Optoelectronic investigation for determination of plastics polymers behavior in surface water

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The increase in synthetic plastic production and the poor management of plastic waste have led to an increase in discharge into our aqueous environment. In this paper we aim to test optoelectronic methods (fluorescence spectroscopy, enhanced darkfield hyperspectral microscopy, spectrophotometry and dynamic light scattering) for the characterization of plastic polymers (polypropylene PP) in surface waters (Carol Lake, Ciorogarla River) and their influence on organic matter. The results obtained showed that these methods could be used for a general assessment of the impact of plastic polymers on aquatic components, being more suitable for samples that have been previously contaminated with microplastics.

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1. Introduction

Called the "great invention of the twentieth century", plastic is currently causing damage to the environment due to improper management of plastic products. [1]. Globally, the latest statistics from 2018 found that plastic production reached 359 million tons [2] and up to 13 million tons of them were discharged into oceans, so that by 2025 a total of 250 million tons of plastics are expected to be discharged [3]. Plastics are a wide range of highly synthetic and semi-synthetic materials that can be machined into a multitude of solid objects. Approximately 40% of plastic production comes from the packaging industry, 19.7% for construction materials, 10% car parts, 6.2% electronic components, 4.2% household and sports equipment, 3.3%, the rest being used for medical, furniture, mechanical engineering, etc. Most of these products are discarded immediately after use. In Romania, over 50% of plastic wastes are deposited at the landfills, which favors environmental pollution [4].

In the environment, plastics polymers can degrade into smaller and smaller fractions, down to nanometer size, which increases their potential to be incorporated by organisms. Due to the high production and the single use nature of several plastic products, small plastic polymers have become ubiquitous. Furthermore, water currents and winds can carry plastic polymers far from their place of origin and affect the biota in different environmental compartments [5]. ECHA (European Chemicals Agency) defines microplastics (MPs) as any (synthetic) polymer or solid or semi-solid particles that contain polymers that are not liquid or gaseous and have a size of less than 5 mm in at least one external direction. The presence of microplastics has been reported for air samples, food and drinking water [6].

In general, plastic waste is released in larger quantities in urban areas compared to rural ones and thus, the risk of contamination is higher [7, 8]. Worryingly, plastics that end up in aquatic environments in the form of MPs are difficult to detect and very difficult to remove. Also, plastic polymers that are not removed by wastewater treatment, end up in surface waters due to their low density [9]. Currently, there is no standardized test method for the analysis of MPs in water. The most used methods of analysis are: fluorescence spectroscopy, imaging coupled with Raman and FTIR spectroscopy, mass spectrometry-gas chromatography, bioanalysis, and electron microscopy (in transmission or scanning) [10]. These optoelectronic methods are often used in several scientific fields for the characterization of bioactive materials [11], in medicine [12], in restoration and conservation interventions [13] etc. They have good sensitivity and high specificity, but also have many limitations such as: long analysis time, or limiting the particles to a minimum size of 1 μm. In addition, plastics can also contain catalysts, stabilizers, antioxidants, and antistatic, processing agents, lubricants and dyes. They can also alter the quality of the water. Moreover, other water contaminants can adsorb on the surface of polymers, altering their properties. On the other hand, MPs change their characteristics depending on the physical, chemical and biological processes in the environment in which they are located. Once in a certain environment, MPs can aggregate with each other or with other nanoparticles, changing their surface / volume ratio. In addition, MPs can undergo biological and chemical transformations that further affect the properties, transport, and toxicity of particles [14]. Therefore, it is necessary to characterize plastic polymers using as many optoelectronic methods as possible, both to identify an optimal analysis technique

and to gain a better understanding of the behavior of plastics in the environment.

The aim of these studies is to test other optoelectronic methods for particle characterization in water, as well as their influence on organic matter. In this sense, samples from two surface water systems (Carol Lake and Ciorogarla River) from the urban and peri-urban environments have been exposed for several weeks to polypropylene. The following combination of optoelectronic techniques has been used for sample characterization: fluorescence spectroscopy, enhanced darkfield hyperspectral microscopy, spectrophotometry and dynamic light scattering (DLS).

