studies.

Compounds	Molecular weight [Da]	Solubility in water [g/L]	Density [g/cm^3]	Melting point [°C]	Boiling point [°C]	Log K_{OW}
1H-BTR	119.12	19.80	1.3600	97–99	204	1.44
4Me-BTR	133.15	3.10	1.2700	139–143	360.6 ± 11.0 (predicted)	1.60
5Me-BTR	133.15	3.10	1.1873	80–82	210–212	1.60
5Cl-BTR	153.57	Soluble in hot water	1.3647	157–159	252.42	2.17
UV-326	315.80	Insoluble	1.3200	144–147	460.4 ± 55.0 (predicted)	–
UV-329	323.43	Insoluble	1.1000	106–108	471.8 ± 55.0 (predicted)	–

Table 2
Ecological risk for the aquatic ecosystem.

Compound	Species	Time of exposition	Toxicity index	Mean value [mg/L]	Reference
4Me-BTR	*Ceriodaphnia dubia*	48 h	LC50	118	Pillard et al., 2001
	Danio rerio	96 h	LC50	59	Damalas et al., 2018
	Aliivibrio fischeri	15 min	EC50	21	Pillard et al., 2001
	Pimephales promelas	96 h	LC50	63	Pillard et al., 2001
5Cl-BTR	*Daphnia magna*	48 h	LC50	28.73	Giraudo et al., 2017
5Me-BTR	*Desmodesmus subspicatus*	72 h	EC10	2.86	Seeland et al., 2012
	Lemna minor	7d	EC10	2.11	Seeland et al., 2012
	Daphnia galeata	48 h	EC50	8.58	Seeland et al., 2012
	Ceriodaphnia dubia	48 h	LC50	79	Pillard et al., 2001
	Aliivibrio fischeri	15 min	EC50	8.7	Pillard et al., 2001
	Pimephales promelas	96 h	LC50	22	Pillard et al., 2001
	Danio rerio	96 h	LC50	128	Damalas et al., 2018
	Aliivibrio fischeri	15 min	EC50	5.91	Cancilla et al., 1997
1H-BTR	*Lemna minor*	7d	EC10	3.94	Seeland et al., 2012
	Desmodesmus subspicatus	72 h	EC10	1.18	Seeland et al., 2012
	Daphnia galeata	48 h	EC50	15.8	Seeland et al., 2012
	Ceriodaphnia dubia	48 h	LC50	102	Pillard et al., 2001
	Aliivibrio fischeri	15 min	EC50	41.65	Cancilla et al., 1997
	Pimephales promelas	96 h	LC50	65	Pillard et al., 2001
	Danio rerio	96 h	LC50	170	Damalas et al., 2018
5Me-BTR, 4-Me-BTR	*Ceriodaphnia dubia*	48 h	LC50	108	Pillard et al., 2001
	Pimephales promelas	96 h	LC50	38	Pillard et al., 2001
	Aliivibrio fischeri	15 min	EC50	7.3	Pillard et al., 2001

studied in rainwater and snowmelt runoff from paved surfaces into the sewer system. This demarcation is a partial view of reality, but it might provide an initial perspective of these compounds' threat to the aquatic environment. For example, direct discharge of Polycyclic aromatic hydrocarbons (PAHs) into stormwater and a receiver (e.g., a river) will reduce their concentrations many times over (dilution process); however, they might represent a significant health risk when there is low dilution capacity, worsened by reduced dissolved oxygen concentrations. High concentrations may also occur in retention ponds in urban areas (Durand et al., 2004; Istenič et al., 2011; Mahler et al., 2012; Stephansen et al., 2020).

3. Results

3.1. BTR concentrations

Table 3 presents the concentration profiles of benzotriazoles and UV stabilizers in the rainwater collected from traffic routes during precipitation. In the case of rainwater (1st series of tests) the frequency of detection of each BTRs has been: for 1H-BTR, 4Me-BTR, 5Me-BTR – 91.7% for 5Cl-BTR – 100% and for UV-326, UV-329 – 0%, the highest concentration of 1H-BTR, amounting to 10,604.6 ng/L, has been detected in the water collected from the L4 measurement point, located in one of the largest car parks within the city. Concentrations exceeding 1000 ng/L have also been detected at points L3, L7, L11, and L2. Only one measurement point (L10 – zone closed to car traffic) did not seem to discharge 1H-BTR in the waters flowing from paved areas.

