# DISTRIBUTION OF BISPHENOL ANALOGUES IN SURFACE WATER FROM VARIOUS LOCATIONS OF INDIA

Lalwani D[1,2], Yamazaki E[2,3], Lin H[2,4,5], Ruan Y[4], Taniyasu S[2], Kumar NJI[1], Lam PKS[4,5], Yamashita N[2]

[1]Institute of Science & Technology for Advanced Studies & Research, Vallabh Vidhyanagar, Anand, India, 388120, lalwani.dipa6@gmail.com; [2]National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan, 305-8569; [3]College of the Environment & Ecology, Xiamen University, Xiamen 361102, China, [4]State Key Laboratory of Marine Pollution, and [5]Department of Chemistry, City University of Hong Kong, Hong Kong SAR, China

## Introduction

Bisphenol A (BPA) is a synthetic phenol belonging to the group of diphenylmethane derivatives, and it is widely used in the manufacture of polycarbonate plastics and epoxy resins. BPA is one of the most widely used chemicals, with an annual production of 5 million tonnes in United States [1]. The toxic effects of BPA have been widely reported[2]; thus, BPA is now being replaced by several bisphenol analogues (BPs) such as bisphenol S (BPS) and bisphenol F (BPF). There have been several studies on the distribution of BPA in various environmental samples including indoor dust[3], sediment[4], surface water[1,5], and drinking water[6]. In spite of the worldwide concern for BPs, their occurrence in India remains largely unknown. A previous study has reported the concentrations of BPA, BPS, and BPF in surface water in India[1], but this investigation was limited to a specific region – Tamil Nadu.

Accordingly, the main objective of the present study was to determine the environmental concentrations of 8 BPs including BPA, BPS, and BPF. This is the first study investigating the BPs in surface water samples (*n* = 74) collected from 12 states and a union territory, representing the whole India.

## Materials and methods

Surface water samples were collected nationwide from December 2017 to May 2018 from main rivers in Jammu & Kashmir (*n* = 6), New Delhi (*n* = 7), Uttar Pradesh (*n* = 11), Bihar (*n* = 2), West Bengal (*n* = 6), Odisha (*n* = 4), Andhra Pradesh (*n* = 2), Tamil Nadu (*n* = 7), Kerala (*n* = 9), Maharashtra (*n* = 8), Gujarat (*n* = 1), Rajasthan (*n* = 3), and Punjab (*n* = 7), India (Figure 1). Wastewater samples were also collected during the same period in each of these studied areas.