2. Methodology

The present preliminary experiment involved the collection of water samples and the performance of tests in the laboratory, in a controlled environment, following their contamination with a predetermined amount of plastic. The type of plastic polymers chosen for this series of experiments was polypropylene (PP) which presents an increased risk of contaminating natural aquatic environments, being the most commonly used polymer in the European market [4]. Used in the manufacture of biscuit packaging, drinking straws, kitchen utensils, as well as food containers, medicines and microwave ovens, polypropylene (PP) is part of the non-recyclable plastics category.

Packing bags were used for the experiments presented in this study. The protocol implemented for the experiments performed in the laboratory is shown in Fig. 1.

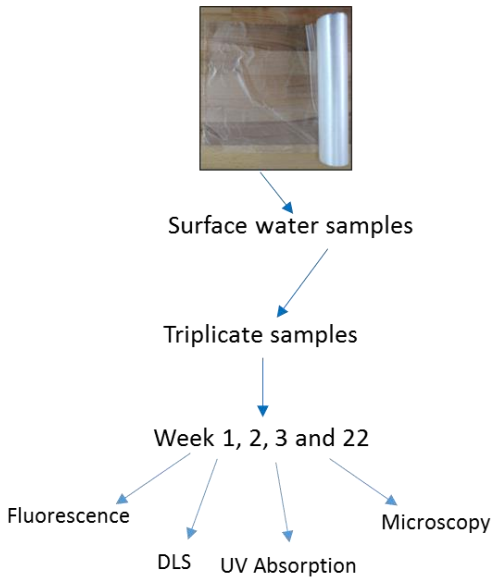

Fig. 1. Protocol implemented for the experiment

Approximately 2 L of water were taken from Carol Lake and Ciorogârla River, in sterile PET containers. The samples were processed in laboratory within a maximum of 8 hours of collection. We consider that the impact of the plastic from the collection container on the water sample is insignificant, the contact time being reduced. Carol Lake was chosen as the collection point, as recent studies [15], showed that this lake has the highest amount of microbial organic matter among the lakes in Bucharest. The collection point for Ciorogarla River was at the Southern limits of Magurele City, Ilfov. Each PP packing bag (0.2 g) was cut into pieces of about 1 cm^2 and added to three identical glass containers with a screw-on lid containing 50 mL of water. The samples were kept at room temperature, away from direct light sources. Measurements were performed at weeks 1, 2, 3 and 22 after plastic contamination.

The first optoelectronic method implemented in the study was fluorescence spectroscopy. Fluorescence spectra were recorded with a Aqualog (Horiba JY, Japan) spectrofluorimeter, equipped with a 150 W Xenon lamp and CCD detector. The following parameters were used for the Aqualog system: excitation and emission wavelengths 200-800 nm, step 3 nm, integration time 0.4 s, measurement temperature 20 ° C, distilled water blank correction. Fluorescence spectroscopy is an optoelectronic method and a very useful tool for examining the excited states of molecules and deactivating their excess energy by emitting photons. Fluorescence spectroscopy can provide insights into the interaction of light with organic matter to track important processes in several areas. One of them is the investigation of the conversion of light energy into electricity in photovoltaic and optoelectronic devices sensitized to organic dyes. In medicine, fluorescence spectroscopy can be very useful in diagnosing cancer cells. Also, dynamic and light-induced inter and intramolecular deactivation processes in molecular systems can be followed by this technique [11, 12, 13].

The water Raman peak was recorded before each set of measurements in order to test the stability of the instrument. The Raman signal showed the value of 2,590 au, SD = 13. The samples were filtered with single-use 0.8 µm pore CME filters to reduce the amount of particles that can affect the fluorescence signal. The Raman scatter line can be used to check for instrument stability and to quantify the degree of contamination from a water sample by using the normalised fluorescence intensity to the Raman peak. The advantages offered by the Raman line are: (a) the independence of the chemistry since it measures the properties of the solvent; (b) the ease of application and sensitivity; (c) versatility since it can be applied at any wavelength between 200 and 500 nm. In the case of water, the Raman line offers the advantage that it is very stable, appearing in the spectrum at the same offset from the excitation wavelength.