The highest concentration of 4Me-BTR, amounting to 3744.4 ng/L, was detected in the water taken from the L7 measurement point, a road with a heavy traffic load. Almost all measurement points exhibited concentrations exceeding 1000 ng/L, except for L1 (469.6 ng/L) and L10 (not observed). Similar results were observed for 5Me-BTR, with the highest concentration detected in L4 (6023.6 ng/L).

The 5Cl-BTR appeared in all the examined locations, with the highest concentration in L1 (24,321.6 ng/L) and the lowest in L8 (1247.4 ng/L). It should be noted that 5Cl-BTR is the only compound detected even at the pedestrian crossing L10 (5311.9 ng/L). On the other hand, UV-326 and UV-329 were not detected in all the collected samples.

Fig. 4 presents in the form of box plots a summary of the results obtained from the first series of tests.

Table 4 presents the concentration profiles of benzotriazoles and UV stabilizers in rainwater collected from traffic routes during snowmelt (2nd series of tests). The frequency of detection of each BTRs has been: for 1H-BTR, 4Me-BTR – 58.3%, for 5Me-BTR – 83,3%, for 5Cl-BTR – 100% and for UV-326, UV-329 – 0%. The highest concentration of 1H-BTR, amounting to 884.7 ng/L, was detected in the water collected from the L12 measurement point. Thus, the above concentrations are much lower than in the case of rainwater. In the case of 5 measurement points (L1, L3, L5, L9, and L10), no 1H-BTR was detected in the samples.

The highest concentration of 4Me-BTR, amounting to 3553.6 ng/L, was recorded in the water taken from the L7 measurement point. Concentrations exceeding 1000 ng/L have been detected at three more measurement points (L8, L9, and L11), while in the case of 5 locations (L1, L2, L3, L4, and L10), no 4Me-BTR was detected in the samples. Similar results have been obtained for 5Me-BTR – the highest concentration was recorded in L7 (4578.4 ng/L), and concentrations exceeding 1000 ng/L were recorded at four other measurement spots (L8, L9, L11, and L12). 5Me-BTR has not been detected at two measurement points (L4 and L6). Concentrations of 5Cl-BTR were detected in all samples, with means ranging between 46,985.6 ng/L (at L10) and 891 ng/L (at L2). As in runoff from rainfall samples, UV-326 and UV-329 were not detected in all the collected samples.

Fig. 5 presents in the form of box plots a summary of the results obtained from the second series of tests.

Comparing results from the 1st and 2nd series of tests indicates that, except for 5Cl-BTR, the concentrations of benzotriazoles and UV stabilizers were higher in the 1st series of samples (rainwater). Additionally, the concentration of BTRs clearly exceeds the suggested limits in previous studies (Beltoft et al., 2013; Janna et al., 2011) or drinking water; therefore, they might represent a risk to drinking water sources.

3.2. Evaluation of the ecotoxicological risk of BTRs

The BTRs-related potential risks in Bialystok vary depending on the sampling location and season. Fig. 6 (rainwater, first series of tests) and Fig. 7 (snowmelt, second series of tests) present the maximal BTRs RQ values obtained based on the parameters given in Table 2 and using four samples from each of the two series. These figures include results for the 1:1 mixture of 5Me and 4Me-BTR prepared according to the procedures described in Pillard et al. (2001). 1H-BTR shows the most significant difference between rainwater and snowmelt, as in the first case, all the analyzed groups of organisms classified within the range of medium risk, varying from 0.16 for invertebrates to 0.89 to algae. Oppositely, the RQ did not exceed the 0.1 low-risks threshold for any group for snowmelt samples.

As previously observed in Table 2, toxicity data is not available for all types of organisms. In the absence of toxicity data for 4Me-BTR, the average

Table 3
Concentration profiles of benzotriazoles and UV stabilizers in rainwater collected from traffic routes during precipitation.

