

DETERMINATION OF HISTORICAL VARIATIONS OF PBDEs IN AN INDUSTRIAL REGION USING TREE CORES

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Introduction

Persistent organic pollutants (POPs) enter the plants from the atmosphere via particle and gas-phase deposition onto the waxy cuticle on the leaf and stem surface or by uptake through the stomata and they are translocated by phloem¹. Although plants are able to take up POPs into the root system followed by their translocation via xylem, root uptake of POPs from soil is generally limited due to their low solubility in soil water². The high lipid content of the xylem of coniferous trees enables tree trunks to store and accumulate atmospheric POPs over time.

Currently, historical variations of environmental POPs are mainly determined by the analysis of dated sediment cores³. Research on historical variations in atmospheric POPs by dendrochemistry has been extremely scarce and had some limitations (i.e., detection problems, coverage of only polycyclic aromatic hydrocarbons and polychlorinated biphenyls, and very small sample sizes)^{1,4,5,6}.

The main objective of this study was to investigate the historical variation of polychlorinated biphenyls (PBDEs) by dendrochemistry in the heavily polluted Aliaga industrial region in Turkey.

Materials and methods

The field studies were conducted in the forested areas of Aliaga, Turkey. The study area includes a large petroleum refinery and a petrochemical complex, several ferrous scrap processing iron–steel plants with electric arc furnaces (EAFs), scrap storage and classification sites, steel rolling mills, a natural gas–fired power plant, a pulp and paper plant, a fertilizer plant, a very intense transportation activities of ferrous scrap trucks, heavy road traffic, ship breaking yards, and busy ports used for product and raw material transportation. Aliaga town with a population of ~60 000, several villages, and agricultural areas are also located within the region (Figure 1). Sampling sites (n=27) were selected to represent locations affected by the industrial emissions (n=21) and the background (n=6) locations. Tree core samples from pine trees (*Pinus brutia* and *Pinus pinea*) were collected from all sampling sites during the period of September 26–October 04, 2011.

Tree core samples were collected using an increment borer. Ages of the sample trees were determined by counting the annual rings using a magnifying glass and they ranged between 28–112 years. All samples were placed into their pre-cleaned glass containers, were transported to the laboratory, and stored at 4°C until they are processed. For 14 sites having trees older than 30 years, core samples were cut into 5-year increments and each increment was processed and analyzed separately. For the remaining 13 sites core samples were processed as single samples. Air samples were also collected on polyurethane foam (PUF) disks using passive samplers (PAS) during a four-month deployment period (October 2011 – January 2012). Before sampling, deuration compounds (DCs) (¹³C–PCB 3, ¹³C–PCB 9, ¹³C–PCB 15, PCB 30, PCB 107, and PCB 198, 17.5–20 ng per sample) dissolved in 10 mL hexane were spiked evenly onto PUF disks.

Prior to extraction, samples were spiked with PBDE surrogate standards (PBDE 77, and ¹³C–PBDE 209). Tree core samples were soaked in 100 mL of 1:1 acetone:hexane mixture overnight. Then, they were ultrasonically extracted for 30 min. Ambient air samples were Soxhlet extracted for 12 hours with a mixture of 1:1 acetone:hexane. The extract volumes were reduced and were transferred into hexane using a rotary evaporator and a high purity N₂ stream. After concentrating to 2 mL, tree component samples were cleaned up using gel permeation chromatography. Then, soil, air and tree samples were cleaned up and fractionated on an alumina–silicic acid column. All samples were analyzed for 7 PBDEs (28, 47, 100, 99, 154, 153, 209) with an Agilent 6890N gas chromatograph (GC) equipped with a mass selective detector (Agilent 5973 inert MSD) using the

negative chemical ionization (NCI) mode. Compounds were identified based on their retention times, target and qualifier ions, and were quantified using the internal standard calibration procedure. Further details for sample preparation and instrumental analysis could be found elsewhere⁷.

