Science of the Total Environment 491–492 (2014) 51–59

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Atmospheric concentrations of persistent organic pollutants over the Pacific Ocean near southern Taiwan and the northern Philippines

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HIGHLIGHTS

- The world's first data on PBDD/Fs, PCDEs, and PBBs in the oceanic atmosphere
- Atmospheric POP TEQ levels over the target ocean were one order lower.
- PCBs and PBDEs were the dominant POPs in the global oceanic atmosphere.
- Atmospheric POPs over the target ocean were influenced by combustion sources.

ARTICLE INFO

Article history:
Received 13 November 2013
Received in revised form 7 March 2014
Accepted 7 March 2014
Available online 28 March 2014

Editor: D. Barcelo

Keywords:
Ocean
Atmosphere
Persistent organic pollutants (POPs)
Dioxins
Polybrominated diphenyl ethers (PBDEs)
Polychlorinated biphenyls (PCBs)

ABSTRACT

This study investigates the atmospheric occurrence of persistent organic pollutants (POPs) over the Pacific Ocean near southern Taiwan and the northern Philippines. We determined sixty-six compounds, including polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), dioxin-like polychlorinated biphenyls (DLPCBs), polybrominated diphenyl ethers (PBDEs), as well as polychlorinated diphenyl ethers (PCDEs), polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs), and polybrominated biphenyls (PBBs), in air samples simultaneously collected from the offshore oceanic atmosphere (n = 6) and over a rural area (n = 2). We calculated the atmospheric World Health Organization 2005 toxic equivalency levels (WHO_{2005}-TEQ), for the total dioxin-like POPs, including PCDD/Fs, DLPCBs, and PBDD/Fs, being 0.00612 pg WHO_{2005}-TEQ/m^3 and 0.0138 pg WHO_{2005}-TEQ/m^3 over the ocean and land, respectively. We found unexpected lower averaged atmospheric PBDE concentrations in the rural area (15.9 pg/m^3) than over the ocean (31.1 pg/m^3) due to higher levels of the BDE209 congener, although the difference was not statistically significant. We have compared and reported our field results with previously published datasets over the global oceans, which suggest PCBs and PBDEs are the dominant chemical contaminants in the global oceanic atmosphere among these halogenated POPs (e.g. PCBs and $\Sigma_{di\text{-}hepta}$ PBDEs could be found in the range of 0.09–48.7 and 8.07–94.0 pg/m^3, respectively, including our dataset). However, there are still very few investigations on the global atmospheric levels of PBDD/Fs, PCDEs and PBBs and our data sums to these earlier studies. Finally, we point out that the halogenated POPs originated from Taiwan or the continental East Asia which could easily reach remote ocean sites via atmospheric transport.

1. Introduction

Halogenated persistent organic pollutants (POPs) are a global concern because of their negative impacts on the environment and health of humans and other animals. Halogenated POPs, including polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), dioxin-like polychlorinated biphenyls (DLPCBs), polychlorinated diphenyl ethers (PCDEs), polybrominated dibenzo-*p*-dioxins and dibenzofurans

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http://dx.doi.org/10.1016/j.scitotenv.2014.03.017
0048-9697/

(PBDD/Fs), polybrominated biphenyls (PBBs), and polybrominated diphenyl ethers (PBDEs), are ubiquitous in the environment. PCDD/Fs and PBDD/Fs are incomplete-combustion byproducts or chemical impurities that are released into the environment (Chang et al., 2014; Lee et al., 2004; Wang et al., 2010a). PCBs are manufactured for industrial purposes and used in capacitors and dielectric fluids in transformers. PBBs and PBDEs are brominated flame retardants (BFRs) used as additives in electronic appliances, paints, textiles, and furnishings (Schenker et al., 2008). A number of studies have shown the importance of the combustion source when considering the release of PBDEs into the atmosphere (Wang et al., 2010b, 2011, 2010c). PCDEs spread into the environment through the use of chlorophenols and as emissions from combustion sources (Wu et al., 2014). Except for PCDEs, the previously mentioned halogenated chemical compounds are all listed as POPs under the Stockholm Convention (Stockholm Convention, 2013).

These organochlorines and organobromines are linked to many adverse health effects (Chao et al., in press; Van den Berg et al., 2006), related to reproductive (Chao et al., 2010, 2007b; Hsu et al., in press), developmental (Chao et al., 2007a; Nishijo et al., 2012), neurological (Chao et al., 2011; Shy et al., 2011; Tai et al., 2013), and immunological toxicities (Lin et al., 2011; Shy et al., 2012), the disruptions of endocrine secretions (Shy et al., 2012; Wang et al., 2006), and the development of cancers (Manuwald et al., 2012; Van den Berg et al., 2006). Their negative impacts are possibly the result of their persistence in the environment, resistance to physical and chemical degradations, and lipophilicity, which means that they accumulate in the fatty tissues of humans and other animals.

The atmosphere is the major transportation pathway for POPs, and long-range atmospheric transport (LRAT) is a rapid method of transporting such chemicals to other locations or remote regions, including oceans, the Arctic, and Antarctica (Booth et al., 2013; Möller et al., 2011a, 2011b; Montone et al., 2005). Oceans are a naturally cumulative reservoir for POPs; therefore, they are associated with the exposure of aquatic organisms to these substances. Oceans act as sinks for the accumulation of airborne POPs through dry and wet deposition and air and water gas exchange, although studies have also suggested that oceans may contribute to the presence of POPs in the oceanic atmosphere via the volatilization of POPs in seawater (Lohmann et al., 2012; Zhang and Lohmann, 2010).

