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Degradation of Bisphenol A in Natural and Artificial Marine and Freshwaters in Turkey

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Abstract

Bisphenol A (BPA), one of the important synthetic chemicals, has been produced at high volumes since the 1960s. These chemicals are commonly detected in the marine and freshwater environments; however, their transformation in aquatic environments depends on many parameters. This study aims to investigate the degradation of BPA in marine and freshwaters under different conditions in terms of microbial degradation, photodegradation, and temperature effect. The results showed that BPA content in samples prepared from the artificial waters did not change significantly in 150 days. BPA concentrations in natural river water started to degrade after day 50, and the degradation rate was faster for the samples at 25°C than ones at 4°C. In natural seawater samples, there was no degradation detected in 150 days at 4°C and 25°C. However, samples prepared in natural seawater, kept outside, and exposed to over 40°C temperature showed degradation after day 50. A treatment exposed to the sunlight showed a higher degradation rate, indicating the additive/synergistic role of the photodegradation. Our study suggests that high temperatures (> 25°C) are required for BPA degradation in seawater. River water is more potent than seawater for BPA degradation. It is suggested that BPA contamination in a marine environment could be more persistent than in a freshwater environment.

Keywords Bisphenol A · Degradation · The mediterranean sea · Half-life

Bisphenol A (BPA) is an endocrine disrupting chemical that can be found all over the world. It is one of the most important synthetic chemicals as it has been produced at high volumes since the 1960s (Staples et al. 1998). Due to the high production volumes and disposal of products made from BPA, polycarbonate plastic and epoxy resins, BPA has entered terrestrial and aquatic environments. Due to the widespread use and inefficient disposal of these products, BPA is released into the environment, mainly through processing of BPA in manufacturing, inefficient/no removal during wastewater treatment, landfill leachates, and leaching from discarded BPA-based materials (e.g., hydrolysis of polycarbonate, recycled paper). When BPA reaches aquatic environments, it does not stay as BPA for long – instead, it transforms through phytodegradation, photodegradation, bacterial degradation, fungi degradation, and reactions with reactive minerals (Im and Löffler 2016). The biotransformation of BPA is performed by vertebrates, invertebrates, and plants (Michałowicz 2014). A variety of biotic and abiotic processes that contribute to BPA transformation and degradation have been documented in the laboratory (e.g., Roh et al. 2009; McCormick et al. 2011; Sun et al. 2012).

In establishing chemical environmental safety, a hazard assessment using environmental exposure and effects information is required. Many bacteria are capable of degrading BPA in aquatic environments but differ in their potential for biodegradation (Im and Löffler 2016). It may not be possible to determine the chemical's fate unless site-specific conditions are present in the experimental test environment. Considering distinct microbial communities and other physicochemical properties of waters, BPA degradation should be investigated in different regions to better understand the global fate of the compound. For this purpose, ultraoligotrophic northeastern Mediterranean Sea, with its indigenous microbial communities, was selected to study BPA degradation under different abiotic and physicochemical conditions to evaluate the regional capacity for BPA degradation.

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Materials and Methods

To monitor the amount of degradation of the BPA, natural and artificial seawater and river water were used (Table 1). Natural seawater and river water were collected from the Mediterranean Sea and Göksu River, respectively. Artificial seawater and river water were directly prepared from Milli-Q water. For the artificial seawater preparation, there was an addition of 35 g/L NaCl and 200 mg/L $NaHCO_3$ into the water. All waters were aliquoted into 500 mL polypropylene plastic bottles and spiked with 100 µg/L BPA. They were kept at 4°C and 25°C, except for one natural seawater treatment; those bottles were kept outside – half in a dark box, the other half in direct sunlight. Samples were taken at days 0, 6, 14, 21, 50, and 150 for the BPA analysis in high performance liquid chromatography (HPLC) system. On each sampling day, one replicate of two bottles was used.

Initially, extraction was achieved, the 500 mL portion of the sample was concentrated and purified through *Thermo Scientific Dionex SolEx* C_{18} *Silica-based solid phase extraction* (*SPE*) *cartridge*s under vacuum. Samples passed through the cartridge at a speed of 7–10 mL/min. At the end, after reaching complete dryness under vacuum, the analyte was collected in 5 mL analytical grade methanol. To assess the efficiency and reproducibility of the analytical procedures, spiked seawater and distilled water samples were recurrently analyzed.