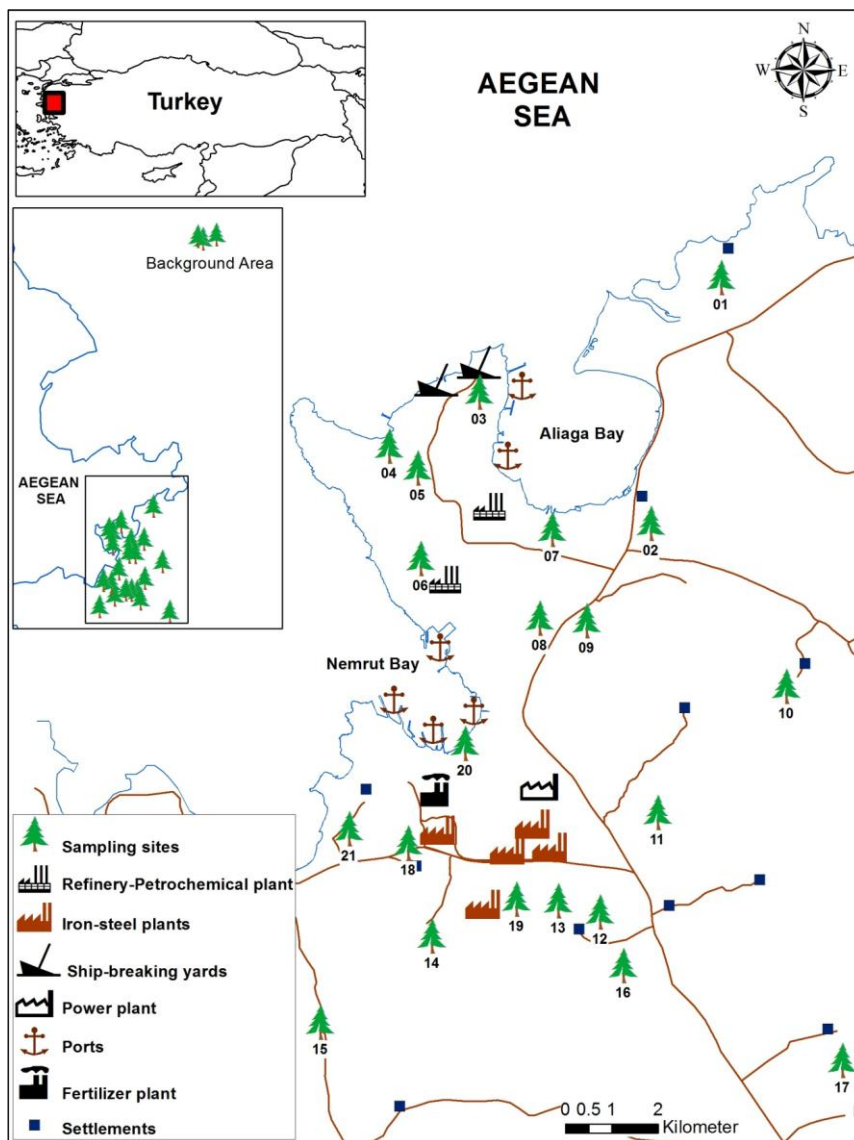


Figure 1. Map of the study area.

Results and discussion

The average concentrations of Σ_7 PBDEs ranged between 21 and 539 pg/m^3 (average \pm SD, 161 \pm 138 pg/m^3) in industrial/residential sites. The lowest concentrations in ambient air were found in background sites without specific local sources (19 \pm 1.0 pg/m^3) (Figure 2).

PBDE concentrations in air decreased with distance from the major sources. Generally, substantially higher concentrations were measured near industrial sites and the lowest ones in background sites. Spatial variations of air concentrations indicated that iron-steel plants and ship breaking yards were the major PBDE emitters in the study area.

Ambient air PBDE profile was dominated by PBDE 209. Compound profiles were similar for ambient air and tree core samples (Figure 3).

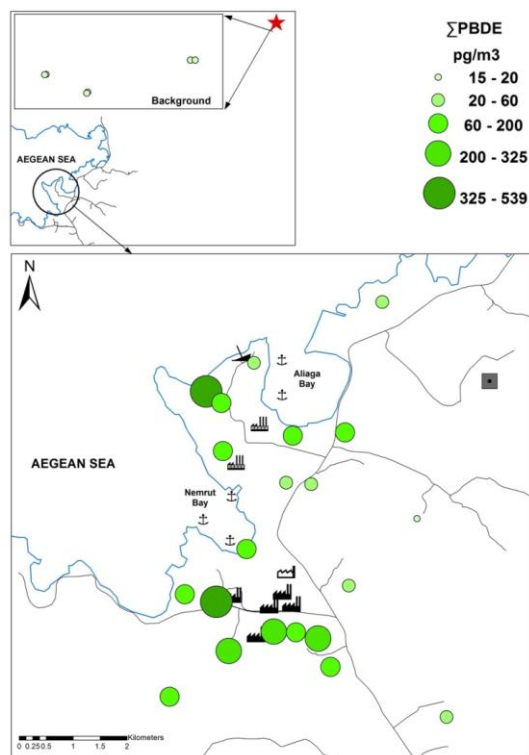


Figure 2. Spatial variation of Σ_7 PBDE concentrations in air.

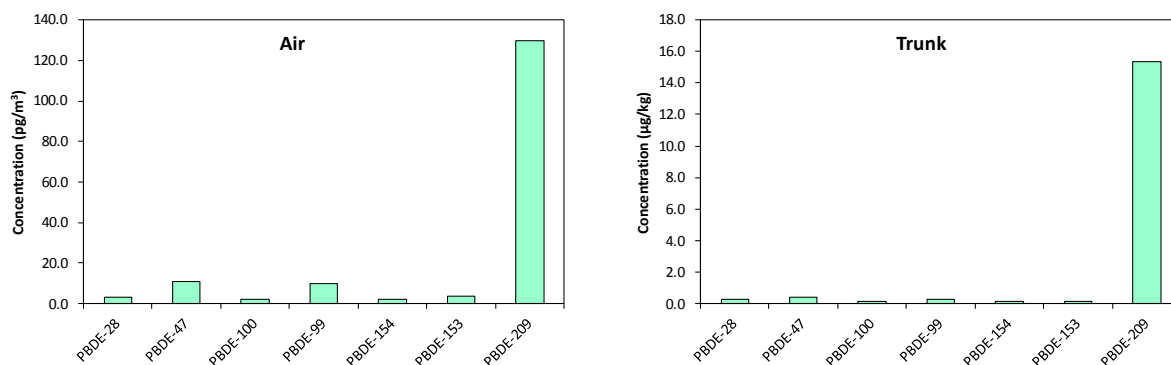


Figure 3. Average concentrations of PBDE congeners in air and core samples.