The hydrodynamic particle size and Zeta potential were measured using a Zetasizer ZS90 system (Malvern, UK), equipped with a 633 nm, 4 mW wavelength laser and APD detector. The measurements were performed at the standard temperature of 22 ° C and by automatically setting the scattering angle. The samples were not filtered because the system does not allow the measurement of a small number of particles. Zeta Potential is an important

tool and a modern optoelectronic technique for understanding the state of the nanoparticle surface and predicting the long term stability of nanoparticles.

The absorption spectra were recorded using the NanoDrop One Microvolume UV-Vis Spectrophotometer (Thermo Scientific USA), equipped with a Xenon lamp, in the spectral range 190-850 nm, blank correction. The samples were filtered with CME filters with 0.8 µm pore size.

For enhanced dark field hyperspectral microscopy, the Cytoviva (USA) system was used, equipped with an Olympus microscope, 10x, 60x and 100x objectives, and VNIR detection (400-1,000 nm). Two or three drops of sample were placed on the slides and allowed to dry completely, after which they were covered with slides. Dark field microscopy directly detects scattering from a sample by rejecting excitation light. This optoelectronic technique has been extensively used for spectral characterization of nanoscopic particles.

3. Results and discussion

Fluorescence spectra were analyzed using the "peak-picking" method [16]. Four peaks were identified: peak B (($\lambda_{excitation}/\lambda_{emission}$ = 230 & 275/305 nm), peak T (($\lambda_{excitation}/\lambda_{emission}$ = ~240 & ~280/~340 nm), peak C (($\lambda_{excitation}/\lambda_{emission}$ = 300-350/400-500 nm), and peak A (($\lambda_{excitation}/\lambda_{emission}$ = 260/400-500 nm). In general, fluorescence peaks B and T indicate a possible microbial contamination of the water sample [17, 18] and are associated with dissolved organic matter (DOM) from domestic sources [16]. Computational chemistry has shown that peaks B and T are represented by compounds with at least one aromatic ring [19], which may include: phenols and indoles derived from plants and algae; amino acids and DNA from proteins; lignin derivatives and plant flavonoids; polyaromatic hydrocarbons and active pharmaceutical compounds from industrial or household waste; detergent bleaching agents [19,20]. Peaks A and C show the presence of compounds with two or more aromatic rings and may indicate a number of fluorophores: humic substances from soil or plants; plant-derived lignin; quinones from microorganisms, fungi and plants; plant alkaloids; polyaromatic hydrocarbons from industrial or household waste [19, 20]. Peak A represents highly processed, biorefractory DOM, of terrestrial origin. Peak C contains a mixture of allochthonous and autochthonous DOM, less processed than that of peak A [21].

Fig. 2 shows the evolution of the fluorescence peaks for samples from Carol Lake and Ciorogarla River with the Aqualog spectrofluorimeter.