HPLC equipped with FLC Cell Agilent 1100 series fluorescence detector was used for BPA detection analysis. The HPLC unit had reverse phase C_{18} column (Vydac, Model: 201TP52, S/N: NE981208-3–1) kept at 25°C during the analysis. Analytical grade methanol at a constant flow rate of 1 mL/min was used as the mobile phase. Standard BPA concentrations were at 100, 500, 1000, 5000, 10,000 µg/L, a linear slope ($R^2 = 0.9998$) was calculated from the peak areas of the standards.

All statistical analyses requiring a comparison of treatments were carried out using SigmaStat 12.3 software (Systat Software, Inc., San Jose, CA, USA). ANOVA and t-tests were performed to evaluate significance of individual differences with a probability threshold of 0.05, followed by a Holm–Sidak test.

Results and Discussion

HPLC extraction efficiency was calculated by BPA spiked seawater and distilled water samples were repetitively analyzed (n = 4). The extraction efficiency was found 99% ± 1.8%. This data indicates that the extraction method and solvents worked well for the BPA analysis.

Seawater samples were kept at 4°C and 25°C and directly sampled for BPA concentrations at days 0, 6, 14, 21, 50, and 150. The analysis showed that neither the artificial nor the natural seawater samples of BPA concentrations changed significantly throughout the 150 days of the experiment (Fig. 1).

River water samples prepared from the natural and artificial waters were kept at 4°C and 25°C. After 150 days, the BPA in artificial river water did not show any significant degradation, but BPA in natural river water samples started to degrade after day 50 (Fig. 2). The natural river water sample kept at 25°C started to degrade quickly after day 50 and reached its half-life at day 91. The concentration of BPA in natural river water samples at 25°C at day 150 was significantly different than the other treatments (ANOVA; $p < 0.05$). BPA in natural river water kept at 4°C started to degrade relatively slowly after day 50 and up until day 150. The concentration difference of this treatment compared to other treatments was not significant at day 150 (ANOVA; natural river water 4°C vs. artificial river water 4°C $p = 0.082$; vs. artificial river water 25°C $p = 0.086$).

Table 1 Experimental conditions

Seawater						River water			
Natural				Artificial		Natural		Artificial	
25°C	4°C	Outside		25°C	4°C	25°C	4°C	25°C	4°C
		Dark	Sunlight						

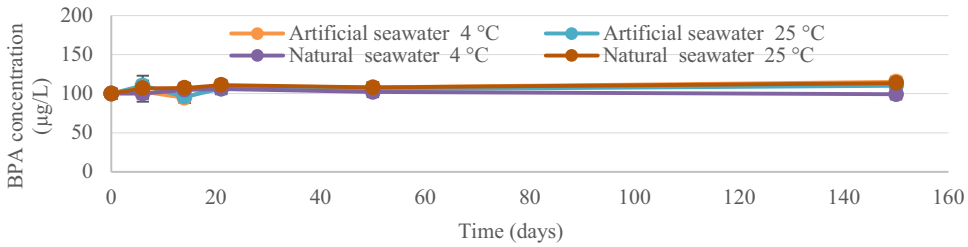

Fig. 1 Bisphenol A concentrations of seawater samples that were kept at 4°C and 25°C

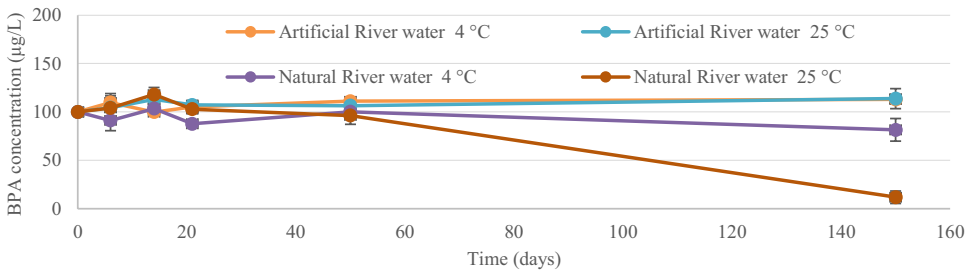

Fig. 2 Bisphenol A concentrations of river water samples that were kept at 4°C and 25°C

The other treatments prepared from natural seawater were kept outside: one treatment was in sunlight and the other one was kept in a dark box. The results showed that both treatments started to degrade after day 50 and reached significant BPA degradation ($p < 0.05$) at day 150 (Fig. 3). The treatment kept in the dark box showed a slower degradation after day 50; however, the treatment kept in direct sunlight degraded at faster rates. The half-lives are > 150 and 98 days for the treatment kept in the dark and sunlight, respectively.

