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# First insight into the levels and distribution of flame retardants in potable water in Pakistan: An underestimated problem with an associated health risk diagnosis

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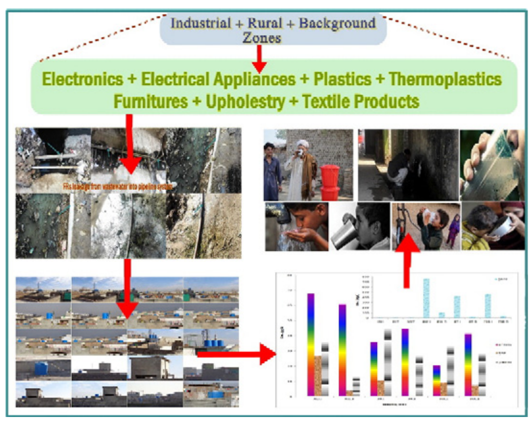
## HIGHLIGHTS

- First report on the occurrence of FRs in the potable water of Pakistan
- High FRs concentration in industrial followed by rural and background zones
- TCPP, anti-DP, BDE-47 and DBDPE were the leading FRs in the potable water.
- HQs for FRs in the Children and adults via potable water consumption were <1.
- FRs leakage in pipelines from wastewater bodies are culprit of water contamination.

## GRAPHICAL ABSTRACT

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## ABSTRACT

To date, very little is known about the occurrence of flame retardants (FRs) in potable water and its associated health risk to the exposed human population. The current study was designed to investigate the differences in the contamination levels of selected FRs in the potable water of industrial, rural and background zones of Pakistan. In addition, the health risk assessment for the exposed human population was estimated. For this purpose, the concentrations of the selected FRs: polybrominated diphenylethers (PBDEs), dechlorane plus (DP), novel brominated flame retardants (NBFRs) and organophosphate flame retardants (OPFRs), were analyzed in a total of 39 samples of potable water from the above mentioned three zones. We found elevated concentrations of $\sum$ OPFRs (BDL-71.05 ng/L), $\sum$ PBDEs (BDL-0.82 pg/L), $\sum$ NBFRs (BDL-1.39 pg/L) and $\sum$ DP (BDL-0.29 pg/L) in the potable water samples from industrial zones, smaller concentrations in the samples from rural zones, and negligible concentrations in the samples from background zones. Among all the FRs analyzed, Tris-(2-chloroisopropyl)-phosphate ($\sum$ TCPP), anti-DP, BDE-47 and 1.2-bis(pentabromodiphenyl)ethane (DBDPE) were the dominant compounds in all three selected zones. Principal component analysis (PCA) revealed that most of the FRs are associated with the industrial zones. The estimated daily intake (EDI) for all selected FRs was found to be higher in children than adults. However, both children and adults were found to be at low

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risk (i.e., Hazard quotient (HQ) < 1) of FRs exposure through potable water consumption. We predict that FRs might be leached out from wastewater bodies and subsequently mixed with nearby potable water facilities. FRs may also spill out from the aluminum or plastic pipes and tanks most commonly used for potable water storage in Pakistan. The present study suggests initiating measures to minimize human exposure to FRs in the future.


## 1. Introduction

Groundwater constitutes about 30% of the world's freshwater resources, 97% of which is available for human consumption (Morris et al., 2003). In addition to drinking purposes, groundwater is widely used for agricultural, industrial, and domestic purposes (Postigo and Barcelo, 2015). Pakistan is among those Asian countries in which both surface and groundwater resources are becoming polluted and therefore may be potentially unsafe for human consumption in the future (Azizullah et al., 2011). Most people in Pakistan (about 60%) live below the poverty line and do not have access to clean drinking water supplies. During the past few decades the observed occurrence of flame retardants (FRs) in potable water has raised a multitude of concerns among scientists and the public.

