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The first countrywide monitoring of selected POPs: Polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and selected organochlorine pesticides (OCPs) in the atmosphere of Turkey

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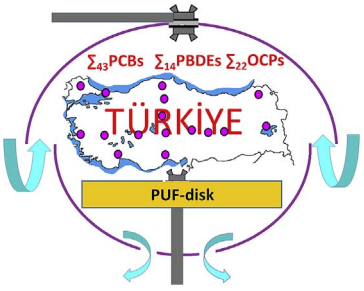
GRAPHICAL ABSTRACT



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ABSTRACT

Atmospheric levels of 43 PCBs, 22 OCPs, and 14 PBDEs were determined in 16 cities at urban and rural sites by passive sampling to generate the first large-scale nationwide dataset of POP residues in Turkey's atmosphere. Sampling campaign was performed from May 2014 to April 2015 with three-month sampling periods at locations on east-west and north-south transects through the country to investigate seasonal and spatial variations, including long range atmospheric transport (LRAT). Factor analysis was conducted to infer on the potential sources. Overall average Σ_{43}PCBs concentration was 108 ± 132 pg/m^3. PCB-118 (26.3 ± 44.6 pg/m^3) was the top congener, and penta-CBs had the highest contribution with 54.3%. ΣDDTs had the highest annual mean concentration with 134 ± 296 pg/m^3 among the OCP groups among which the highest concentration compound was *p'p*-DDE (97.6 ± 236 pg/m^3). Overall average concentration of Σ_{14}PBDEs was 191 ± 329 pg/m^3 with the highest contribution from BDE-190 (42%). Comparison of OCPs and PCBs concentrations detected at temperatures which were above and below annual average temperature indicated higher concentrations in the warmer periods, hence significance of secondary emissions for several OCPs and Σ_{43}PCBs, as well as inference as LRAT from secondary emissions. The first nationwide POPs database constructed in this study, point to current

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use, local secondary emissions, and LRAT for different individual compounds, and indicate the need for regular monitoring.The first country-wide passive sampling of selected POPs showed no unequivocal trends reflecting transitional location of Turkey.

1. Introduction

It was decided by the Grand National Assembly in April 2009 that Turkey was to become a party to the Stockholm Convention (Official Gazette, 2009a). The decision was accepted by the Council of Ministers in July 2009 (Official Gazette, 2009b) whereas the legal procedure was completed in January 2010. As is the case for many Stockholm Convention ratifying countries, certain persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) were never produced in Turkey. However, many products such as transformers, capacitors and flame retarded consumer products containing these chemicals were/are in use in the country. As a country with intensive agricultural practices, organochlorine pesticides (OCPs) were also widely used in Turkey until they were banned. Moreover, Turkey receives air masses from Europe, former Soviet countries, the Arabian Peninsula, and North Africa, which makes it an interesting country in terms of POPs due to its transitional location. PCBs, PBDEs, and OCPs are considered as POPs that are best known for their persistence to degradation in the environment. Therefore, they can undergo long range atmospheric transport (LRAT), and are subject to bioaccumulation in fatty tissues and in the food chain (Li et al., 2006). Most of the subject POPs (such as heptachlor, lindane, dieldrin, chlordane, etc.) were banned around the 1980s in Turkey.

One of the main obligatory tasks required under Stockholm Convention for ratifying countries is to monitor environmental levels of banned/phased out chemicals. In this manner, many of ratifying countries have conducted long-term systematic monitoring programs. Although the country is under the obligations of the Convention since 2010, Turkey is unfortunately lacking such long-term spatial and temporal monitoring activities of POPs. There exist studies to determine occurrence and seasonality of PCBs (Gedik and Imamoglu, 2010; Yenisoy Karakas et al., 2012; Kuzu et al., 2014, 2016; Kuzu, 2016; Kuzu and Saral, 2017; Dumanoglu et al., 2017), PBDEs (Cetin and Odabasi, 2007, 2008; Odabasi et al., 2016) and OCPs (Yenisoy-Karakas et al., 2012; Kuzu, 2016) in the country. However, these studies are limited to several specific industrial and urban locations to measure seasonality of chemicals of interest.