There are controversial studies in the literature about BPA degradation in aquatic systems. While some of the studies show rapid biodegradation and very short half-lives of BPA in river and seawater (Klecka et al. 2001; Robinson and Hellou 2009; Im and Löffler 2016), the others claimed that there was no degradation or very high half-lives of BPA observed during the course of their evaluations (Howard 1989; Ying et al. 2003) (Table 2).

Natural seawater and river water samples contain native microbial communities that are potentially able to degrade BPA. Biodegradation is a significant way to remove or detoxify BPA from the aquatic environment or aquatic organisms. Bacteria capable of biodegrading BPA are distributed in aquatic environments. Many different organisms – not only diverse taxa of bacteria but also fungi, algae and even higher plants – metabolize BPA (Im and Löffler 2016). One of the earliest studies regarding BPA degradation showed that BPA concentration within experimental research about 15%–25% of BPA disappeared during the first 48 h then a sharp reduction of BPA occurred in the following 2 days; therefore, on the fourth day, BPA was reduced below detection limit (Dorn et al. 1987). BPA was also assessed in surface waters from seven different rivers across the US and Europe (Klecka et al., 2001). Rapid biodegradation of BPA was observed in all the rivers, regardless of geographic location, following lag phases ranging from 2 to 4 days (Klecka et al. 2001). Most of the studies report average half-life for BPA biodegradation is less than 10 days. On the other hand, BPA concentrations in groundwater remained unchanged after 70 days (Ying and Kookana 2003; Ying et al. 2003) and half-life of BPA in surface waters extended until 160 days (Howard 1989).

Biodegradability of BPA in seawater varies due to microbial communities was altered by environmental factors such as nutrients, temperature, and water flow (Sakai et al. 2007). Efficiency of photolytic degradation depended on pH, turbidity, water turbulence, and other factors (Howard 1989; Chen et al. 2006). There are also many natural materials that can remove or reduce the concentration of BPA from aquatic environments via adsorption (reviewed by Bhatnagar and Anastopoulos 2017). So, it is likely to observe very distinct half-lives of BPA depending on locations as biological and physicochemical parameters vary around the world. Particularly, metagenomics and metatranscriptomic studies are required to indicate organisms responsible from biodegradation. In this study, half-lives of BPA in natural river waters were found > 90 days and > 150 days at 4°C and 25°C, respectively (Fig. 3). It is a good example for the location and temperature dependency of the BPA degradation.

Over 150 days, BPA concentrations in seawater at 4°C and 25°C did not show any significant degradation (Fig. 2). On the other hand, the treatments prepared from the same seawater kept outside were significantly degraded in 150 days. The only differences between the treatments were temperature and sunlight effects. The samples kept outside were exposed to temperatures higher than 40°C in summer. While outside temperatures reach up to 40°C in July and