Punjab province is located in the central part of Pakistan and has a high population and extensive industrial and agricultural activities. These activities result in the potential release of various legacy and emerging flame retardants into the environment. FRs such as polybrominated diphenyl ethers (PBDEs), dechlorane plus (DP), novel brominated flame retardants (NBFRs) and organophosphate flame retardants (OPFRs) are used in various consumer products to prevent and retard fires (EFRA, 2005). These flame-retarding organic compounds have been added to a large number of commercial products such as foams, paints, plastics, furniture and textiles (Marklund et al., 2003) and have also been used as additives in lubricants and hydraulic fluids and in electrical and electronics materials, paints, glues, varnishes, lacquer and rubber (Marklund et al., 2005; Reemtsma et al., 2008; Yang et al., 2014). Due to their toxicities and high levels in the environment, brominated flame retardants (BFRs) such as PBDEs (Penta and Octa) and chlorinated DP have been phased out through regulation via various regional, national and international agreements (Möller et al., 2012; Wang et al., 2015). In replacement, NBFRs such as bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (TBPH), pentabromoethylbenzene (PBEB), hexabromobenzene (HBB), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), 1,2-bis(2,4,6-tribromophenoxy)ethane (TBE) and 1,2-bis(pentabromodiphenyl)ethane (DBDPE) and OPFRs have been used in various commercial products due to their low cost and effective fire-retarding capacities. OPFRs, due to their additive behavior and solubility in water, are released into environmental water either by abrasion, volatilization or leaching (Marklund et al., 2005; Sundkvist et al., 2010; Li et al., 2014). Few previous studies have revealed the occurrence of OPFRs in the groundwater, reflecting its origin through the process of infiltration/leaching from wastewater and other contaminated sources (Cordy et al., 2004; Heberer et al., 2004). The groundwater quality is usually deteriorated due to the inclusion of different chemicals especially from point and diffuse sources (Postigo and Barcelo, 2015). Further, concentration levels of FRs in groundwater may be potentially influenced by the octanol-water (logKow) and organic carbon-water (logKoc) partition coefficients, water solubility and biodegradation activities (Lapworth et al., 2012). OPFRs are known to have medium–high polarity (logKow, 1.4–4) and they prefer the water phase (Estevez et al., 2012; Regnery et al., 2011; Focazio et al., 2008; Teijon et al., 2010). In contrast to OPFRs, all other BFRs (PBDEs, DP and NBFRs) are slightly soluble in water and may be attached to the residual or suspended particles in the potable water. But the dust-bound FRs may be available both in the air particulate and gaseous phases that have their potential to be transported in the potable water through the wet/dry deposition process. Previous studies from Pakistan have revealed the occurrence of PBDEs, NBFRs and OPFRs in soil dust samples (Ali et al., 2012, 2013, 2014), as well as PBDEs and DP in air samples (Mahmood et al., 2015a; Syed et al., 2013; Ali et al., 2015). In addition to these pathways, potable water is transported to local populations through pipelines that were stretched in the drainage system or wastewater. It is also possible that the pipelines in study areas were badly damaged due to the prolonged use of cheap, low quality materials and binding spaces in pipelines further boost the leakage of FRs from wastewater. Therefore, with the passage of time, potable water becomes contaminated with FRs due to the above mentioned practices.

Several studies have highlighted the incidence of OPFRs in different environmental matrices (atmospheric, aquatic and terrestrial) as a result of their utility in many commercial products (Andresen and Bester, 2006). Due to their toxicity, OPFRs have been surveyed widely and detected in various aquatic (surface water, groundwater) environments of Austria, Germany, Japan, United States, Italy, Spain and China (Benotti et al., 2009; Fries and Puttmann, 2001; Martineze-Carballo et al., 2007; Bacaloni et al., 2008; Rodil et al., 2012; Wang et al., 2011; Cristale et al., 2013a; Cristale et al., 2013b; Regnery and Puttmann, 2010; Focazio et al., 2008; Schaider et al., 2014; Li et al., 2014; Hu et al., 2014; Wang et al., 2015; Ding et al., 2015). To date, very few studies have been carried out to measure BFR concentrations in surface water (Oros et al., 2005; Wurl et al., 2006; Qi et al., 2010; Cristale et al., 2013a; Venier et al., 2014; Schreder and La Guardia, 2014; Zheng et al., 2015; Mahmood et al., 2015b). However, no study so far has investigated the concentrations of PBDEs, DP and NBFRs in potable water samples.

It is important to evaluate the health risk associated with the levels and distribution of FRs in drinking water. For this purpose, the current study not only presents the concentration levels, distribution and overall profile composition of FRs in the potable water in three different zones, but also emphasizes the risks to human health associated with the consumption of contaminated water. This study will be helpful in developing the first baseline data of FRs in drinking water in Pakistan.

## 2. Materials and methods

### 2.1. Study area

Potable water samples were collected from three sampling zones: industrial, rural and background. The industrial and rural samples were taken from Gujrat, Gujranwala and Faisalabad, while the background samples were collected from Azad kashmir, Swat and Chitral (Fig. 1). The sample collection was carried out from June to November 2014.

### 2.2. Sampling strategy

A total of 39 drinking water samples (five from each industrial and rural zone (Gujrat, Gujranwala, Faisalabad) and three from each background zone (Azad kashmir, Swat and Chitral) were collected as depicted in Fig. 1. A detailed sampling strategy for the potable water collections is given in the Supplementary information text 1. A composite sample (3–5 sub-samples) of potable water in an area of about 1–2 km was allocated, from where random sampling of the proposed site was carried out. Water stored in tanks used for drinking purposes was preferred for sample collection. All the potable water samples were preserved in amber glass bottles already pre-rinsed with 10% nitric acid solution followed by distilled water and stored at 4 °C. After collection, all the potable water samples were transported to State Key