Sampling point	Compounds concentration (ng/L)											
	1H-BTR		4Me-BTR		5Me-BTR		5Cl-BTR		UV-326		UV-329	
	Avg. Min Max	±SD	Avg. Min Max	±SD	Avg. Min Max	±SD	Avg. Min Max	±SD	Avg.	±SD	Avg.	±SD
L1	286.8	5.2	469.6	9.1	415.7	6.5	24,321.6	177.5	n.o.	–	n.o.	–
	281.6		460.5		409.2		24,319.7					
	291.7		472.9		419.4		24,326.8					
L2	1267.3	11.3	1545.0	30.1	2267.2	31.9	11,938.1	132.4	n.o.	–	n.o.	–
	1262.2		1514.9		2235.3		11,805.7					
	1278.6		1558		2282.1		12,004.3					
L3	2748.4	17.3	1570.8	18.4	2016.8	30.1	4474.2	46.0	n.o.	–	n.o.	–
	2731.1		1552.4		1999.8		4437.4					
	2758		1779.5		2046.9		4520.2					
L4	10,604.6	105.7	3434.0	25.1	6023.6	101.6	6355.7	45.3	n.o.	–	n.o.	–
	10,540.8		3422.5		5922		6337.4					
	10,710.3		3459.1		6069.7		6401					
L5	359.8	7.7	1250.7	20.0	1572.6	29.3	2167.9	29.7	n.o.	–	n.o.	–
	352.1		1238.9		1543.3		2139.1					
	363.9		1270.7		1590.3		2197.6					
L6	383.0	6.2	2921.8	14.4	3462.9	41.0	2938.1	31.3	n.o.	–	n.o.	–
	376.8		2914.1		3436.3		2906.8					
	386.3		2936.2		3503.9		2951.2					
L7	2151.2	19.3	3744.4	41.7	4176.8	44.3	3027.3	61.4	n.o.	–	n.o.	–
	2145.3		3730.8		4147.7		2965.9					
	2170.5		3786.1		4221.1		3069					
L8	600.1	25.9	2347.8	19.5	2911.5	39.9	1247.4	22.7	n.o.	–	n.o.	–
	588.7		2328.3		2871.6		1224.7					
	626		2353.3		2925.1		1259.8					
L9	309.4	10.1	1224.0	13.0	1269.6	12.7	1653.1	21.9	n.o.	–	n.o.	–
	299.3		1220.2		1262.8		1634.1					
	317.1		1237		1282.3		1675					
L10	n.o.	–	n.o.	–	n.o.	–	5311.9	61.0	n.o.	–	n.o.	–
							5250.9					
							5361.2					
L11	1795.2	17.7	1918.4	7.7	2020.7	51.2	1313.9	47.4	n.o.	–	n.o.	–
	1777.5		1916.3		1987		1285.5					
	1801.4		1926.1		2071,9		1361.3					
L12	319.0	2.1	1093.7	9.5	1265.7	19.4	2332.0	31.9	n.o.	–	n.o.	–
	317.1		1084.2		1246.3		2300.1					
	321.1		1100.8		1277.9		2355.9					

n.o. - not observed.

risk level was estimated only for microorganisms, and our findings showed that differences between samples taken at different times were negligible. The increased risk values for 5Me-BTR were also due to the high sensitivity of the microbial tests, and the maximum values were always slightly higher for precipitation than for snowmelt. Contrary to the other compounds, 5Cl-BTR exhibited higher values (and well above the high-risk level) in the runoff from snowmelt samples. However, it is worth mentioning that this

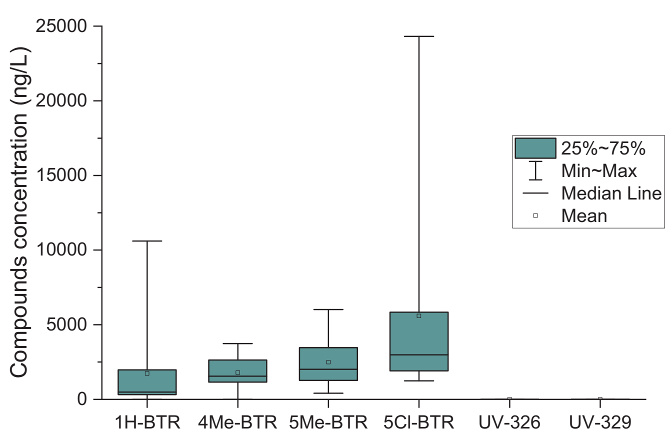

Fig. 4. Concentration profiles of benzotriazoles and UV stabilizers in rainwater collected from traffic routes during precipitation.

assessment was conducted only on *Daphnia* sp., in the absence of any data besides from the study of Giraudo et al. (2017). Moreover, there is a lack of data on temperature's effect on the transformation and toxicity of PAHs, including BTRs, although studies conducted on single invertebrate species tend to indicate that their toxicity increases with increasing temperature (Gan et al., 2021).

