Archives of Environmental Contamination and Toxicology (2019) 76:246–254
https://doi.org/10.1007/s00244-018-00594-6

Temporal and Spatial Distributions of Bisphenol A in Marine and Freshwaters in Turkey

Koray Ozhan[1] · **Emel Kocaman**[1]

Received: 17 August 2018 / Accepted: 29 December 2018 / Published online: 4 January 2019

Abstract

Bisphenol A (BPA), a chemical component used in the manufacture of plastics, is commonly introduced to and detected in aquatic environments. This is the first study conducted to understand the distribution of BPA in the marine and freshwaters of Turkey. The purpose of this study is to report BPA concentrations measured from a time-series conducted in coastal waters of Erdemli and regional rivers located in the northeastern Mediterranean region. Furthermore, seawater samples obtained from other Turkish coastal areas—The Black Sea, Bosphorus, Sea of Marmara, and the Mediterranean Sea—also were investigated to gain a better understanding of regional and seasonal variations of BPA concentrations in Turkish Seas. Whilst spatial variation in BPA concentrations was very low, temporal variation was found to be high. It has been shown that BPA can reach the deep sea environment (> 500 m depth). This study indicated that BPA contamination has reached serious levels at another location in the world.

Bisphenol A (BPA) is an endocrine-disrupting chemical (EDC) and is present globally. It is one of the most important synthetic chemicals produced in high volumes since the 1960s (Staples et al. 1998). Since then, it has been widely used commercially in the plastics industry for the production of epoxy resins and flame retardants and in other industrial fields. In polycarbonates, due to its advantageous properties, BPA is used in optical media, construction materials, and the electrical and electronics industries, a small fraction is used for the manufacture of bottles and other food-contact applications and for medical and healthcare applications (Zielińska et al. 2019). In epoxy resins, it is a component of coatings for consumer and industrial applications, protective coatings for automotive and marine use, electrical and electronic laminates, adhesives, paving applications, and also internal coatings of coils and food and beverage cans (Zielińska et al. 2019). Consequently, all of these commonly used products are potential sources of BPA contamination.

According to the European Food Safety Authority (EFSA), BPA is one of the most extensively studied compounds (EFSA 2010). BPA has been found to be weakly estrogenic and therefore of both environmental and human health interest (Staples et al. 1998). It has been shown to interact with estrogen receptors and to act as an agonist or antagonist via endocrine receptor (ER)-dependent signaling pathways and play a role in the pathogenesis of several endocrine disorders, including female and male infertility, precocious puberty, hormone-dependent tumours, such as breast and prostate cancer, and several metabolic disorders, including polycystic ovary syndrome (PCOS) (Diamanti-Kandarakis et al. 2009; Konieczna et al. 2015). During the past few decades, due to possible adverse health risks, such as cancer and infertility, BPA usage was banned or restricted in some products (Tsai 2006). BPA levels have been detected in human urine samples at extremely high frequency (up to 99%) (Ye et al. 2015), indicating extensive contamination. The EFSA performed its first full-risk assessment of BPA in 2006, repeating in 2008, 2009, 2010, 2011, and 2016 with new scientific information on BPA following consideration of hundreds of scientific publications. In January 2011, the European Commission approved Directive 2011/8/EU, prohibiting the use of BPA for the manufacture of polycarbonate infant feeding bottles. The EFSA also published a comprehensive reevaluation of BPA exposure and toxicity and reduced the TDI (dose/tolerable daily intake) for BPA from 50 to 4 µg/kg bw/day (bodyweight) in January 2015 (Authority EFS 2015).

Laboratory studies, which focus on the impact of BPA on aquatic species, indicate that in nonmammalian

✉ Koray Ozhan
korayozhan@gmail.com

[1] Institute of Marine Sciences, Middle East Technical University, Erdemli, Mersin, Turkey

vertebrates, in particular aquatic species, BPA causes harmful developmental and reproductive effects, including reduction of male hormones, death of testicular cells, decreased sperm density and motility, inhibition of spermatogenesis and egg production, along with delayed or absent ovulation and an impairment in the sex ratio (Canesi and Fabbri 2015). Considering its prevalence and impact as an endocrine disruptor, BPA is included in the MSFD (Marine Strategy Framework Directive), OSPAR commission, and WFD (Water Framework Directive) list of priority substances.

Due to the excessive production volumes and disposal of products made from polycarbonate plastic and epoxy resins, BPA has entered terrestrial and aquatic environments. BPA reaches the sea mainly via rivers, wastewater treatment plants, landfill leachates, and leaching from discarded BPA-based materials (e.g., hydrolysis of polycarbonate, recycled paper) (reviewed by Im and Löffler 2016). Detection of BPA in water began in the late 1990s. Since then, many studies have been conducted on BPA in aquatic environments (reviewed by Corrales et al. 2015). However, due to a lack of data from the majority of developing countries around the world, an understanding of global patterns in BPA levels remains challenging. Because this lack of information on riverine and marine BPA distributions also is the case for Turkey, this study attempts to provide the first comprehensive data set presenting BPA surveys obtained from rivers, surface, and deep sea waters in the Mediterranean Sea, Black Sea, and Sea of Marmara. The main objectives in our study were (1) to indicate spatial and temporal distributions of BPA levels in rivers and for the monthly Erdemli Time Series (ETS) in the NE Mediterranean Sea over a 1-year period, (2) to illustrate spatial distribution throughout the Mediterranean Sea, and (3) to determine BPA concentrations in the vicinity close to the megacity Istanbul.