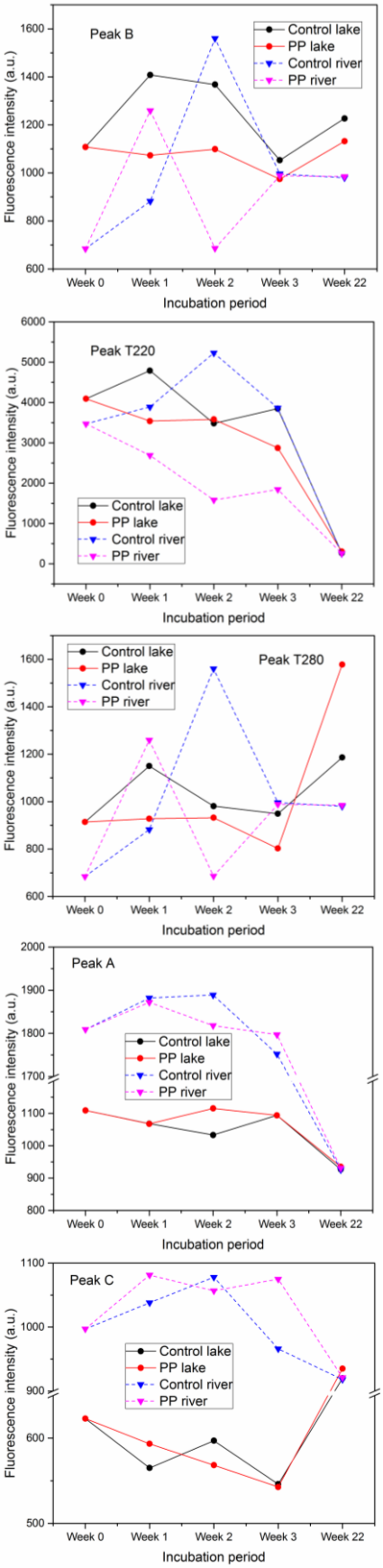

Fig. 2. Evolution of fluorescence peaks for samples from Carol Lake and Ciorogârla River contaminated with PP (color online)

Control samples showed an increase in peaks B, T220 and T280 in the first two weeks of the experiment, in the case of Carol Lake, and only in the first week, in the case of the Ciorogarla River. This tendency is determined by the increase of the metabolic activity of bacteria in water [22], which leads to the release of fluorescent derivatives such as proteins, amino acids, indoles, etc. After two weeks, the metabolic activity decreases significantly, depending on the amount of microbial matter in each sample. On the contrary, peaks A and C showed a gradual decrease in the first weeks of the experiment, followed by a sudden increase until week 22. Recent studies have shown that microorganisms contribute to the consumption and formation of reprocessed and / or refractory organic matter [22]. These processes would explain the fluctuation of peaks A and C for the control samples. Different values of the peaks' fluorescence intensity were observed in the plastic samples compared to the control samples, but the tendencies on the time scale are generally similar (Fig. 2). Peak B showed higher values in all plastic samples added to the water in Carol Lake than in the control sample. PP could increase this peak due to the release of toluene. Previous studies have shown that toluene can migrate from plastic bags composed of PP [23, 24]. However, the migration rate of toluene depends on the type and concentration of solvent used, which could explain the presence of small amounts of contaminant in the water samples. PP can also release methanol if this substance has been used in the production process of PP [25]. Furthermore, phenolic derivatives emit a fluorescence signal in the spectral range of the peak B [26]. The fluorescence of peak B decreases in the first weeks of the experiment possible due to the migration of toluene to the water surface or the degradation of methanol by the microorganisms present in the sample. Phenolic compounds, on the other hand, are severely degraded in the environment and inhibit the growth of microorganisms in water [27]. This could explain the reduction in fluorescence intensity of T220 and T280 peaks associated with microbial activity in plastic samples. Peaks A and C generally show the same upward trends in plastic samples compared to the control sample. The results show that plastic-derived substances could affect the metabolic activity of microorganisms in water, influencing the formation of reprocessed and refractory organic matter.

Absorption spectra confirmed the presence of substances migrating from plastic to water samples (Fig. 3). The samples from Carol Lake with plastic showed a higher absorption, at 254 nm wavelength, compared to the control samples, possibly due to the migration of oligomers and antioxidants from plastic. Instead, the samples from the Ciorogârla River, with added plastic, showed lower values of absorption at the two wavelengths, compared to the control sample. The results show that the substances released from the plastic behave differently depending on the composition of the organic matter in the water sample.