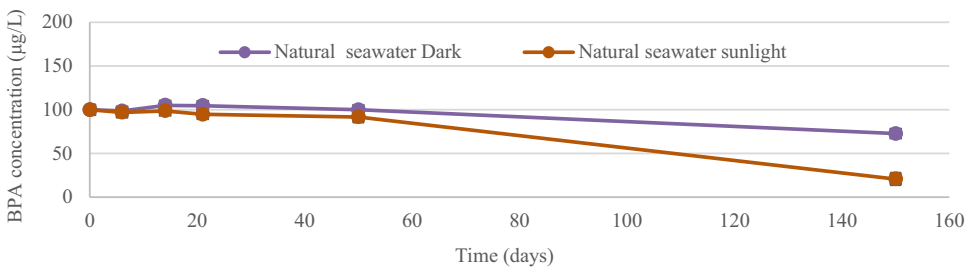

Fig. 3 Bisphenol A concentrations of seawater samples that were kept outside

Table 2 Bisphenol A (BPA) degradation studies and reported half-lives of BPA

Degradation speed/half-life	Degradation medium/conditions	References
Short half-life/2 days	3 mg/L BPA was added to the samples and analysed 8-day	Dorn et al. (1987)
No degradation-long half-life/extended until 160 days	In surface waters	Howard (1989)
2 to 5 days	Investigated in 3 activated sludge and 44 river water microcosms	Ike et al. (2000)
2 to 4 days	Observations from rivers	Klecka et al. (2001)
< 10 days	Seven different fresh and estuarine water samples with inoculated with different BPA concentrations analysed 28-day	West et al. (2001)
2–3 days (aerobic); slow to no degradation (anaerobic)	In river water under aerobic and anaerobic conditions	Kang and Kondo (2002)
14.5 days to no degradation in seawater and sediments	35–42 days (seawater), 14.5 days (aerobic, sediment), no degradation in 56 days (anaerobic, sediment) from the coastal Australia	Ying and Kookana (2003)
No degradation in 70 days; long half-life	In the aquifer media under the aerobic and anaerobic conditions, BPA remained unchanged over 70 days	Ying et al. (2003)
3 to 60 days at different conditions	3–5 days (non-autocleaved river water)/slow degradation (non-autoclaved seawater)/no degradation in 60 days (autoclaved seawater)	Kang and Kondo (2005)
20 to 40 days	By *Sphingomonas* sp. strain BP-7 and several strains	Sakai et al. (2007)
12 to 21 days	Natural and artificial seawaters in the Bay of Osaka, Japan	Danzl et al. (2009)
4 to 14 days	Seawater and sediment samples near a major sewage effluent	Robinson and Hellou (2009)
26 days	BPA in the Mediterranean mussel in the Aegean Sea (Greece) unfiltered seawater and clean water	Gatidou et al. (2010)
7 days	The algae, *C. sorokiniana*, were cultivated with 10, 20, and 50 mg/L BPA for 7 days	Eio et al. (2015)
Long half life/ > 90 days	No degradation for autoclaved river and seawater	This study

August, the temperature inside the bottles in direct sunlight can reach up to higher temperatures. It is expected to observe higher temperatures in bottles in the sunlight than the bottles kept in the dark box. Even though how much sunlight penetrate through the polypropylene bottles is unknown, the transparent bottles kept in the sunlight might have been exposed to photodegradation. The higher rate of degradation of BPA in the bottles kept in the sunlight compared to bottles kept in the box might be affected by the joint effect of the high temperatures and the photodegradation. Unchanged BPA concentrations in the same seawater kept at 4°C and 25°C might indicate that microorganisms were present in the bottles, but they were not activated until the water reached higher temperatures.

In this study, unchanged BPA concentrations in artificial waters and lack of native microbial communities shows that microorganism could be the major contributor to the BPA degradation by means of elevated temperatures and photodegradation. Similar results from a study by Kang and Kondo (2005) showed that while river water samples degraded rapidly at 25°C and 35°C, seawater samples remained unchanged in the autoclaved seawater at 4°C, 25°C, and 35°C for 60 days. But non-autoclaved seawater BPA content decreased after 40 days with the increasing temperature (Kang and Kondo 2005).

Like other studies (e.g., Nie et al. 2012) suggesting that higher temperatures accelerate the degradation of BPA, it is likely summer is the most potent season regarding BPA degradation in the region where seawater temperature reach around 33°C. It is also expected that high BPA residence time found in the northeastern Mediterranean Sea, make the region more potent for BPA bioaccumulation compared to other regions. And, slower degradation rate of BPA in the seawater compared to the river water propose BPA contamination in a marine organism could be higher than that in freshwater organisms.

To the best of our knowledge, this is the first study showing BPA degradation in the Mediterranean Sea, so there is no way to compare our results to studies performed on the other parts of the Mediterranean Sea. It is still unknown what really causes the very slow degradation of BPA in the Mediterranean Sea. However, there are some possible reasons such as physicochemical properties of the Mediterranean Sea, bacterial community structure (amount of present BPA degrading bacteria), their long acclimation time requirements, or the BPA degradation abilities among

different strains. Microbial community analysis, quantification and identification of species involved, on BPA degradation could be the next step towards better understanding the fate of BPA in the Mediterranean Sea.

In this study, artificial river and surface seawater samples were evaluated in terms of BPA degradation at different temperatures for 150 days. In seawater samples, there were no degradation observed at 4°C and 25°C in 150 days regardless they are prepared from natural or artificial seawaters. The seawater sample treatments that were kept outside (prepared from natural seawater) started to degrade after day 50. The samples kept outside in dark degraded at lower rates than the ones kept in direct sunlight. In river waters, the artificial ones did not degrade at all in 150 days, but natural river water samples started to degrade after day 50. This study shows the impact of the temperature since different degradation rates were observed at different temperatures. The higher the temperature, the faster BPA degradation. In addition, photodegradation potentially contributed to the BPA degradation either additively or synergistically. Microbial communities could be effective on BPA degradation since the artificial water samples were not degraded at all after 150 days. Different half-lives of BPA depending on the location is an indication that different biological compositions and physicochemical properties of the aquatic systems can play an important role in BPA degradation. More regional data are required around the globe for the global assessment about the fate of BPA in aquatic systems.

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