Original Article

Environmental Monitoring of Bisphenol A in Ardabil's drinking water source as san endocrine disrupting chemical

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Abstract

Bisphenol A is a chemical used as the monomer of epoxy resins and polycarbonate plastics. Therefore, the aim of the present study was the monitoring of Bisphenol A as an endocrine disrupter chemical in drinking water sources of Ardabil. In this research, the first step was the sampling along the Nir Chay River in four seasons, which is the main supplier of Ardabil's drinking water. The amount of samples taken in each season from each of the 5 stations was 4 liters. Then Samples were analyzed using HPLC. In all seasons, the measured parameters values was below the standard limit. The lowest level of detection in all five sampling stations was in winter. There was not any significant quantitative relationship between the values the seasons, which may be due to other factors such as temperature and secondary inflammation caused by the presence of tourists.

Keywords: Bisphenol A; Ardabil; drinking water

Introduction

Water is the most abundant compound worldwide and the main source of life. The water availability affects the life and health of all living beings, including humans, plants, and animals [1]. The availability of clean water is of tremendous importance as water consumption increases, especially in industries; water resources are being contaminated by pollutants in different ways and these issues will result in problems in the future. Roughly, three decades ago, World Health Organization (WHO) and the United Nations Global Environment Monitoring System (GEMS) have recognized environmental quality regarding air and water quality, food contamination; moreover, the biological indicators have been monitored [2]. The presence of endocrine disrupting compounds (EDCs) in the environment and their harmful effect on human and animal health has been favored recently [3].

Bisphenol A (BPA; 4, 4′-dihydroxy-2, 2-diphenyl propane; CAS#80-05-7) is a monomer used extensively in the production of polycarbonate, epoxy resins and as a non-polymer additive in water pipes and plastics such as polyvinyl chloride (PVC). Therefore, the global demand for BPA raised from 3.9 million tons in 2006 to about 5 million tons in 2010 [4-7]. Major end-use applications for polycarbonate include electronic storage media, electrical and electronic goods, sheeting and glazing, and household equipment including containers utensils, and bottles. Epoxy resins are utilized as protective coatings for printed circuit boards, container coatings, marine and car coatings, and architectural structures. BPA is also used in the production of phenolic, phenoplast, and unsaturated polyester resins, thermal paper, and polyvinyl chloride. The presence of BPA in the consumer products and environment has been the subject of regulatory and public attention, primarily due to concerns about its weak endocrine activity. The ecotoxicological properties and environmental fate of BPA have been extensively assessed [8-11]. In addition, a number of risk assessments have been carried out by regulatory authorities worldwide [12, 13]. Compared to fresh surface waters, only limited data are available for sediments and less for marine ecosystems. Many of these studies characterized the sample locations as being downstream of wastewater discharges, receiving waters for

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areas susceptible to contamination, industrial facilities, industrial ports, or urban waterways. Measurements of BPA in drinking water and its source waters have been reported in numerous studies by government agencies and other researchers [14-17]. Several studies have described national monitoring programs. For most of these investigations, BPA is of the long list of analytes, while other investigations have only focused on BPA measurements. The available data have not been summarized, statistically analyzed, nor correlated with human exposures been assessed, so far. The treatment of drinking water usually involves adding a coagulant to the surface water to aid with flocculation of finely divided suspended matter that may be eliminated by sedimentation and filtration, and then chemical especially chlorine-based methods, or physical methods such as UV radiation are utilized to disinfect filtered water, [18]. Depending upon the surface water, additional processes may be used, including activated carbon treatment for the removal of dissolved organic material, demineralization for the reduction of dissolved ions (usually through advanced membrane treatment), and hydrogen sulphide/iron/manganese removal. Human exposure to BPA has been assessed by the determination of its concentration in media such as air, dust, and diet [9, 19-21]. Willhite et al [19] and AIST [12] demonstrated that water consumption is a minor source of exposure in comparison to food consumption. Snyder et al. [17] determined a safety margin of 72,000 by evaluating a relatively small dataset of drinking water samples from the US. The aim of this study was to perform a comprehensive review of BPA measurement in drinking water and source waters (surface water) and to determine the relative contributions of drinking water to overall exposure and potential human health risk of Nir Chay River and Balighli Chay that are the main supplier of drinking water of Ardabil. Therefore, the aim of the present study was the monitoring of Bisphenol A as an endocrine disrupter chemical in drinking water sources of Ardabil.