Materials and Methods

Sampling and Sampling Stations

Seawater samples were obtained using a CTD rosette sampler with Niskin bottles; 500-ml duplicate samples were acquired during research cruises of the Institute of Marine Sciences METU (RV Bilim 2). Sampling was performed in three distinct categories (locations are shown in Fig. 1: (1) Surface seawater samples obtained from the monthly Erdemli Time Series (ETS) and four regional rivers (Göksu, Lamas, Berdan, and Seyhan) between August 2016 and October 2017 from a transect (ETS 20 m, ETS100 m, and ETS 200 m) (Fig. 2); (2) Surface seawater samples obtained from the Black Sea, Bosphorus, and Sea of Marmara in December 2016 (Fig. 3); (3) District samples obtained along the coastal Northeastern (NE) Mediterranean Sea in August 2017 (Fig. 4).

Sampling stations in the Mediterranean Sea were incorporated from the Erdemli Time Series (long-term monthly sampling stations) and from the national pollution-monitoring programme for district samples.

The geostrophic circulation of the central and eastern Mediterranean waters demonstrates a considerable stability in winter and autumn and is mainly characterised by a vast cyclonic gyre in the Levantine Sea (Said 1990). The main Asia Minor Current with Cilician Current, which flowfrom east to west along the shores of the Turkish Mediterranean Sea (Robinson et al. 1991), encloses the stations that were

Fig. 1 Bisphenol A sampling stations

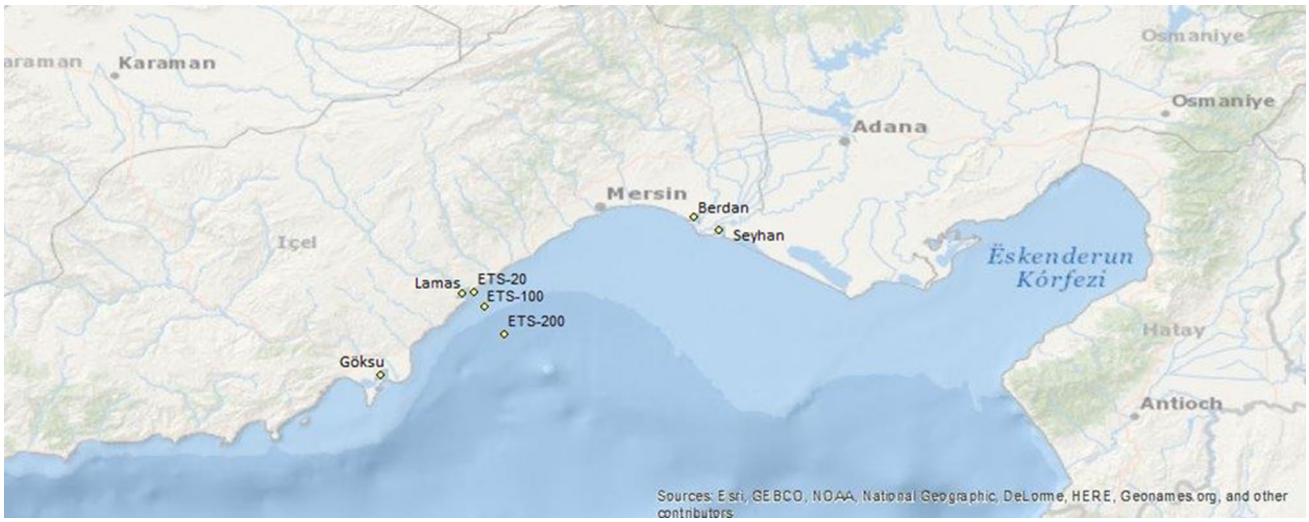

Fig. 2 Erdemli time series (ETS) stations and locations of the rivers, Göksu, Lamas, Berdan, and Seyhan, on the northeastern Mediterranean coast