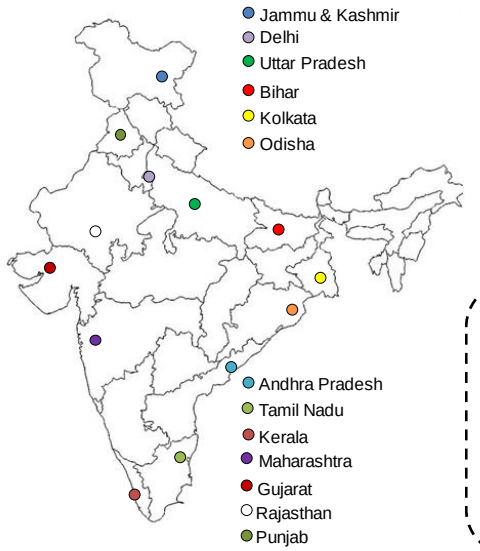


Figure 1. Sampling locations

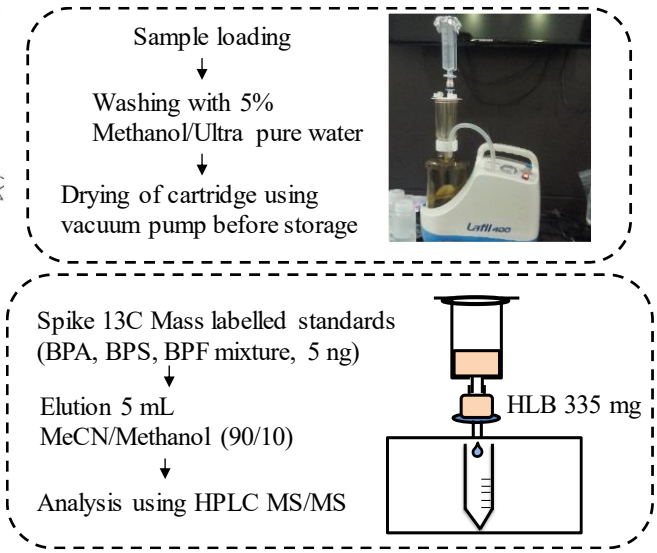


Figure 2. Schematic diagram for sample extraction

Samples were analyzed using previous established methods with modifications[1]. All samples were filtrated on site using portable vacuum filtration device with nylon filters (pore size: 5.0 µm). 15 mL of sample was diluted to 200 mL with ultrapure water and pH was adjusted to 3 by adding 0.3 mL of acetic acid[1]. The diluted sample was then loaded onto a PRiME HLB Plus Short cartridge and washed with 5 mL of 5% methanol in water to remove impurities, followed by drying under vacuum. The cartridges and filters were covered with alumina foil

and stored at 4 °C until further treatment. The elution and instrumental analysis were performed at the National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan. Prior to elution, cartridges and filters were brought to room temperature. Then cartridges were spiked with 5 ng of $^{13}$C-labelled internal standard (ISTD) mixtures of BPA, BPS, and BPF. The cartridge was eluted using 5 mL acetonitrile/methanol (v/v 9:1). The nylon filters ($n$ = 54) were extracted using 2 mL of methanol in order to determine BPs associated with particles in water. Then both final extracts were subjected to high-performance liquid chromatography–tandem mass spectrometry analysis (Figure 2)[1,3].

The risk assessment for BPA to human health due to ingestion of river water was also calculated following previous study[5]. The calculated adult exposure values were compared to total daily intake (TDI) values to check the safety status. The measured BPA concentrations were compared with predicted no effect concentration (PNEC) given by EU (2008) for a preliminary assessment.

**Results and discussion**

Among the 8 analyzed analogues, only BPA, BPS, and BPF were detected in the present study (Figure 3); other analogues were not found in any of the samples.