Materials and Methods

Instruments

A Rigol high-performance liquid chromatography (HPLC) model L3000 (China) equipped with a UV/Vis detector was used to separate and quantify estrone and 17β-estradiol. The separation was carried out on the Knauer ODS column, 250×4.6, 5 µm (Germany) using acetonitrile: water mixture (80:20) with 1 mL min^{-1} flow rate as the mobile phase.

The Study Area

Ardabil is the capital of Ardabil Province in the north-west of Iran (N 38° latitude and E 48° 02' longitude); it is placed west south of the Caspian Sea and between two mountains of "Sabalan and Baghro" (Fig.1). Ardabil is 70 km far from the Caspian Sea and 210 km from the city of Tabriz; it is located on the basin of the Baliqly Chay River. It has an average altitude of 1263 meters (4144 ft) and a total area of 18011 km^2 (6954 sq mi). Neighboring on the Republic of Azerbaijan and the Caspian Sea, Ardabil is of great economic and political significance throughout history, especially within the Caucasus region. It is also located in the east of Mount Sabalan (4811 m), where its peak is covered with snow throughout the year. According to the reports of the Statistics Center of Iran, the population of this city in 2011 was about 485,153 persons and the density of the city was 74 persons in a hectare and in 2016 was about 605,992 persons. Yamchi dam in Ardabil Province, with the aim of providing safe water for the needs of agriculture and drinking water in Ardabil, was constructed on the Baliqly Chay River. This dam is designed to provide 65 million m^3 of water for agriculture and 20 million m^3/year for urban use in Ardabil.

Climate

Due to its cool climate during hot summer months, many tourists come from regions with semi-arid climate. The winters are cold and long, with record low temperature of -33 °C. The annual rainfall is around 380 mm per year. Ardabil's temperature is between 35 °C to -33 °C during a year.

Sampling

This study was conducted over a 12-month period including four sampling periods (four seasons) from March 2018 to February 2019 and 23 samples were collected from the Ardabil drinking water supply river (BaliqlyChay River). Samples were collected from 5 stations in the specified areas along the Baliqly Chay River, the sewage outlet of Nir fish farms, crude sewage of Nir city, sewage treatment plant of Ardabil city and Ardabil drinking water distribution network according to the standard sampling procedure of water and sewage using 250 mL glass containers. The samples were transferred to the lab in an ice-cold box at 4 °C. Sampling areas were selected based on the research objectives as follows using the GPS device, the geographic coordinates were presented in (Fig. 1).

Analysis of the samples by HPLC: HPLC machine, the Dionex model is equipped with an Ultimate 3000 pump with two solvent inputs, Degasser gasification system CSI6150, P5 ODS Hichrome column (C_{18}), 250 mm long and 4/6 mm internal diameter, filled with particles of 5µm in size, Detector model Dionex Fluorescence RF2000, a wavelength of excitation is 330, and emission wavelength is 550 nm, and gradient elution, is a moving phase in two parts. To prepare standard solutions of bisphenol A for a calibration line of between 10-1000 µg L^{-1}, a Sigma solution of 1000 µg L^{-1} is used as a solvent in a methanol matrix. The sample size injected into the device to determine the quality of bisphenol A of µL. The type of injection into the machine was in the form of a spitlass, and the selected ions were 213 and 228 mass on the bisphenol A load.

Accuracy: The accuracy is calculated using the recovery value. 20 µl of the specimens determined at 40 µg.L^{-1} levels, and 3 of them each, were injected into the HPLC by the amount of recovered bisphenol A and the percentage of deviation. The relative RSD% criterion was also calculated.

Precision: Calculation of the accuracy of the method was carried out by repeatability in one day and for 3 consecutive

days. In order to check the precision of the day, the specimens presented in 40 µg L^{-1} were injected into the machine three times. The surface area under the curve of each peak and the relative percentage deviation of each peak were calculated.

Fig. 1. Location of sampling sites in the river basin

Sample-Preparation Procedures

Solid-phase extraction was performed with an SPE-12G vacuum system (Baker SPE). Cartridges containing C_{18} bonded-phase silica adsorbent (Baker SPE) were placed on the vacuum manifold and conditioned with 10 mL deionized water and 5 mL MeOH.

For investigations of recovery and analytical precision, samples (500 mL) of deionized tap water were spiked with BPA. After preconcentration, the adsorbent was air-dried using a vacuum system for 20 min. The compounds retained were eluted with 2 mL MeOH. The extracts were then evaporated to dryness, reconstituted in 0.25 mL mobile phase, and analyzed by MLC.