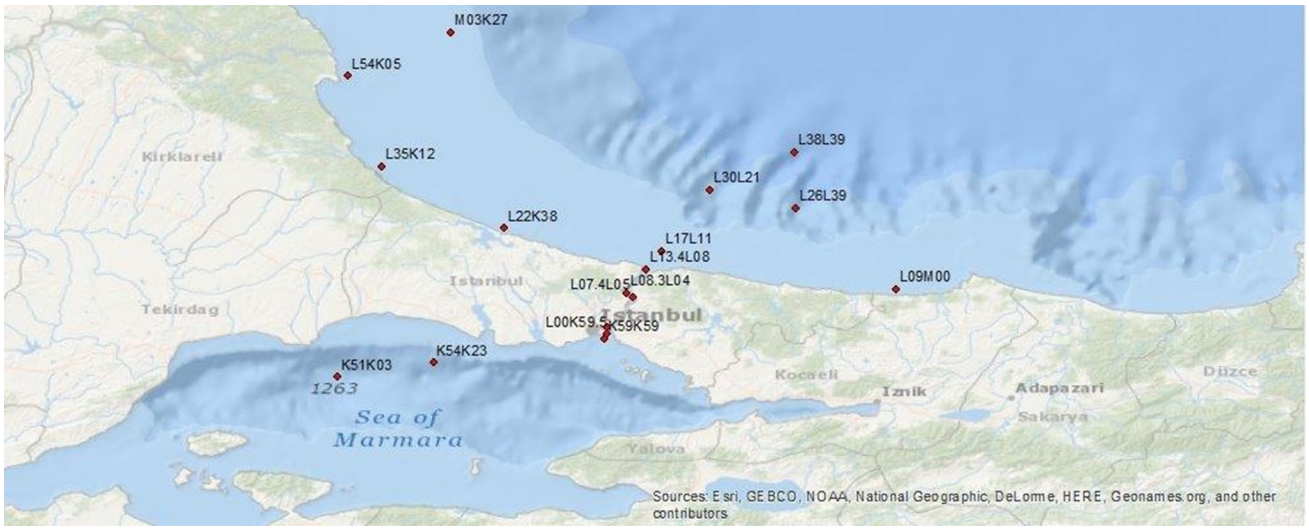

Fig. 3 The Black Sea, Bosphorus, and Sea of Marmara stations

sampled. Major rivers are located to the east of ETS stations. In summary, this contributes to surface waters in the region becoming riverine dominated.

A transect was mapped through the Bosphorus to observe any transition in BPA levels from the Black Sea to the Sea of Marmara. Additional stations were added for both seas to better understand BPA level distribution in the region within a close proximity to Istanbul. Three major rivers (Danube, Dniepr, and Dniestr) provide important freshwater input to the Black Sea. The relatively less saline water from the north flows southward into the Bosphorus Strait, which is a strongly stratified two-layer system with less saline Black Sea water in the upper layer. In brief, major river dominated seawater covers all stations sampled in the Black Sea and the Sea of Marmara.

Extraction of Water Samples

Initially, extraction was achieved by purification and concentration of the 500-ml portion of the sample through *Thermo Scientific Dionex SolEx C18 Silica-Based solid phase extraction (SPE) cartridge*s under vacuum. Samples were passed through the cartridge at a speed of 7–10 ml/min. After complete drying under vacuum, the analyte was collected in 5-ml analytical grade methanol. Matrix spikes quality control was used to calculate sample matrix

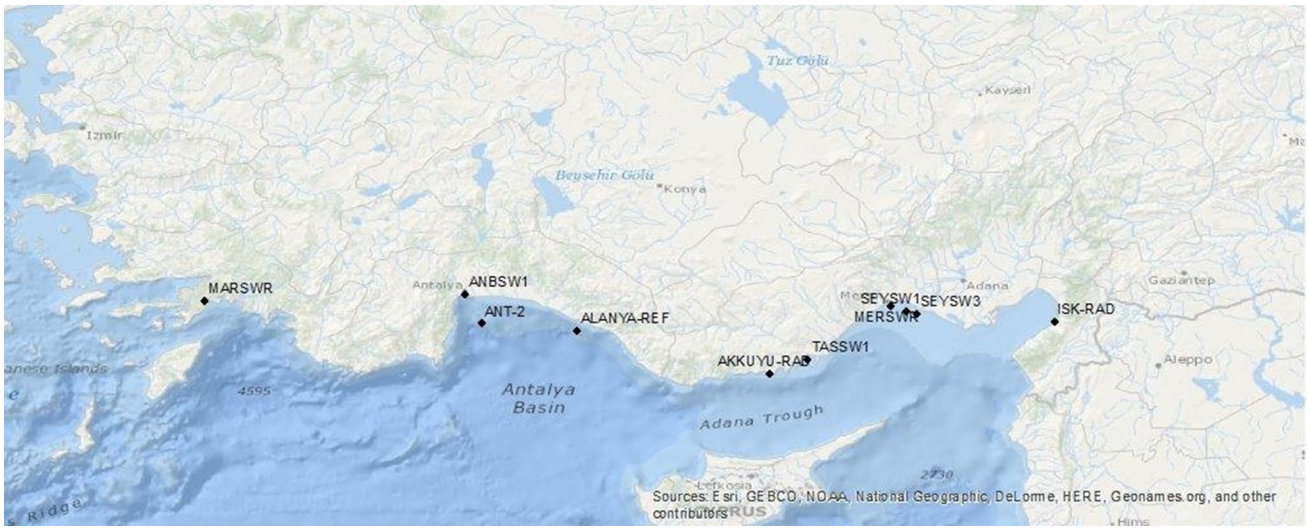

Fig. 4 The northeastern Mediterranean Sea stations

interference. To assess the efficiency and reproducibility of the analytical procedures, spiked seawater and distilled water samples were repeatedly analyzed.

HPLC Analysis

High-performance liquid chromatography (HPLC) equipped with FLC Cell Agilent 1100 series fluorescence detector was used for BPA detection analysis. The HPLC unit had a reverse phase C18 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. Concentrations of BPA (Sigma-Aldrich, product no: 239658 Lot no: MKBS0991V) standards were 10, 50, 100, 500, 1000, and 5000 µg/l. The linear slope ($R^2 = 0.9998$) was calculated from the peak areas of the standards. Matrix spike triplicates, providing a means of measuring method precision, were used to calculate the method precision. Accuracy was assessed by analyzing a certified reference material (CRM) (Sigma-Aldrich, product no: 42088 Lot no: BCBN9199V).

