EVALUATION OF POLYCICYCLIC AROMATIC HYDROCARBONS IN WATER AND MICROPLASTICS.

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ABSTRACT

Polycyclic Aromatic Hydrocarbons (PAHs) are a group of environmental contaminants, classified as potentially toxic, mutagenic and carcinogenic, being an important public health concern. In the present study, we assayed different samples of water (superficial water, groundwater and tap water) for five PAHs: pyrene (Pyr), 1-chloro-pyrene (1-ClPyr), 1-bromine-pyrene (1-BrPyr), benzo-a-anthracene (BaA) and 7-chloro-benzo-a-anthracene (7-ClBaA) by gas chromatography - mass spectrometry (GC-MS) after sample concentration by solid phase microextration. The most abundant PAHs was Pyr. Taken this in account we performed a study to evaluate Pyr adsorption by PET (polyethyleneterephthalate), HDPE (high density polyethylene), LDPE (low density PE), PP (polypropylene) and PS (polystyrene) particles with circular shape of 4 mm diameter (microplastics) dispersed in freshwater. Our data showed that, all types of plastic adsorbed Pyr withouth any statiscally significant difference. This process enhances Pyr stability contributing to its persistence /accumulation in the environment and consequent toxicity through the trophic chain.

Keywords: Polycyclic aromatic hydrocarbons (PAHs); pyrene (Pyr); microplastics.

1. INTRODUCTION

Polyciclic aromatic compounds (PAHs) are a group of persistent organic pollutants, formed by two or more fused benzene rings, widely distributed within the environment representing an ecological and public health concern. These pollutants arise from natural (e.g., forest fires, volcanic eruptions, etc) and anthropogenic processes (e.g., burning of fossil fuels and wood, production of charcoal, petroleum refining, petroleum spills, etc) (Billiard et al., 2007) and can move between environmental compartments (Tidwell et al., 2017). Wind and rain are responsible for the transportation of PAH from the atmosphere to different terrestrial or aquatic biospheres (Azhari et al., 2011) as shown by the detection of these compounds in remote areas (Guzzella et al., 2016).

In southern European countries several demographic factors such as the decline of population density in inland regions, the abandonment of farming activities led to forest expansion. On the other hand, the climate changes with less rainfall and atmospheric temperature increase increased the risk of ignition resulting in a higher incidence of forest fires. In Portugal, the incidence of wildfires has been increasing overtime and affecting both air (Vicente et al., 2013; Vicente et al., 2017) and water quality (Mansilha et al., 2014) due to a more intense emission of trace gases and particles to the atmosphere. The physicochemical characteristics of these compounds favours its accumulation within the soil and sediments, which could later release the PAHs to the water or other living organisms.

Water pollution resulting from domestic and industrial use of non-biodegradable materials such as plastics is a major concern. Most plastics are only fragmentable giving rise to small fragments that will persist within the environment and interact with all elements that make up the ecosystem. To date, research has focused largely on the pollution of the oceans with plastics, but the impact of this of pollution on freshwater bodies and soils is as large or as relevant.

In the present work, we focused on water contamination by PAHs in water samples of different origins. Since pyrene was detected in several water samples, we decided to follow the possible role played by different plastics in the persistence of this pollutant in the environment.

2. RESULTS AND DISCUSSION

First 20 samples of water samples from different natures (superficial marine or freshwater, groundwater and tapwater) and origins were assayed for five PAHs: Pyr, 1-ClPyr, 1-BrPyr, BaA and 7-ClBaA (table 1). Pyr, one of the 16 priority pollutants assigned by the US Environmental Protection Agency, was found in 4 samples of waters with different natures (superficial marine and freshwater, groundwater and tap water) and origins in concentrations above the detection limit (8 ngL^{-1}) but under the quantification limit (25 ngL^{-1}) of the GC-MS method. The chlorinate derivative (1-ClPyr) was either absent or under the detection limit of the method in all samples (table 1). This result is in good agreement with previous studies showing that Pyr is among the most abundant PAHs in water samples of different natures (WHO, 1998; Zhang et al., 2016; Li et al., 2017). The detection of these pollutants in water raises ecological and public health concerns especially in water reservoirs used for capitation of water for human use. In this study all the superficial freshwater samples with exception of the sample positive for Pyr collected in Setubal (38°22'54.6''N 8° 28' 15.9''W) were collected in dams with water collection points for human consumption. In addition, a groundwater that might be used for human consumption and a tap water sample were positive for this PAH. Despite the low levels of Pyr the ability to concentrate in lipophilic compartments represents a threat to human beings health in the long run. This concern was expressed by the World Health Organization taking into account the toxicity of individual PAHs in water and the total uptake estimated on a water consumption of 2L per day (WHO, 2010). Ingestion of water and food contaminated with PAHs is only one of the possible routes of human exposure to these pollutants, being inhalation of air and dust and dermal contact other possibilities (Menzie et al., 1992). The exposure by dermal route might be a concern in the case of marine superficial samples collected in beach areas, such as the one in the present study. Setubal bay presents the duality of being located in the Nature Park of Arrabida, housing some of the beaches most frequented by the inhabitants of Lisbon and near sea routes to fishing ports (Setubal and Sesimbra) and other commercial ports located in Lisbon and Sines. Another possible route for human exposure is by ingestion of contaminated food, namely seafood. The high lipophilic character of PAHs favours its bioaccumulation in species living in the environmental compartments polluted with these compounds. For this reason, several organisms such as mollusks, crustaceans and fish were referred by the WFD as ecological and chemical indicators of water bodies (EU, 2008; EU, 2013). Our concern is supported by the data reported by others showing occurrence of persistant organic pollutants in biota that are part of human diet in Portugal (Ribeiro et al., 2016) and other countries (Loh et al., 2017).