Tree core Σ_7 PBDE concentrations indicated an increasing trend with time in industrial and background sites. Concentrations in background sites were generally lower. Increases in concentrations followed a similar trend with the number of the industries in the study area (Figure 4). Temporal trends of PBDE congeners at site 13 are shown in Figure 4 as an example. All congeners followed a similar temporal trend.

In summary, the highest atmospheric concentrations were measured at sites located near the iron–steel plants and ship breaking yards indicating that they are the major PBDE emitters in the region. According to the tree cores analyzed for historical variation, PBDE concentrations have substantially increased during the last three decades. The results of this study showed that tree cores could be used to investigate the historical variation of PBDEs.

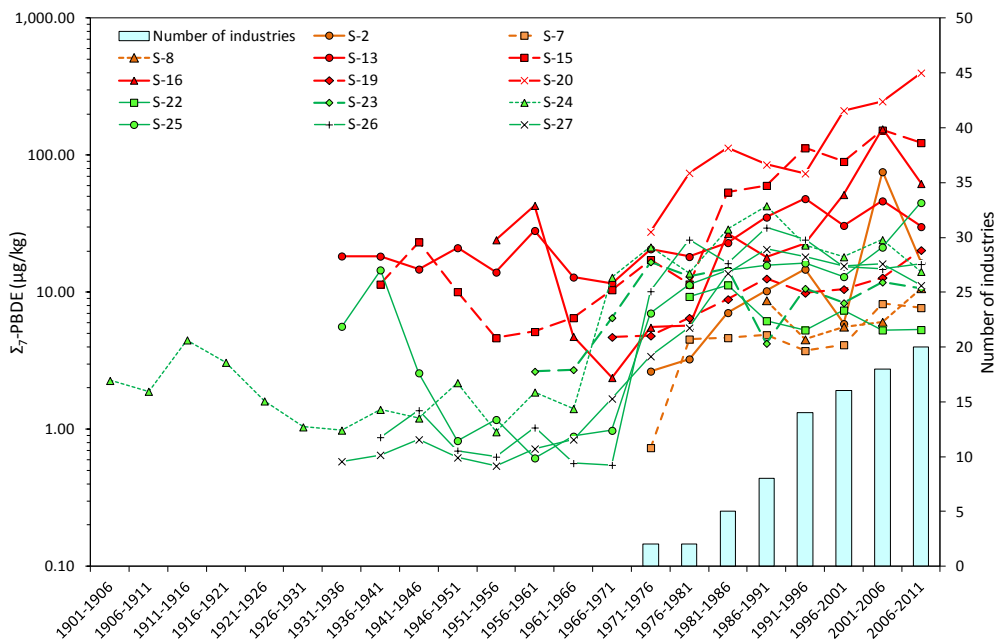


Figure 4. Historical variations of Σ_7 PBDEs in dated tree core samples (n=14).

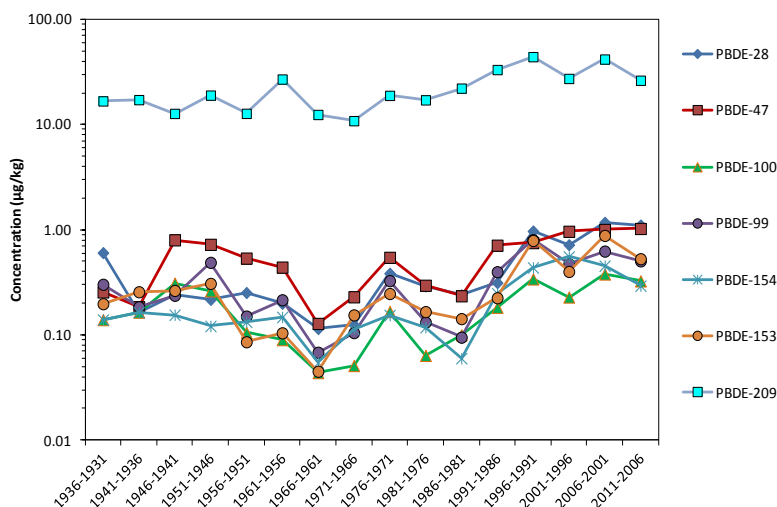


Figure 5. Historical variations of PBDE congeners at site 13.

Acknowledgements

This study was supported by The Scientific and Technological Research Council of Turkey (project no: TUB/110Y096).

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