Statistical Analysis

All statistical analyses that required a comparison of treatments were performed using SigmaStat 12.3 software (Systat Software, Inc., San Jose, CA). Analysis of variance (ANOVA) and *t*-tests were performed to evaluate the significance of individual differences with a probability threshold of 0.05, followed by a Holm-Sidak test.

Results and Discussion

HPLC extraction efficiency, calculated by spiked seawater and distilled water samples, was found as 99% ± 1.8%. This validates the efficiency of the employed extraction method and solvents used in our analysis.

Samples obtained from the time-series stations (ETS) during the same period displayed very similar trends in BPA concentration changes while no significant spatial variations were observed (Fig. 5). These results suggest that BPA can impact not only the coastal sites but also offshore stations (ETS 200 m lies 16 km offshore). However, seasonal variations in BPA concentrations were observed at ETS stations. BPA concentrations measured at ETS stations over a 1-year period ranged between 4.16 and 29.92 µg/l. BPA concentrations in seawater were at the lowest levels in October–November 2016 and September 2017. Peak levels occurred in January–February 2017.

In a similar pattern, BPA river concentrations varied between 4.62 and 29.92 µg/l (Fig. 6). In the same sampling periods, BPA concentrations found in all four rivers were very similar (Fig. 6). Spring-time river and seawater BPA concentrations were closest to each other; however in summer, a difference was observed in BPA distribution and concentration (Fig. 7). Annual mean water discharge rates for the Seyhan, Göksu, Berdan, and Lamas Rivers were found to be 168, 45, 6, and 3 m^3/s, respectively (Kocak et al. 2010). Additionally, the annual mean BPA concentration calculated for these four rivers was 12.33 µg/l, yielding a total combined load of 86.3 kg of BPA/year. Other rivers located in the region are the Asi and Ceyhan