Analyzing the percentage share of risk quotients levels between all the sampling points provides additional information (Fig. 8). In one-third of the sites, the 1H-BTR risk qualified in the middle range for the runoff from rainfall and can be considered safe in the case of snowmelt samples. Regarding 4Me-BTR, 17% of the sites present a medium-risk level for snowmelt. Particular attention should be paid to 5Me-BTR and 5Cl-BTR compounds, as significant shares of their RQ_x classify at medium-risk and high-risk levels.

It is also conceivable that soil organisms living in urban areas in contact with paved surfaces from which rainwater is not effectively channeled (e.g., temporary yards, minor roads, railway tracks) may be exposed to such concentrations. Finally, a limited number of organisms, representing all trophic levels studied, primarily microorganisms but potentially vertebrates (*Mammalia*) as well, may occur directly in the sewer system itself and at the rainwater discharge/retention system or accumulate near the outlet of the sewer system at the receiving water body (e.g., *Actinopterygii*).

Bacteria are particularly susceptible to the adverse effects of chemical compounds as they are present in each of these environments. On the one hand, they have an extreme potential to reduce and transform pollutants and disseminate newly created mutations, and exchange genetic information

Table 4
Concentration profiles of benzotriazoles and UV stabilizers in rainwater collected from traffic routes during snowmelt.

Sampling point	Compounds concentration (ng/L)											
	1H-BTR		4Me-BTR		5Me-BTR		5Cl-BTR		UV-326		UV-329	
	Avg. Min Max	± SD	Avg. Min Max	± SD	Avg. Min Max	± SD	Avg. Min Max	± SD	Avg. Min Max	± SD	Avg. Min Max	± SD
L1	n.o.	–	n.o.	–	447.9 444.7 459.3	11.4	5254.6 5160 5329	94.6	n.o.	–	n.o.	–
L2	379.6 374.7 382.9	4.9	n.o.	–	339.2 324.5 344.7	14.7	891.0 885.1 893.6	5.9	n.o.	–	n.o.	–
L3	n.o.	–	n.o.	–	429.7 421.6 439.1	9.4	7369.1 7302.8 7396.2	66.3	n.o.	–	n.o.	–
L4	425.7 419.3 435.6	9.9	n.o.	–	n.o.	–	22,330.9 22,198.7 22,529.6	198.7	n.o.	–	n.o.	–
L5	n.o.	–	146.5 144.9 150	3.5	391.1 379.4 395.7	11.7	12,751.5 12,593.2 12,968.9	217.4	n.o.	–	n.o.	–
L6	363.6 358.8 371	7.4	128.0 123.7 135.9	7.9	n.o.	–	28,301.5 27,997.6 28,479.2	303.9	n.o.	–	n.o.	–
L7	753.8 748.7 762.5	8.7	3553.6 3526.3 3569.8	27.3	4578.4 4538.7 4603	39.7	36,132.0 35,828.5 36,509.4	377.4	n.o.	–	n.o.	–
L8	527.5 517.3 531.9	10.2	1924.6 1891.2 1942.9	33.4	2261.2 2238.3 2295.3	34.1	40,866.0 49,588.5 41,054.3	277.5	n.o.	–	n.o.	–
L9	n.o.	–	1075.3 1067.4 1100.9	25.6	1231.0 1201.2 1249.1	29.8	20,023.7 19,936.4 20,169.3	145.6	n.o.	–	n.o.	–
L10	n.o.	–	n.o.	–	213.8 213 216.4	2.6	46,985.6 4663.4 47,387.3	401.7	n.o.	–	n.o.	–
L11	594.2 590.7 605.5	11.3	2924.0 2901.2 2933.4	22.8	4248.7 4239.4 4266	17.3	14,263.4 14,049.1 14,429.6	214.3	n.o.	–	n.o.	–
L12	884.7 872,6 905.9	21.2	764.0 760.5 764.7	3.5	1320.9 1304.3 1349.5	28.6	44,233.0 43,729.3 4469.5	503.7	n.o.	–	n.o.	–

n.o. - not observed.

on resistance and degradation mechanisms horizontally. Stouten et al. (2000) summarized studies conducted on in vitro bacteria and mammalian cells assessing the genotoxic effects of benzotriazoles.