For the analysis of drinking water, the samples (500 mL) were percolated through previously conditioned cartridges at a flow rate of approximately 1 mL min^{-1}. Retained bisphenol A was eluted with 2 mL methanol, the MeOH was evaporated, and the residue was reconstituted in 0.25 mL micellar mobile phase.

Results and Discussion

The results of this study showed that the highest amount of BPA for spring and summer for Jurab and Borjelu, respectively were 0.86 and 1.10 µg L^{-1}. The maximum amount of BPA for the output of the dam and outlet of the refinery and city water network in the summer were, 1.64, 2.59, and 0.67 µg L^{-1}, respectively. In the autumn, the amount of bisphenol was lower than in spring and summer, and in winter it was below the detection limit. In this study, it was shown that the amount of BPA in the summer was higher than the other seasons, and outlet of the refinery was higher than the BPA content compared to the studied station (Table 1). High levels of BPA in summer and low in winter (especially below the detection limit) and lack of significant changes in pH mentioned in Table (2), as well as lack of significant quantitative correlations in other seasons other factors that contribute to increasing or decreasing BPA levels, Particularly the increase in inflammation in summer and spring alerts human beings to pollution by increasing the number of tourists to these areas. This is because the Borjelu and Jurab stations are the best places for tourists to visit, the most common collected items are all forms of plastic debris. Decreased BPA levels after dam outflow indicate that standing time, sedimentation, or biological activities during the time the water is behind the dam can have a significant impact on reducing BPA. The decrease in BPA at the first point after the transmission line to a distribution network that exceeds 20 km can be due to deposition inside the pipe or due to biological activity. It is noteworthy that no disinfectant was injected after the water discharged from the treatment plant and this was done in the first storage tank after the transmission line was completed, and the effect of polyethylene pipes on BPA increases was practically overshadowed because if it had been effective, it would have had to show up along this long route.

In general, the amount of BPA in Ardabil drinking water was not significant and its source is the secondary pollution caused by direct human impact.

Table 1. The amount of BPA in the rivers in four seasons

Area	Spring µg L^{-1}	Summer µg L^{-1}	Autumn µg L^{-1}	Winter µg L^{-1}
Borjelu	0.86	0.55	0.85	Under the detection limit
Jurab	1.10	dry	0.96	Under the detection limit
Outlet dam	0.41	1.64	0.38	Under the detection limit
Outlet of the refinery	0.55	2.59	0.51	Under the detection limit
City water network	0.18	0.67	0.16	Under the detection limit

Table 2. The amount of temperature (oC) and pH in the rivers in four seasons

		Spring	Summer	Autumn	Winter
Raw water	Temperature (°C)	11	18.5	13	5.5
	pH	8.26	8.35	7.98	7.82
Outlet water	Temperature (°C)	13	20	16.5	7
	pH	7.28	7.32	7.49	7.58

The determination of BPA was performed with a mobile phase. An example of a chromatogram obtained under these conditions from a standard mixture of bisphenol A (1.0 µg L^{-1}) is shown in Fig. 2.

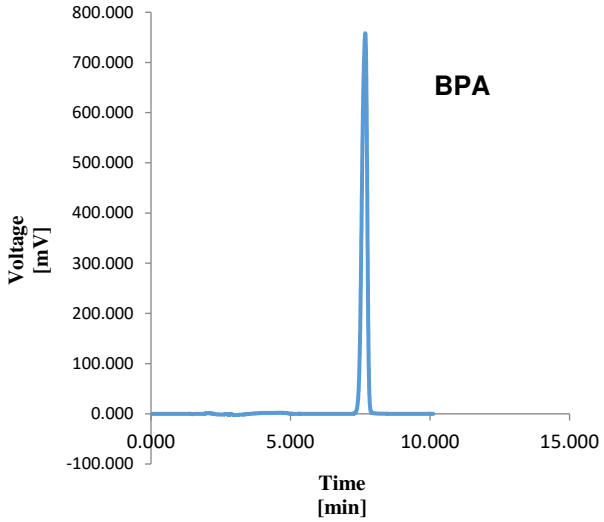

Fig. 2. The chromatogram obtained from a standard solution of BPA (7.68 min).