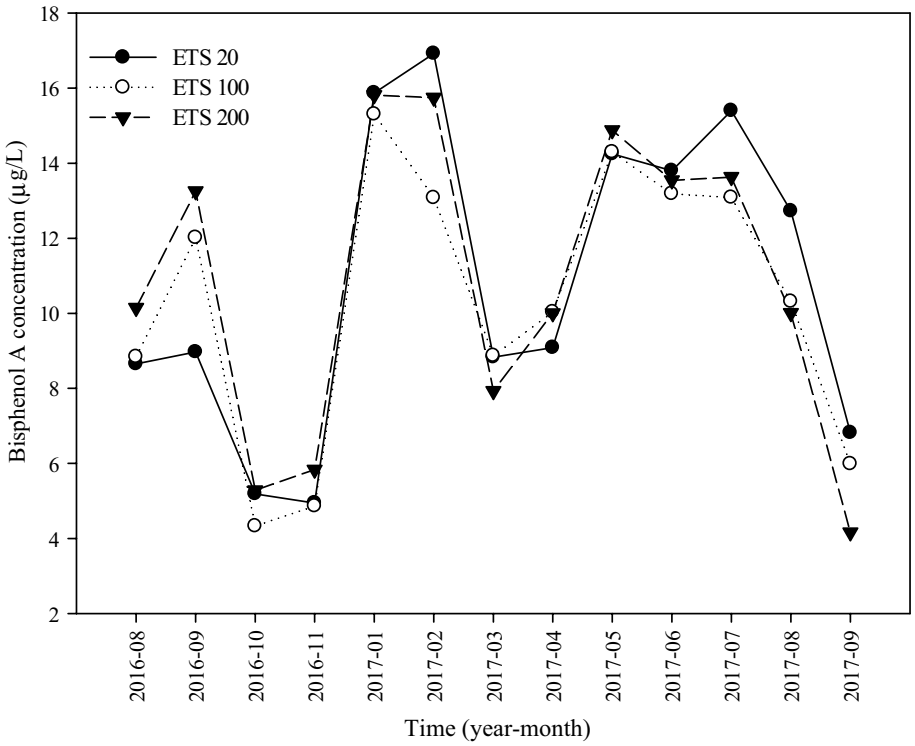

Fig. 5 Bisphenol A concentrations at Erdemli Time Series (ETS) stations

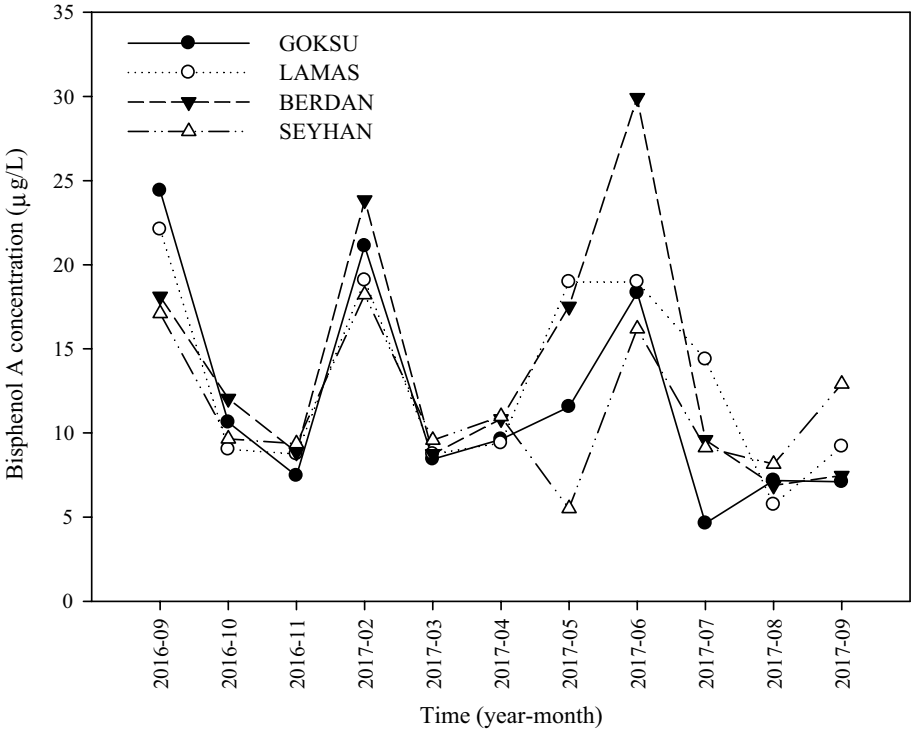

Fig. 6 Bisphenol A concentrations in regional rivers on the northeastern Mediterranean Sea

Rivers with discharge rates of 235.1 m^3/s (Kılıç et al. 2018) and 144 m^3/s (Kocak et al. 2010) respectively. On the assumption that these rivers exhibit similar concentrations of BPA, calculations reveal a BPA load of 223.7 kg/year only from the rivers located in the eastern part of the study region. Due to the lack of data on wastewater treatment plant discharge levels and BPA content, the present study was unable to evaluate the share of this contributory factor to the seawater BPA levels.

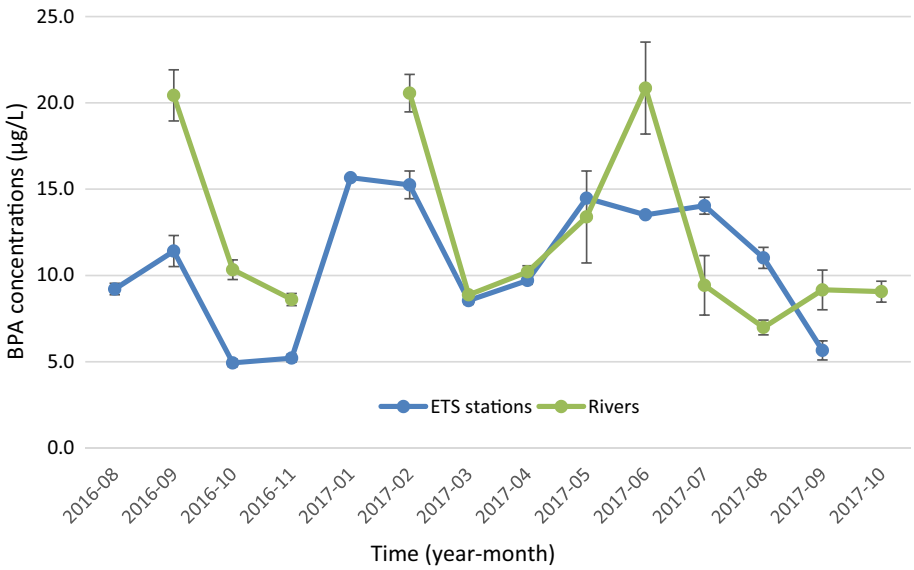

Fig. 7 Average BPA concentrations at ETS stations and regional rivers on the northeastern Mediterranean Sea

The impact of megacities on coastal pollution is well known. In this study, the largest Turkish city, Istanbul (population 15 M), surrounded by the Black Sea, Sea of Marmara, and Bosphorus, was investigated regarding BPA concentrations. BPA levels in the Black Sea, Bosphorus, and Sea of Marmara were found to be in a narrow range of 8.85–14.76 µg/l (Fig. 8). Highest concentrations were observed in a river mouth in the Black Sea and at stations in the Bosphorus where wastewater discharge of Istanbul occurs. Lowest BPA concentrations were measured at stations located further away from the northwest of the shelf where rivers dominate and at some stations in the Bosphorus (stations: L3021, L26L39, L38L39, K54K23, and