There is almost no information on the toxicity of chlorinated benzotriazole derivatives. The only source is a study by Giraudo et al. (2017) investigating the effects of 5Cl-BTR towards *Daphnia magna* in a 48-h acute test. The toxicity of this compound was much higher (LC_{50} = 28.73) than 5Me-BTR (LC_{50} = 50.89) or 1H-BTR (LC_{50} = 93.3); however, the analysis of differential gene expression showed that 5Cl-BTR down-regulates only 28 genes and up-regulates 8, while the rest of above mentioned BTRs changed the activities of several times more genes (even over a hundred). The quantitative analysis of chitinase expression also correlates with the reduction of molt frequency and has been proposed as a potential marker of 5Cl-BTR exposure. The present study results for the *Daphnia magna* with AF1000 indicated an RQ value close to high-risk for runoff from rainwater and displayed a considerable high-risk value when tested for snowmelt. This compound exhibits the highest RQ values in this research, which justifies further research in this direction.

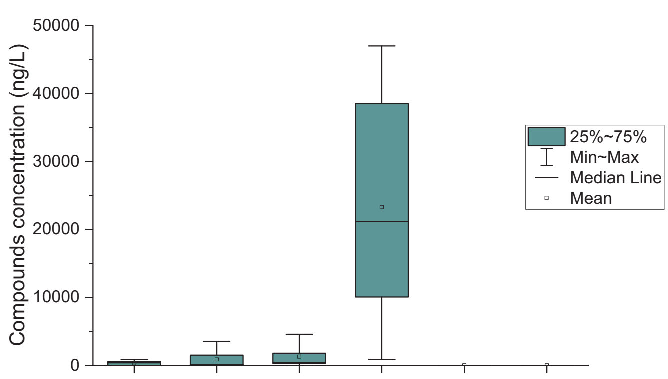

Fig. 5. Concentration profiles of benzotriazoles and UV stabilizers in rainwater collected from traffic routes during snowmelt.

This research also contributes to the literature related to the interaction of BTRs in mixtures of two or more elements. Using the 1:1 4Me-BTR and 5Me-BTR mixture as employed in Pillard et al. (2001), the results in Figs. 6 and 7 suggest that these calculations seem worthy of further discussion and studies assessing different proportions. For instance, the maximum RQ values for 4Me-BTR and 5Me-BTR obtained in this study equaled 0.0037444 and 0.0060236 in rainwater, while they were 0.0035536 and 0.0045784 for the snowmelt runoff, respectively. Thus, the 4Me/5Me ratio accounted for 0.62 in the first case and 0.78 in the second. As this ratio also varies between sampling sites and over time, and other compound occurrences are not considered, we do not know precisely how these combinations could affect various model organisms, which is an aspect to be considered in a follow-up paper. In this paper, we followed the assumption of using the sum of the maximum observed 4Me-BTR and 5Me-BTR concentrations and the toxicological data in Table 2 for these compound mixtures to estimate the environmental risk assessment. Both for precipitation and

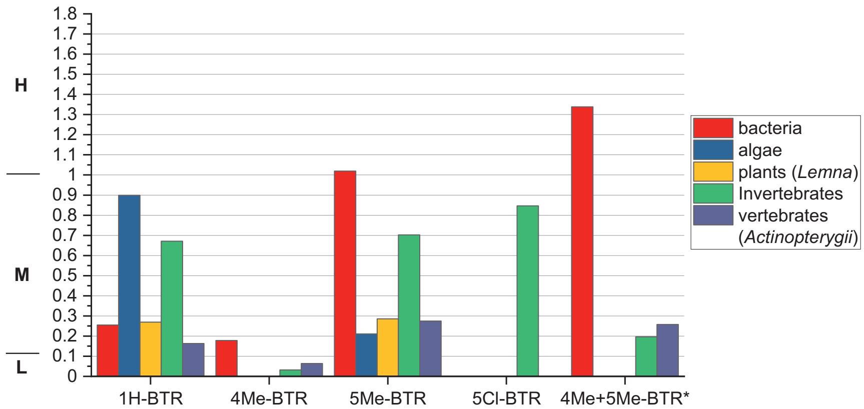

Fig. 6. Maximal RQ values (based on available literature) calculated from samples of rainwater runoff from paved surfaces in Białystok. Risk thresholds: (H)igh, (M)ean, and (L)ow.