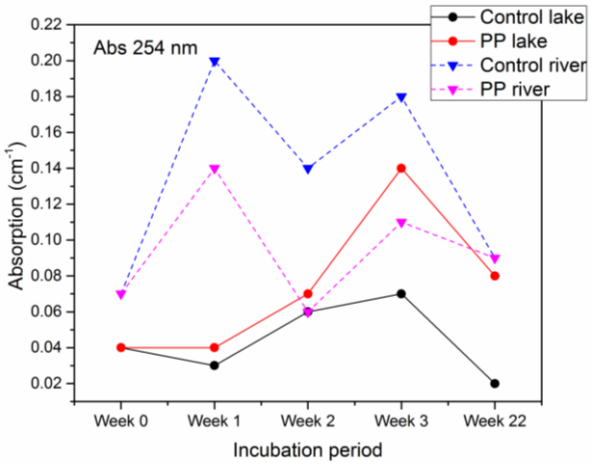

Fig. 3. Absorption spectra of lake and river samples with added plastic (color online)

To study the hydrodynamic diameter of the particles in the studied samples we used the method of dynamic light scattering (DLS). Fig. 4 shows the results obtained for the water samples from Carol Lake and those with water from the Ciorogarla River. Water samples from Carol Lake showed, in the first three weeks after plastic contamination, higher values than those recorded for control samples, but in week 22 control samples recorded the highest values. In contrast, for Ciorogarla River samples, the values during the first three weeks of contamination measurements were lower than those of the control samples. The evolution of particle size in the case of water samples taken from Carol Lake shows an influence of substances that migrate from plastic on organic matter by modifying the aggregation processes of suspended particles. Recent studies [28] have shown that suspended particles, with an average size of 300 nm, present in lake environments are characterized by a very low tendency to form agglomerations. However, the presence of plastic migrating substances favors the agglomeration and sedimentation of particles, the results being confirmed by measuring the zeta potential (<-20 mV). In the Ciorogarla River samples, the decrease in particle size probably reflects the degradation of microorganisms by plastic migrating substances.

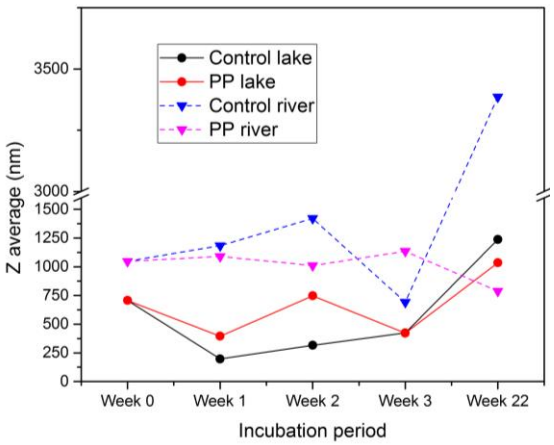

Fig. 4. Hydrodynamic diameters of particles in water samples (color online)

Microscopy images showed water, particulate matter and biological matter, as well as spores and bacteria of various forms (spindle bacilli, coccus, and spirilium) at the control samples (Fig. 5). It has been observed that water samples with added plastic show a relatively higher number of particles from the first week. In the following weeks of the experiment, the particles agglomerate and towards week 22 only debris could be observed in the samples. Degradation of biological matter in plastic samples was also observed. The results of the particle analysis with the DLS system and enhanced darkfield microscope confirm the fluorescence and absorption data.