Marine environmental scientists have examined the presence of organochlorines, such as organochlorine pesticides and PCBs, in the oceanic atmosphere (Gioia et al., 2012; Montone et al., 2005; Wurl et al., 2006b; Zhang and Lohmann, 2010). An investigation of PCBs and hexachlorobenzene (HCB) in the surface ocean-lower atmosphere of the open Pacific Ocean revealed that the levels of these substances in the Northern Hemisphere were significantly higher than in the Southern Hemisphere, although no notable differences were found in the seawater between these two areas (Zhang and Lohmann, 2010). Recently, several studies were conducted on the levels of BFRs in the oceanic atmosphere, especially PBDEs, to determine the related spatial and latitudinal distributions and time trends for different oceans (Li et al., 2011; Möller et al., 2011a; Xie et al., 2011). Möller et al. (2012a, 2012b) indicated that elevated levels of atmospheric PBDEs were generally observed in the marginal seas, such as the East China Sea or North Sea, and among the global oceans, such as the Pacific, Atlantic, Indian, Arctic, and Antarctic Oceans. Although a considerable number of oceanic studies of airborne PBDE and PCB contamination have been conducted, very few works have focused on investigations of PCDEs and dioxin-like POPs, such as PCDD/Fs, PBDD/Fs and DLPCBs, in the oceanic atmosphere (Lohmann et al., 2001).

Taiwan and the Philippines are located in the marginal sea of the West Pacific Ocean. Background levels of POPs in these countries may be influenced by LRAT during specific events (e.g., the burning of biomass in Southeast Asia) (Chang et al., 2012) or the monsoon season (e.g., the winter or northeast monsoon from Siberia, Mongolia, and northern China) (Huang and Liang, 2011). During biomass burning in Southeast Asia, atmospheric PCDD/F and PBDE levels were shown to be significantly increased at a high-altitude background station in central Taiwan, which was most likely a result of the LRAT of PCDD/Fs and PBDEs from various Southeast Asian countries (Chang et al., 2012). Li et al. (2011) reported that Σ_{21}PBDE (the sum of BDE17, 28, 32, 35, 37, 47, 49, 51, 66, 71, 75, 77, 99, 100, 126, 128, 138, 153, 154, 166, and 183) in the oceanic atmosphere of the East and South China Seas was 10.8 pg/m^3, which is higher than the figures given in other published marine atmospheric studies of the open oceans (Möller et al., 2012b). To the best of our knowledge, no reports to date have investigated the oceanic atmospheric levels of halogenated POPs in the West Pacific Ocean between Taiwan and the northern Philippines. Therefore, it is still unknown whether the marine atmosphere over the Pacific Ocean near these areas is influenced by the LRAT of POPs from continental East Asia or Taiwan Island.

Our previous studies have established the levels of PCDD/Fs, PBDD/Fs, DLPCBs, PBDEs, and PBBs in different atmospheric environments in Taiwan (Chang et al., 2012; Lee et al., 2004; Shih et al., 2006; Wang et al., 2007, 2010d, 2011); however, there is still a lack of data on the levels of POPs in the marine atmosphere surrounding this island. This study was the first to investigate atmospheric levels of PCDD/Fs, PBDD/Fs, DLPCBs, PBBs, PCDEs and PBDEs over the Pacific Ocean near southern Taiwan and the northern Philippines. Although the halogenated POP concentrations in the oceanic atmosphere are considered to be at global background levels, as a result of the extremely low levels in the atmosphere over the ocean compared to such levels over the land, only PBDEs and indicator PCBs in the oceanic atmosphere have received much research attention. This study presents details of the background levels of halogenated POPs in the oceanic atmosphere over the West Pacific Ocean to compensate for part of the current lack of data on the oceanic atmosphere for the area from Aomori to Okinawa, Japan, to Taiwan and the northern Philippines.

2. Materials and methods

2.1. Air sample collection

The ambient air of the atmospheric boundary layer over the ocean was sampled between November 1 and November 6, 2012 by two high-volume air samplers installed on the compass deck of the Research Vessel Ocean Researcher V (R/V OR5), which is a 2700-tonne research vessel from the Taiwan Ocean Research Institute, National Applied Research Laboratories (TORL/NARL). The R/V OR5 sailed to the target ocean from Kaohsiung (Kaohsiung Harbor, 22.60° N, 120.29° E) and returned to Tainan (Anping Harbor, 22.97° N, 120.17° E). The atmospheric air samples were collected along three routes, A (22.49° N, 120.13° E), B (20.05° N, 123.57° E), and C (19.26° N, 123.09° E), which were over the Pacific Ocean near southern Taiwan and the northern Philippines between 22.49° N, 120.13° E and 17.94° N, 124.63° E (Fig. 1). Concurrently, the ambient air in a rural area (D) was sampled by two high-volume air samplers deployed on the top floor (4 F) of the Engineering College Building of National Pingtung University of Science and Technology (NPUST) in southern Taiwan (22.65° N, 120.61° E). The rural area was far from the seacoast and industrial and urban areas and has historically provided background levels of POPs in southern Taiwan.

Each air sample was collected for approximately 40 h (1–2 days, ~600 m^3) using a PS-1 sampler (Graseby Andersen, GA, USA) following US EPA Reference Method TO9A. A quartz fiber filter was followed by a glass cartridge containing polyurethane foam (PUF) to capture the particle and gas phases. After the collection, the quartz fiber filter and PUF of each air sample were combined and analyzed for PCDD/Fs, DLPCBs, PCDEs, PBDD/Fs, PBBs, and PBDEs.

One of PS-1 samplers did not work on the NPUST campus after November 2. Consequently, only eight air samples were collected in