snowmelt, *Allovibrio* (representing the decomposers) proved to be the most sensitive model, exceeding high-risk levels (>1.3 and >1.1, respectively). Also, risk assessment for the mixture is higher than the sum of risk assessments, and 5Me-BTR constitutes the main factor, which supports the claim that assessing toxicity assessing the interaction between BTRs derivatives in mixtures is a relevant research direction. Also, apart from water, the potential risk of BTRs in other aquatic ecosystems media, e.g., sediments, remains relatively unexplored (Careghini et al., 2015).

According to the authors (Franco et al., 2017), current regulatory practice for risk assessment of pollutants suffers from a lack of realism. Among the limitations of the approach used is the axiom of using acute toxicity laboratory data. This favors typical poisons in risk calculations, while substances with long-term effects, such as carcinogens, mutagens, hormone analogs affecting reproduction, etc., may be underrated. This problem stems from a preference for standardizing data sources rather than a case-by-case approach and may grow with increasing knowledge of the mechanisms of formation and degradation of micropollutants, some of which have the ability to bioaccumulate and biomagnify in the trophic chain. Therefore, also in the context of assessment methodology, a shift should be made from the dilution paradigm as the primary mechanism for reducing the environmental risk of pollution, to the "boomerang" paradigm rather (Newman and Unger, 2003).

Moreover, attention is drawn to the significant, even by several orders of magnitude, spatial and temporal variability of the real dilution of a pollution source in the environment, which implies the modification of the calculation methodology taking into account local geographic, populational (e.g. density), technical (the ability for partial removal, e.g. in slime separators), climatic (e.g. water availability, hydrological balance) or seasonal factors. For example, for central European countries, including Poland, Keller et al. (2014) suggest to use predicted values of annual median dilution factor between 10 and 40.

Therefore, when discussing the role of dilution on the real expected ecological threat, first of all, the specific conditions for the studied case must be characterized, which consist of: (1) the hydrological regime of the main receiving body of rainwater runoff, and (2) the land management of the Białystok. The main receiver of wastewater and rainwater from the city area is a small river *Biała* – its length is only 32.7 km, of which 20 km flow within the city boundaries (the catchment area is 133.4 km^2 and about 83 km^2, respectively). This causes the hydrological regime of the river to be strongly disturbed under the influence of urbanization - low flows dominate in the rainless periods, with the mean lowest (MLQ) placed at 0.53 m^3/s, and the lowest of the lowest (LLQ) reaching even 0.05 m^3/s. On the other hand, during precipitation and immediately after, as well as during the snowmelt, short-term peaks are observed, up to 21.5 m^3/s (HHQ). A significant ratio of this flow is represented both by treated wastewater and rainwater. Only the inflow from the municipal WWTP (PE ≈ 640 k including industry), can be about $Q_s \approx 0.81$ m^3/s, which is already a significant proportion of the mean annual flow (MMQ), placed at 1.2 m3/s (ratio 0.3). In turn, the total area of the city within its administrative boundaries is now 102 km^2, but due to the consistent development of all the land incorporated in recent years, the area impermeable to precipitation has increased dramatically. Currently, 49.2% of the catchment area is covered by the existing and planned stormwater drainage system, making a total of 5027.5 ha. Even if we conservatively assume for the calculations, the catchment area reduced by the runoff coefficient to 1603.9 ha, with an average annual rainfall of 715 L/m^2, another $Q_S \approx 0.36$ m^3/s of