Calibration, Limits of Detection and Quantification, and Recovery

Calibration was performed with mixed standard solutions of the compounds. To determine the range in which response was a linear function of the amount injected, standard solutions containing 0.5; 1.0; 2.0; 5.0; 10.0; 20.0; 50.0; 100.0 µg L^{-1} BPA in the mobile phase were injected (40 µg L^{-1} injection). Each solution was injected in triplicate. Good correlation coefficients (>0.9973) were obtained.

The resulting calibration plots, regression data, and correlation coefficients are presented in Fig. 3. The limits of detection (LOD) and limits of quantitation (LOQ), and the linear range are listed in Table 3.

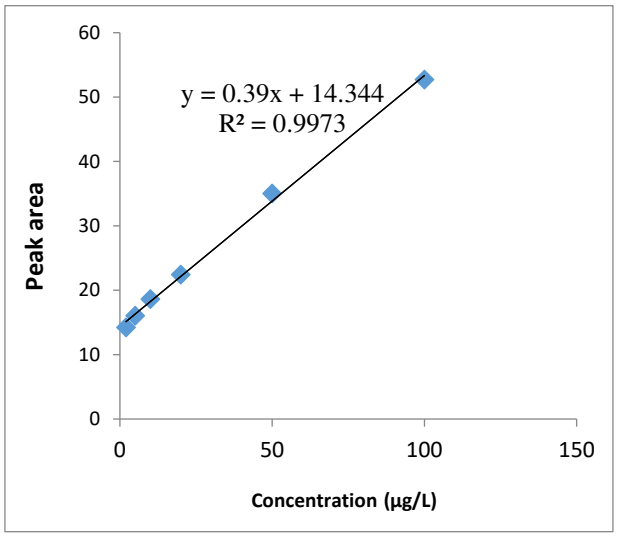

Fig. 3. Calibration plots for BPA

Table 3. Limits of detection and quantitation, and the linear range

	Linear range (µg L^{-1})	LOD (µg L^{-1})	LOQ (µg L^{-1})
BPA	0.50-100	2	5

Recoveries of BPA from water, with relative standard deviations, are given in Table 3. The compounds were added to the water at a concentration of 1.0 µg L^{-1}. The method proposed is characterized by high recovery.

Table 4. Recovery of BPA from 500 mL tap water spiked At 1 µg L^{-1} after SPE on C_{18} (n = 6)

	Recovery (%)	RSD (%)
BPA	89	5.7

Determination of BPA in Water

Five types of water samples were collected from the areas Jurab, Borjelu, outlet dam, outlet of the refinery and city water network located along the Nir Chay river as the main supplier of drinking water of the city of Ardabil in Iran. The amount of BPA was determined by the standard-addition method after SPE on C_{18}. The results are presented in Table 5.

Table 5. Results from the analysis of drinking water (n = 4)

Sample	BPA (µg L^{-1} ± SD)	RSD (%)
Borjelu	0.18±0.75	2.3
Jurab	0.10±1.03	0.96
Outlet dam	0.72±0.81	8.8
Outlet of the refinery	1.19±1.22	9.7
City water network	0.29±0.34	8.5

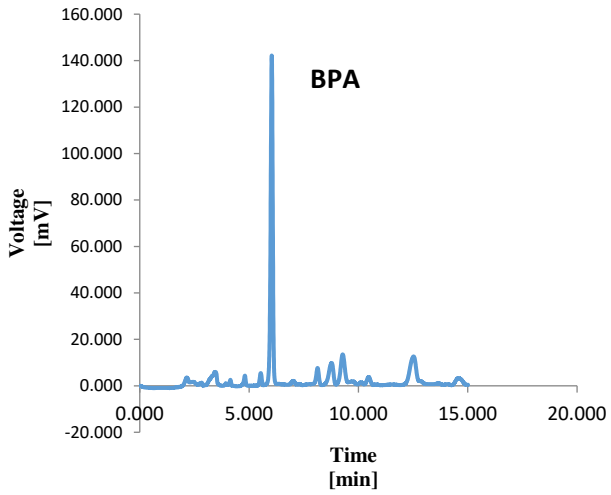

Fig. 4. HPLC chromatograms obtained from the analysis of a water sample.

Conclusions

The proposed method involves the concentration of BPA residues in drinking water samples by solid-phase extraction then analysis by micellar liquid chromatography with UV detection. The method is simple, sensitive, rapid, and is characterized by high recovery; for example, the recovery of BPA was 89%. The detection limit for BPA was 2 µg L^{-1} in water samples studied.

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