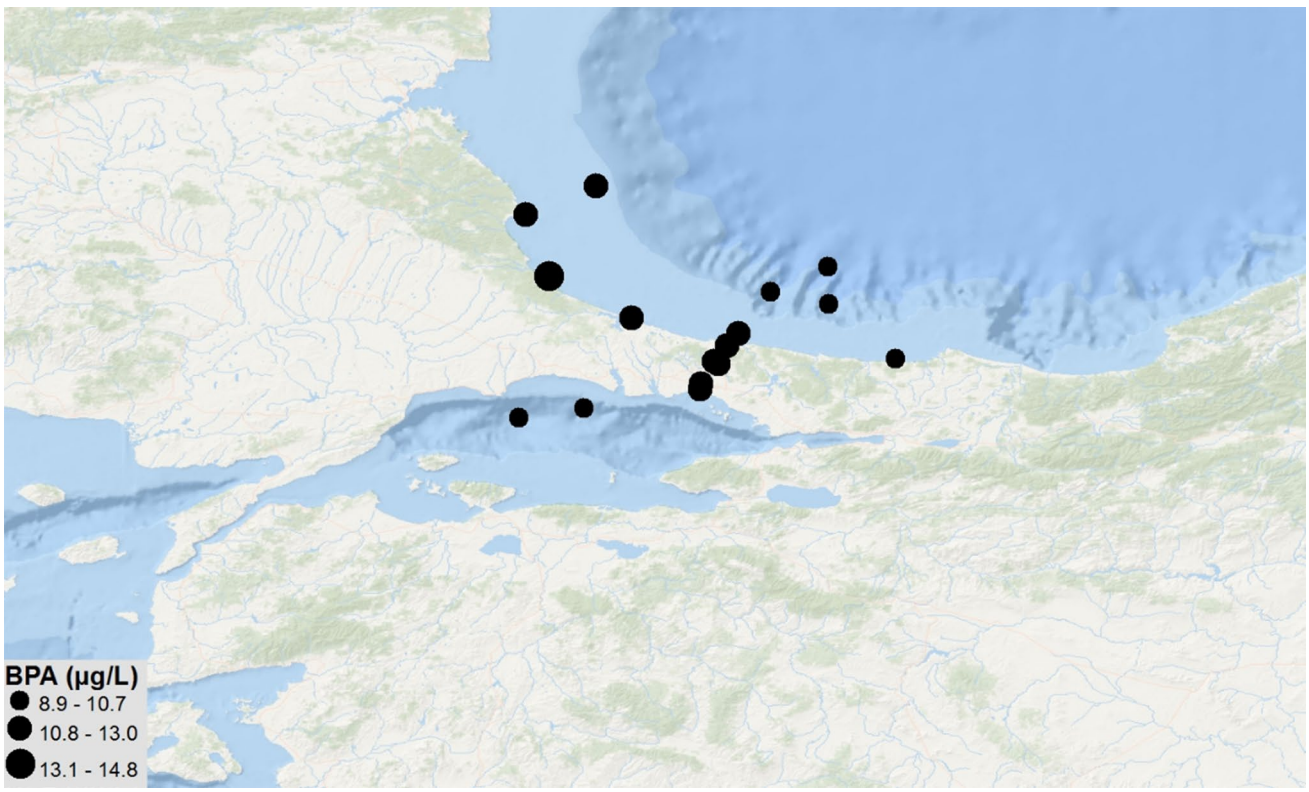

Fig. 8 Bisphenol A concentrations in the Black Sea, Bosporus, and Sea of Marmara

K51K03). It is an indication of the direct impact of rivers and wastewater discharges in this region.

Similarly, the Mediterranean Sea survey showed that BPA concentrations in surface seawater lie in a narrow range from 13.80 to 15.34 µg/l (Fig. 9). Spatial variation in BPA concentrations among stations was very low. To investigate the depth profile of BPA concentrations in the Mediterranean Sea, two stations were chosen with samples obtained from different depths (Fig. 10). Results obtained did not differ significantly (Fig. 10), indicating BPA to be vertically diffused throughout the water column.

According to the available literature, BPA surface water concentrations range from 0 to 56 µg/l (Corrales et al. 2015) around the world and in sediment from 5.32 to 15.52 µg/kg in the Adriatic Sea (Andelic et al. 2015). Corrales et al. (2015) analyzed all peer-reviewed literature results regarding BPA concentrations in seawater and ranked them using the Weibull formula. According to this ranking, the current study's results are higher than almost 80% of the literature values. BPA Predicted No Effect Concentrations (PNECs) were reported for different regions, such as in Canada (750 ng/l), the European Union (1500 ng/l), and Japan (1600 ng/l) (Corrales et al. 2015). All of our results are higher than the PNECs values already determined for different regions illustrating serious levels of BPA pollution in Turkish seas and rivers.

It is widely believed that hard plastics are the main source of BPA in oceans (ACS 2010). The team analyzed sand and seawater from more than 200 sites in 20 countries, mainly in Southeast Asia and North America. All contained a