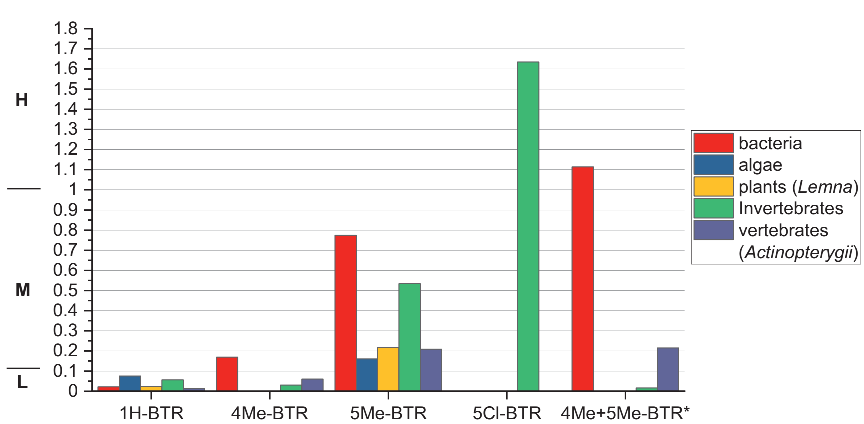

Fig. 7. Maximal RQ values (based on available literature) calculated from samples of snowmelt runoff from paved surfaces in Białystok. Risk thresholds: (H)igh, (M)ean, and (L)ow.

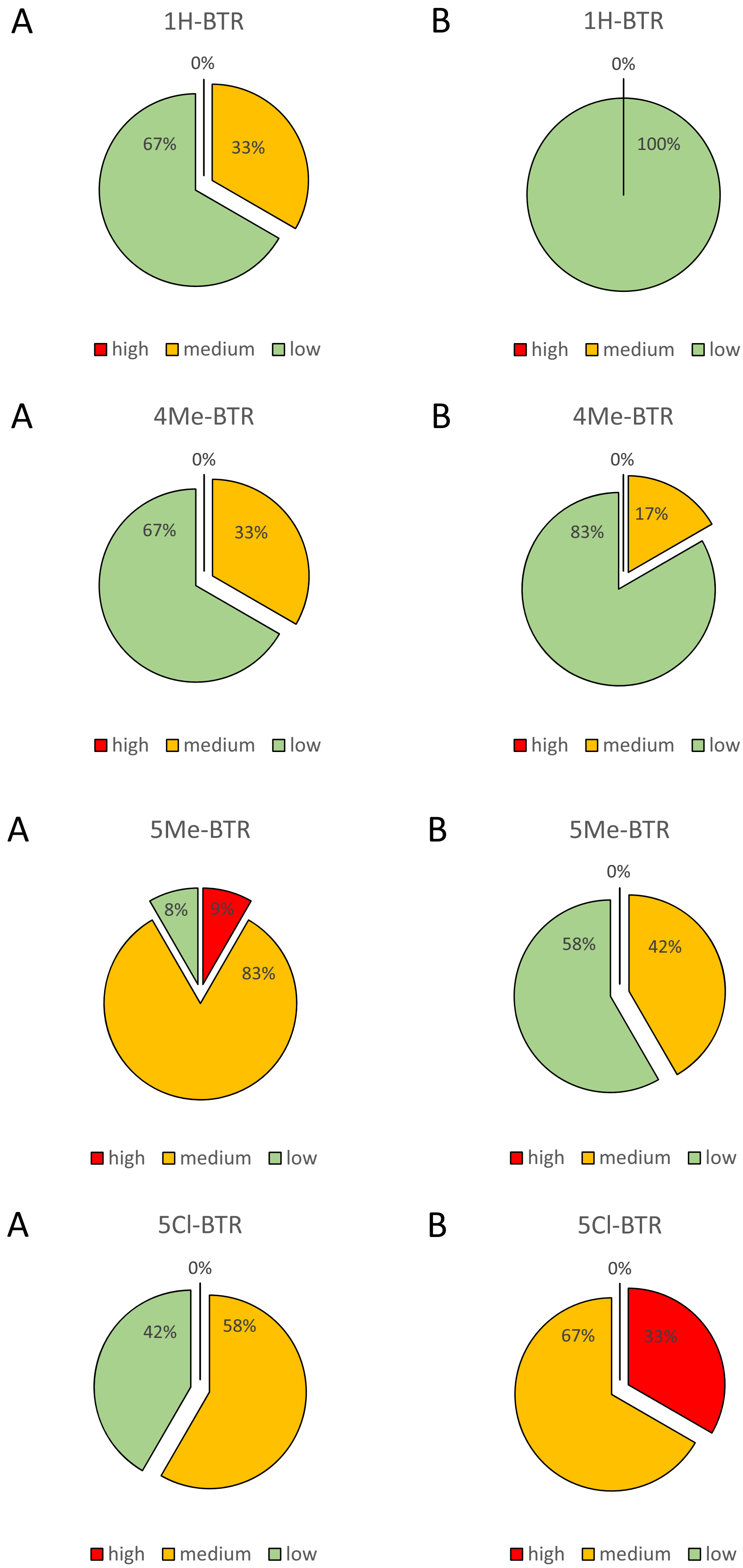

Fig. 8. Comparison of percentage share of risk quotients levels calculated for four BTRs in (A) runoff from rainwater and (B) snowmelt waters sampled in 12 points localized in the urban area of Bialystok.