Compared to the western part of the world, number of studies on investigation of occurrence and fate of POPs including PCBs, OCP, and PBDEs in environmental compartments in Turkey is still limited, it is certainly of an increasing interest. Sources of PCB contamination was reported to be petrochemical plants, iron steel-plants, and ship demolishing sites in the studies conducted in Aliaga (Kaya et al., 2012; Odabasi et al., 2015) and waste landfill in Hamitler (Esen, 2013). Odabasi et al. (2016) reported average concentration of Σ_{41}PCBs in background and industrial sites in Iskenderun (Turkey) as 180 ± 140 pg/m^3 and 1600 ± 900 pg/m^3, respectively. Summer concentrations of Σ_{41}PCBs in Kutahya province were reported in the range of 31.6 pg/m^3 to 230.2 pg/m^3 (average value of 125.3 ± 33.5 pg/m^3) while concentration range was 19.6 pg/m^3 to 675,1 pg/m^3 with an average value of 187.9 ± 132.9 pg/m^3 in winter (Dumanoglu et al., 2017). Average ambient gas-phase Σ_7PBDE concentrations were between 189 ± 61 (summer) and 76 ± 65 pg/m^3 (winter) in Izmir (Cetin and Odabasi, 2007). Kurt-Karakus et al. (2017) reported Σ_{12}PBDEs concentrations range between 110 and 620 pg/m^3 in Istanbul. Gas phase Σ_{23}OCPs average concentration were in the range of 1.10 pg/m^3 and 42.5 pg/m^3 in Izmir (Ugranli et al., 2016). Alpha-HCH showed the lowest concentration (2.10 pg/m^3) while endosulfan II showed the highest concentration (73.01 pg/m^3) in samples collected from Bursa province in 2008–2009 (Cindoruk and Tasdemir, 2014). The congener pattern of PCBs was similar in air of Aegean but PBDE levels were different between Greece and Turkey (Lammel et al., 2015). Additionally, uniform concentration levels of long-lived chemicals were reported to be dominated by LRAT or distribution within a region.

High volume active air sampling of POPs is a widely favored technique around the world. However, after the awareness of the fact that remote areas might also been polluted by POPs due to LRAT (Bowes and Jonkel, 1975), an alternative technique was required that provides easy access, less operation cost and labor, and, above all, has no electricity requirement. Development of passive air samplers (PAS) met these requirements, and they have been widely used for measurement of relatively long term average gas phase concentrations of POPs. Besides studies to determine ambient air POPs levels using active air samplers in Turkey (Birgul and Tasdemir, 2012; Cindoruk and Tasdemir, 2014; Kuzu et al., 2014; Odabasi and Cetin, 2012; Yolsal et al., 2014; Ugranli et al., 2016) there are limited studies conducted in Turkey using polyurethane foam passive samplers (PUF-PAS) (Kaya et al., 2012; Aydin et al., 2014; Odabasi et al., 2015, 2016; Kurt-Karakus et al., 2017; Cetin et al., 2017a,b). However, these studies were conducted in particular regions of the country and there are no studies to investigate the levels of PCBs, PBDEs and OCPs concurrently on a countrywide scale.

The aims of this study were (a) to measure atmospheric air concentrations of PCBs, OCPs, and PBDEs at a total of 32 urban and rural places located in 16 provinces at an east-west and a north-south transect in Turkey using PUF-PAS samplers, (b) to investigate spatial and seasonal variations of target chemicals, and (c) to generate the first large-scale nationwide dataset of atmospheric PCB, PBDE, and OCP levels in Turkey.

2. Materials and methods

2.1. Study area and sampling program

Sixteen provinces with urban and rural sites in Turkey were selected on the centerline from East to West and North to South in addition to the three corner locations of Turkey (Figs. 1, 3 and 4; Supplementary Material Table S1). It was recommended that the rural sites should represent a diameter of a circular area of at least 100 km so the distance between the sampling locations was about 250–300 km (UNEP, 2007). Ease of transport, existence of contact people to take care of the samplers, and travel safety were the other criteria considered for sampling point selections. Urban sampling locations were representative of typical urbanized areas. Background sites were chosen to be remote from any potential sources such as populated/industrialized/agrochemical application areas, to ensure that they were representative of background levels.

Three-month sampling was performed in four periods; May–July 2014 (1st period), August–October 2014 (2nd period), November 2014–January 2015 (3rd period), and February–April 2015 (4th period). The sampling durations varied from 80 to 118 days depending on the availability and travel conditions on the field (Supplementary Material Table S1). Mean temperature ranges during the sampling periods were 12.9–25.6 °C (1st period), 10.6–24.2 °C (2nd period), −3.6–12.8 °C (3rd period), and 3.5–15.6 °C (4th period).

2.2. Chemicals and reagents

All chromatography-grade solvents (acetone, hexane, dichloromethane, iso-octane), anhydrous sodium sulfate (granulated for