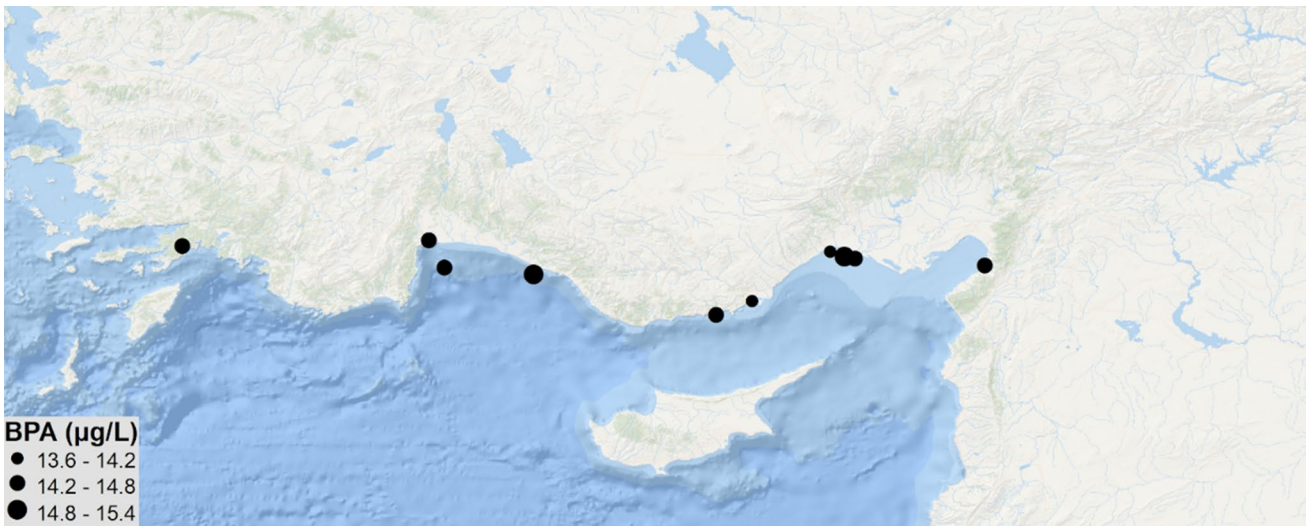

Fig. 9 Surface seawater Bisphenol A concentrations in the Mediterranean Sea

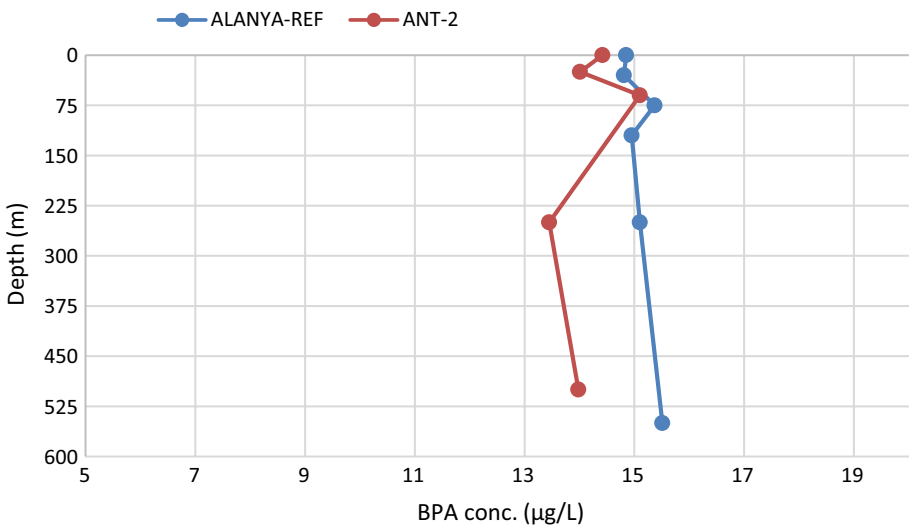

Fig. 10 Concentration profiles of Bisphenol A in the Mediterranean Sea at different depths

"significant" amount of BPA, ranging from 0.01 to 50 µg/l. They concluded that polycarbonates and epoxy-resin coatings and paints were the main sources of BPA. The high concentrations of BPA found in the present study potentially indicate serious plastic pollution in the Mediterranean.

One of the important outcomes of this study is the very low spatial variation regardless of the different Turkish seas studied. In Turkey, many wastewater treatment plants (WWTPs) lack tertiary/advanced treatment systems providing no preventative measures against BPA, thereby making BPA marine pollution unavoidable. This study also revealed high levels of BPA in rivers; therefore, continuous riverine discharge is a substantial contributor to the BPA marine pollution.

The majority of aquatic toxicity data for BPA from various sources show EC_{10}, EC_{50}, and LC_{50} values for microorganisms, invertebrates, and fishes to be higher than 1000 µg/l (Alexander et al. 1988; Hendriks et al. 1994). However, a recent review (Kang et al. 2007) found that BPA's adverse endocrine-disruptive effects occur in aquatic organisms at concentrations as low as 1.75 µg/l in Brown trout (Lahnsteiner et al. 2005), 1–25 µg/l in mud snails (Jobling et al. 2003), and 50 µg/l in mussels (Ortiz-Zarragoitia and Cajaraville 2006). Thus, the values detected in our seas apparently exceed those levels that can potentially produce adverse endocrine-disruptive effects in marine life.

One of the limitations of this study is the determination of BPA sources other than rivers. Future studies should include BPA source assessment, input levels, and trend analysis from those sources. In addition, other studies that focus on mitigation of BPA in rivers will be essential to reduce the impact of BPA in aquatic systems.

Conclusions

The occurrence of BPA was investigated in the marine environment and rivers of Turkey. Concentrations of BPA ranged from 4.16 to 16.92 µg/l in seawater and 4.62–29.92 µg/l in rivers. Rivers contain high levels of BPA, and their continuous discharge is a substantial contributor to the BPA marine pollution. The spatial distribution was investigated in different seas, but the variation was very low. In the northeastern Mediterranean Sea, temporal variation was high, but no clear pattern was observed regarding BPA concentration in surface seawater. It has been determined that BPA reaches the deep sea with no significant difference between deep sea and surface seawater concentrations. This is the first study to demonstrate spatial and temporal distributions of BPA in Turkish Seas and will aid lawmakers in Turkey in terms of precaution and prevention of BPA in both freshwater and marine environments.