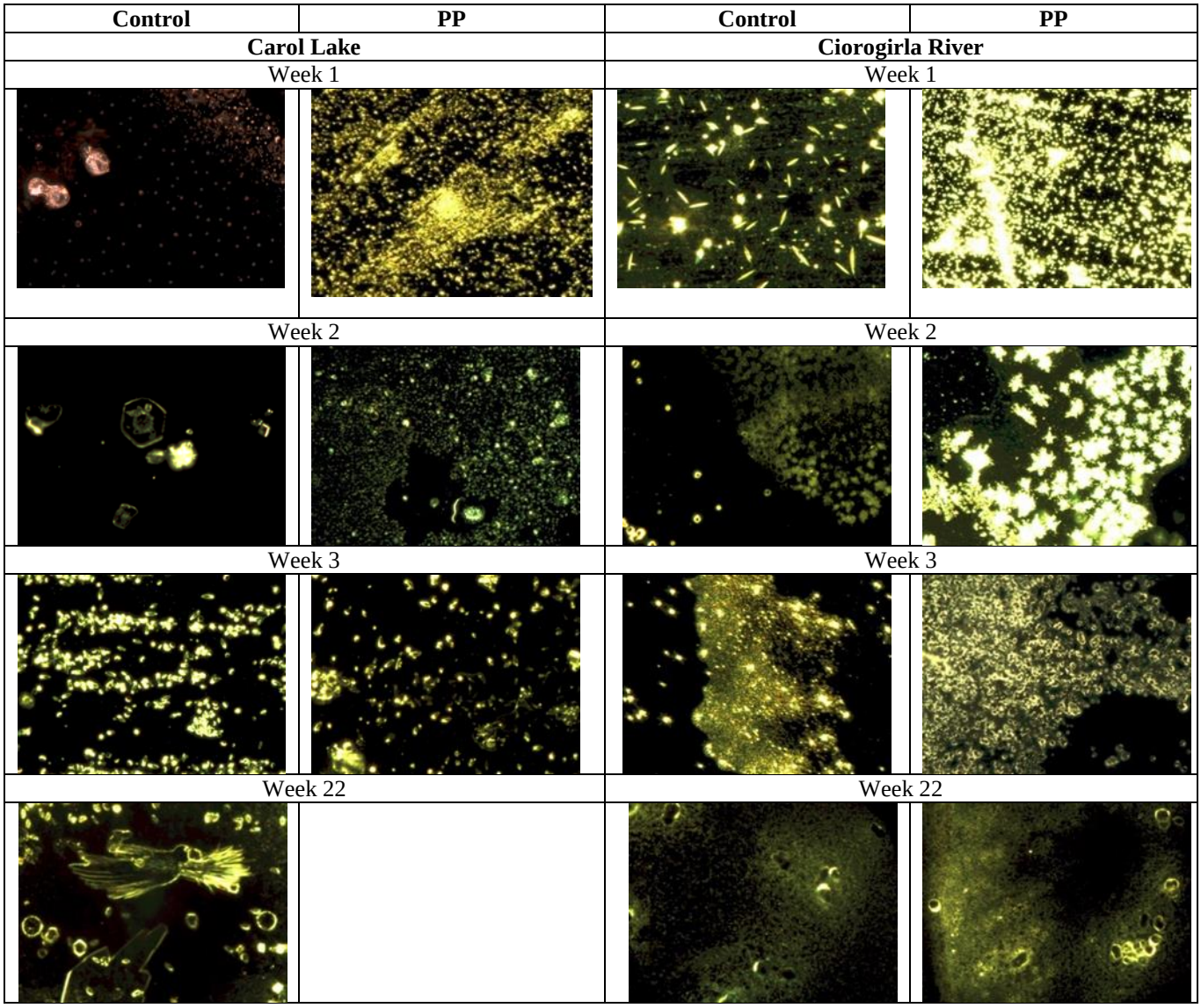

Fig. 5. Microscopy images on water samples from Carol Lake and Ciorogarla River

4. Conclusions

To identify an effective method for detecting plastic particles and substances migrating from plastic in aquatic systems, a number of optoelectronic characterization techniques were used. Fluorescence spectroscopy showed a clear influence of migrating plastic substances, such as toluene, phenols, styrene or methanol on organic matter, by degradation of microorganisms and the possible formation of complexes, over a period of 22 weeks of exposure to PP. These results were also supported by data obtained by DLS, which showed a marked change in the particle size and aggregate formation at the samples subjected to plastic exposure. All these results lead to the conclusion that these optoelectronic methods could be used for an overall assessment of the impact of plastics on aquatic components, being more appropriate for samples where a prior contamination with plastic is known.

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