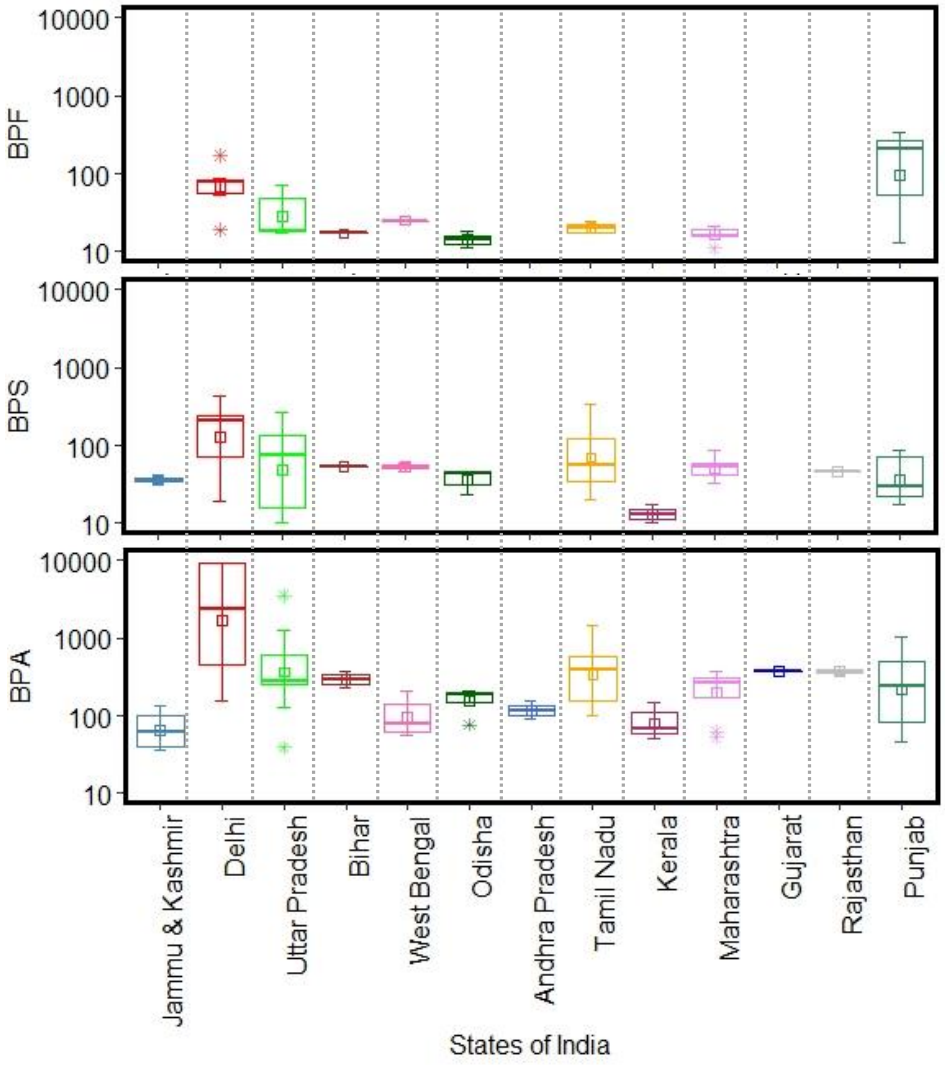


Figure 3. Concentrations (ng L$^{-1}$) of BPA, BPS, and BPF in surface water collected from different locations of India (no boxplot = not detected, whiskers = min to max values, middle square in each box plot = mean value, points apart from boxplot = outliers)

The distribution of the 3 detected BPs is demonstrated in Figure 4. The detection frequencies of these BPs were found as BPA (100%) > BPS (53%) > BPF (31%) among samples. BPA was found at the highest concentrations (38.3-14800 ng/L) in all samples. Among sampling locations, the Yamuna River exhibited the highest BPA and BPS concentrations, ranging from 154 to 14800 ng/L and from 19.2 to 246 ng/L, respectively. The wastewater from Punjab had the highest concentration of BPF (333 ng/L). In Leh, Patna, Kolkata, Bhubaneswar, and Kochi, higher BPS and BPF concentrations were found in wastewater compared to those in river water; meanwhile, a higher BPF concentration (<17.2-333 ng/L) was found in river samples from Punjab. The lowest BPA concentrations (38.3-83.7ng/L) were found in the Indus River.