Acknowledgements This work was partially funded by the Scientific and Technological Research Council of Turkey (TUBITAK) under Grant Number TUBITAK 115YE627; "Impacts of Microplastic Particles and Bisphenol A as a Chemical Additive on Zooplankton Species in the Mersin Bay."

References

Alexander HC, Dill DC, Smith LW, Guiney PD, Dorn P (1988) Bisphenol A: acute aquatic toxicity. Environ Toxicol Chem 7(1):19–26

American Chemical Society (2010) Hard plastics decompose in oceans, releasing endocrine disruptor BPA. ScienceDaily. www.sciencedaily.com/releases/2010/03/100323184607.htm Accessed 24 July 2018

Andelić I, Matijević S, Ujević I (2015) Preliminary investigation of bisphenol A in sediments and suspended matter in Kaštela Bay (Adriatic Sea, Croatia). Acta Adriatica Int J Mar Sci 56(2):259–268

Authority EFS (2015) Scientific opinion on the risks to public health related to the presence of bisphenol A (BPA) in foodstuffs. EFSA J 13(1):3978

Canesi L, Fabbri E (2015) Environmental effects of BPA: focus on aquatic species. Dose-Response 13(3):1559325815598304

Corrales J, Kristofco LA, Steele WB, Yates BS, Breed CS, Williams ES, Brooks BW (2015) Global assessment of bisphenol A in the environment: review and analysis of its occurrence and bioaccumulation. Dose-Response 13(3):1559325815598308

Diamanti-Kandarakis E, Bourguignon JP, Giudice LC, Hauser R, Prins GS, Soto AM, Gore AC (2009) Endocrine-disrupting chemicals: an Endocrine Society scientific statement. Endocr Rev 30(4):293–342

EFSA Panel on food contact materials, enzymes, flavourings and processing aids (CEF) (2010) Scientific opinion on Bisphenol A: evaluation of a study investigating its neurodevelopmental toxicity, review of recent scientific literature on its toxicity and advice on the Danish risk assessment of Bisphenol A. EFSA J 8(9):1829

Hendriks AJ, Maas-Diepeveen JL, Noordsij A, Van der Gaag MA (1994) Monitoring response of XAD-concentrated water in the Rhine delta: a major part of the toxic compounds remains unidentified. Water Res 28(3):581–598

Im J, Löffler FE (2016) Fate of bisphenol A in terrestrial and aquatic environments. Environ Sci Technol 50(16):8403–8416

Jobling S, Casey D, Rodgers-Gray T, Oehlmann J, Schulte-Oehlmann U, Pawlowski TCR (2003) Comparative responses of mollusks and fish to environmental estrogens and an estrogenic effluent. Aquat Toxicol 65(2):205–220

Kang JH, Aasi D, Katayama Y (2007) Bisphenol A in the aquatic environment and its endocrine-disruptive effects on aquatic organisms. Crit Rev Toxicol 37(7):607–625

Kılıç E, Akpınar A, Yücel N (2018) The Asi River's estimated nutrient load and effects on the eastern Mediterranean. Aquat Sci Eng 33(2):61–67

Kocak M, Kubilay N, Tuğrul S, Mihalopoulos N (2010) Atmospheric nutrient inputs to the northern levantine basin from a long-term observation: sources and comparison with riverine inputs. Biogeosciences 7(12):4037–4050

Konieczna A, Rutkowska A, Rachon D (2015) Health risk of exposure to Bisphenol A (BPA). Roczniki Państwowego Zakładu Higieny 66(1):5–11

Lahnsteiner F, Berger B, Kletzl M, Weismann T (2005) Effect of bisphenol A on maturation and quality of semen and eggs in the brown trout, *Salmo trutta f. fario*. Aquat Toxicol 75:213–224

Ortiz-Zarragoitia M, Cajaraville MP (2006) Biomarkers of exposure and reproduction-related effects in mussels exposed to endocrine disruptors. Arch Environ Contam Toxicol 50:361–369

Robinson AR, Golnaraghi M, Leslie WG, Artegiani A, Hecht A, Lazzoni E, Ünlüata Ü (1991) The eastern Mediterranean general circulation: features, structure and variability. Dyn Atmos Oceans 15(3–5):215–240

Said MA (1990) Horizontal circulation of the Eastern Mediterranean waters during winter and summer seasons. Acta Adriatica AADRAY 31(1/2):5–21

Staples CA, Dome PB, Klecka GM, Oblock ST, Harris LR (1998) A review of the environmental fate, effects, and exposures of bisphenol A. Chemosphere 36(10):2149–2173

Tsai WT (2006) Human health risk on environmental exposure to bisphenol A: a review. J Environ Sci Health Part C 24(2):225–255

Ye X, Wong LY, Kramer J, Zhou X, Jia T, Calafat AM (2015) Urinary concentrations of bisphenol A and three other bisphenols in convenience samples of US adults during 2000–2014. Environ Sci Technol 49(19):11834–11839

Zielińska M, Wojnowska-Baryła I, Cydzik-Kwiatkowska A (2019) Sources and properties of BPA. In: Bisphenol A removal from water and wastewater. Springer, Cham, pp 3–28