Table 1. PAHs in water.

GPS coordinates	District	Sample	Pyr	BaA	1-BrPyr	1-ClPyr	7-ClBaA
41°22'42.2"N 6°21'05.2"W	Bragança	Superficial	-	-	-	-	-
41°05'10.1"N 8°07'53.2"W	Porto	freshwater	-	-	-	-	-
40°20'16.7"N 8°11'36.9"W	Coimbra		-	-	-	-	-
41°39'10.3"N 8°13'50.6"W	Braga		-	-	-	-	-
41°35'24.5"N 8°07'56.6"W	Braga		-	-	-	-	-
40°02'53.6"N 7°00'55.4"W	Castelo Branco		-	-	-	-	-
38°22'54.6''N 8° 28' 15.9''W	Setúbal		+	+	+	-	-
38°24'15.1"N 7°22'36.6"W	Évora		-	-	-	-	-
38°11'51.0"N 7°29'45.2"W	Beja		-	-	-	-	-
38°41'59.6"N 9°10'35.6"W	Lisboa	Superficial	-	-	-	-	-
38°41'31.0"N 9°25'08.7"W	Lisboa	marine	-	-	-	-	-
38°30'04.3"N 8°55'24.8"W; 38°28'54.8"N 8°49'16.9"W	Setúbal*		+	+	-	-	-
38°22'54.7''N 8° 28' 15.0''W	Setúbal	Groundwater	+	-	-	-	-
38°08'38.1"N 7°26'58.9"W	Beja	Tap water	+	-	-	-	-

* Seven samples were collected between these two GPS coordinates. PAHs concentrations in the sample were bellow (-) or above (+) the detection limit (0.008 μgL^{-1}). Quantification limit 0.025 μgL^{-1}

Another aspect that might contribute to enhance Pyr toxicity to human beings is its concentration in micro and nanoplastics that could enter the throphic chain by ingestion and progress/ accumulate throught it. In order to explore this hypothesis we evaluate the ability of PET, LDPP, HDPP, PP and PS to adsorb Pyr from freshwater over a period of 3 and 30 days (Fig.1). After 3 days in contact with 100 μg/L Pyr, was possible to recovered from the microplastics at least 10 μg/L of this PAH. No significant difference between the five plastics for Pyr adsorption was identified. In order to explore the possible accumulation of Pyr in the plastic particles overtime we determined Pyr concentration after 30 days. At a first glance, the results presented in figure 1 seemed to contradict our hypothesis. Nevertheless, when we take in to account that Pyr halflife in the water is approximately 16 days this scenario changes. In fact, the ratio between the expected Pyr concentration at 3 and 30 days based on the halflife and the Pyr concentrations recovered from the plastics was smaller for all plastics except PET. This result shows that Pyr adsorption to the majority of the tested plastics enhanced its persistence in the environment.

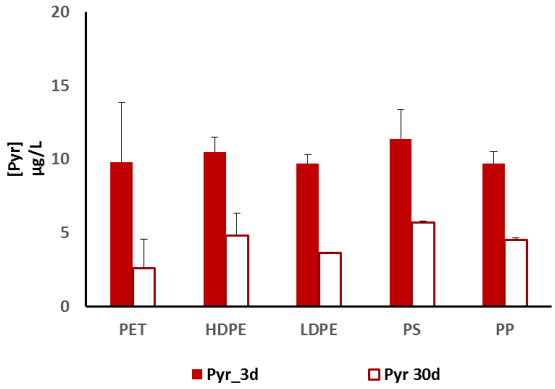

Fig. 1. Pyr recovered from microsplastics.

3. CONCLUSIONS

The present work show that Pyr is a persistent pollutant present in different water samples (superficial marine and freshwater, groundwater and tap water). Futhermore, a synergistic relation between Pyr and microplastics was identified that could extend the persistence of Pyr in the environment with hazardous impact on the ecosystem.

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