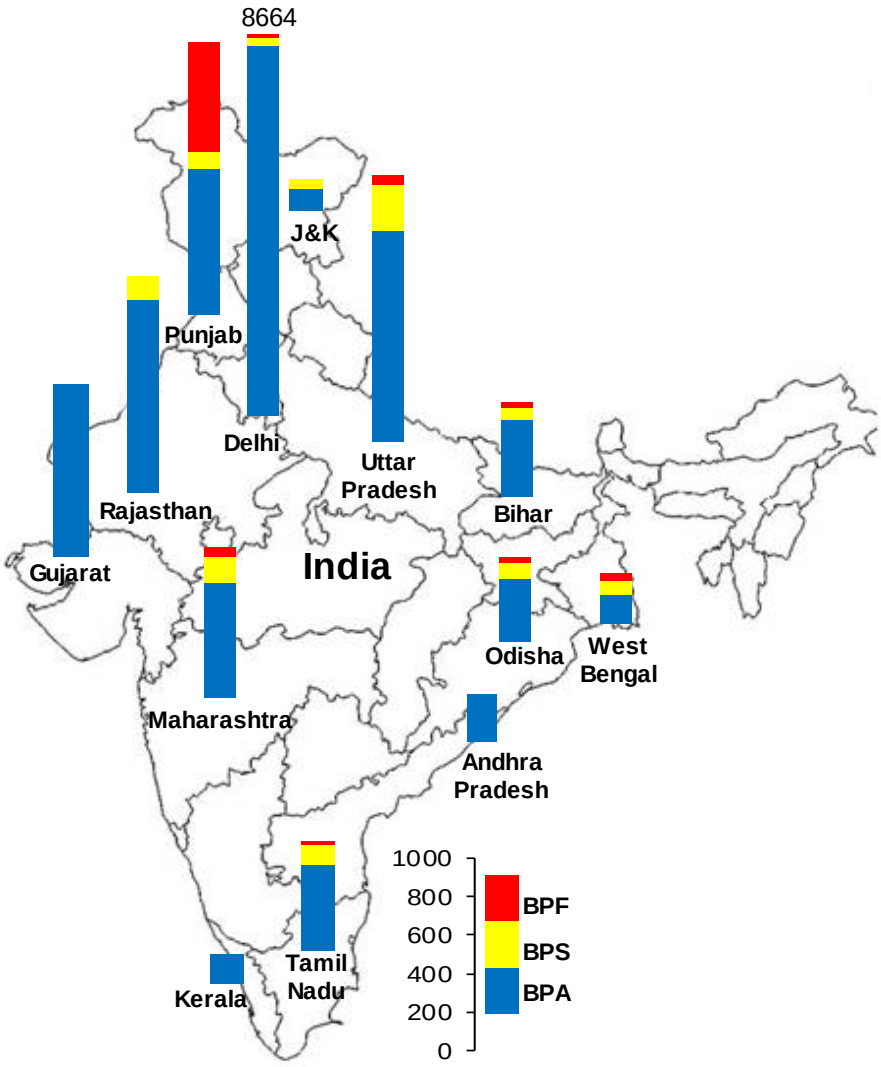


Figure 4. Nation wide distribution of Bisphenol analogues (average, concentration = ng $L^{-1}$) in surface water of India (J&K=Jammu & Kashmir)

Few measurements have been conducted on BPs concentrations in surface waters of India, mostly limited to the Tamil Nadu. BPA was found in the Kaveri, Vellar, and Tamiraparani Rivers with concentrations at the ranges of 6.60-136 ng/L, 2.80-6.00 ng/L, and 9.80-36.0 ng/L[5] respectively, which are 10 to 100 times lower than the highest concentration (1490 ng/L) recorded in Cooum River in present study. The large volumes of untreated wastewater discharge from highly urbanized and industrialized regions nearby might be the prime reasons for the high BPA contamination4. A significant positive correlation ($p < 0.05$) was found between BPA and BPS concentrations in Punjab ($R^2 = 0.73$) and Uttar Pradesh ($R^2 = 0.61$), whereas BPS and BPF were found significantly correlated in from Punjab ($R^2 = 0.82$), Delhi ($R^2 = 0.92$), and Uttar Pradesh ($R^2 = 0.67$). These findings indicate a similar pattern of usage and sources of BPS and BPF in these states of Northern India. One of the reasons could be the application of BPF-based resins used in wastewater treatment facilities including storage and aeration tanks[7] as well as in water pipes for irrigation. Indeed, the FCCI report (2014) mentioned that

the total consumption of plastic products in Northern India was 23% in 2012-2013, although the use of particular BPs in plastic products remains unknown in India.
An inconsistency of the contamination pattern of BPS and BPF was observed between India and other countries (China, Korea, and Japan) where BPF was the major contaminant as compared to BPA in India. The frequent occurrence of BPS and BPF in Indian samples implies the release of these analogues into the environment via usage, although their concentrations were several times lower than those of BPA. In the present study, the human exposure of BPA through drinking river water was much lower (0.01-0.5 µg/kg bw/day) than the reference TDI (4 µg/kg bw/day). In comparison, the European Union has suggested a PNEC of BPA at 1500 ng/L (EU, 2008)[1] to protect aquatic organisms, while the highest concentrations of BPA in water samples from the Yamuna River and Cooum River as well as wastewater samples were recorded 2 to 10 times higher the PNEC value for aquatic organisms. These results suggest an urgent need of further studies on the monitoring and management of BPA usage in India.

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**References**

1. Yamazaki E, Yamashita N, Taniyasu S., et al. (2015) Ecotox. Environ. Safe. 122: 565–572
2. Chen D, Kannan K, Tan H et al., (2016) *Environ. Sci. Technol.* 50(11): 5438–5453
3. Liao C, Liu F, Guo Y, et al. (2012a) *Environ. Sci. Technol.* 46(16): 9138−9145
4. Liao C, Liu F, Moon HB, et al. (2012b) *Environ. Sci. Technol.* 46(21): 11558−11565
5. Kumar, K., Shanmugam, G., Sampath, S. et al., (2014). *Ecotox. Environ. Safe.* 99: 13–20.
6. Santhi VA, Sakai N, Ahmad ED, et al. (2012). *Sci. Total Environ.* 427: 332–338
7. Lee S, Liao C, Song G, et al., (2015) *Chemosphere* 119: 1000–1006