theoretical average rainwater outflow to the environment is obtained. Thus, we are faced with a situation where, paradoxically, there are often the periods during the year, when it is not the runoffs carrying micropollutants being diluted by the water, but the riverine water is being diluted in the runoffs. In this case, even BTR concentrations of moderate risk should be considered as having a potential impact on ecosystem components.

4. Conclusions

Road traffic is one of the largest BTR emitters to the environment. These emissions are uncontrolled and unmonitored; thus, they are directly discharged into human habitats and crucial water resources. This paper quantitatively and qualitatively assessed the environmental risk resulting from four low molecule benzotriazoles (1H-BTR, 4Me-BTR, 5Me-BTR, 5Cl-BTR) and two benzotriazole UV stabilizers (UV-326, UV-329) in runoff produced from rainwater (first series of experiments) and snowmelt (second series of experiments) in the urban environment. The case study corresponds to Białystok, a Polish metropolitan area encompassing 102 km^2 and 300,000 residents.

Dangerous micropollutants were present in all of the analyzed water samples, and the comparison of both series shows a constant and dynamic renewal of the micropollutants loads accumulated on impervious surfaces. Even if it is difficult to accurately determine the source/origin of the detected pollutants, the results suggest that it is possible to correlate them with the type of cover, traffic intensity, and type of vehicles. In general terms, samples from rainwater runoff displayed higher pollutant concentrations and RQ_x than those from snowmelt. BTR group UV stabilizers are insoluble in water, and that might have avoided their detection following the procedures described in the Methods section.

The environmental risk assessment in this research uses conventional acute and, more rarely, chronic toxicity indices (EC, LOEC), following the regulations specified in EMA (2006). The main advantages of this approach are the relatively low cost of obtaining a minimum sample size, allowing statistically significant differences to be obtained even for data with low strength of dependence, the simplicity of performing the test, and the possibility of replicating the procedure if different laboratories. The number of data collected and the ease of their statistical processing also allow comparing many substances of similar origin or use, their derivatives and transformation products, and they make it possible to compare data obtained many years ago with new data.

The scientific community agrees that there are still significant knowledge gaps regarding the acute risks or chronic toxicity of BTRs derivatives, which commonly have the potential to accumulate in the environment. Moreover, with the development of knowledge and research techniques about these compounds, there are also new possibilities to determine the adverse sublethal effects of pollutants on organisms, which include: changes in the production rate of specific metabolites, genetic expression expressed by RNA transcription or protein translation, and changes in the structure of the genetic material itself (genotoxicity). These advances would also help in the risk assessment of the sublethal effects of micropollutants characterized by low toxicity in classical terms, as in the case of BTRs, but whose chronic effects may affect the endocrine system and reproductive processes, the process of embryonic development, or DNA damage.

Based on the results, the authors conclude that intake water, tap water, wastewater, and treated wastewater must be tested to detect and monitor the residence time of the pollutant loads. Besides the discussed potential research directions that involve assessing the effect of proportions and interactions in the mixtures, future research on BTRs should include developing effective methods for removing these micropollutants in water treatment plants and from the polluted environment and water resources.

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CRediT authorship contribution statement

Joanna Struk-Sokołowska: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Joanna Gwoździej-Mazur:** Conceptualization, Investigation, Formal analysis, Writing – original draft. **Łukasz Jurczyk:** Methodology, Data curation, Writing – original draft. **Piotr Jadwiszczak:** Data curation, Writing – original draft, Writing – review & editing. **Urszula Kotowska:** Methodology, Investigation. **Janina Piekutin:** Writing – review & editing. **Fausto A. Canales:** Formal analysis, Writing – review & editing. **Bartosz Kaźmierczak:** Conceptualization, Investigation, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.156246.

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