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Background levels of polybrominated diphenyl ethers (PBDEs) in soils from Mount Meru area, Arusha district (Tanzania)

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HIGHLIGHTS

- PBDEs contamination in mountain soils from Mount Meru, Tanzania, was measured.
- Moderate PBDE levels showing relationship with altitude were found.
- Mount Meru PBDE levels were similar to those from other high mountain areas.
- Levels were comparable to those found in mountain soils from the northern hemisphere.

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ABSTRACT

This study investigates the contamination by 13 polybrominated diphenyl ether (PBDE) congeners in an altitudinal soil transect on Mt. Meru area, Northern Tanzania. A $\sum_{13}$PBDEs mean concentration of 386 ± 200 pg/g d.w. (4900 ± 3500 pg $\sum_{13}$PBDEs/g soil organic matter — SOM) was measured, pointing out that, in a prevalently agricultural area from the southern hemisphere, PBDE contamination can be even higher than in similar semi-remote environment of industrialized country of the northern one. The Mt. Meru PBDE pattern of contamination was characterized by the prevalence of intermediate brominated congeners (tetra- and penta-BDEs). Among the detected compounds, BDE-47 was the main congener, followed by BDE-99, BDE-190 and BDE-100. The distribution of PBDEs confirmed that organic carbon had a substantial impact on their accumulation in Tanzanian soils. The altitudinal profile of PBDEs (log TOC-normalized concentrations) fitted a second order polynomial model with altitude, with an initial concentration decrease, interpreted as a dilution effect from local/regional sources, and a following consistent increase with altitude according to the cold condensation theory. Evidences of distillation effect among PBDE congeners were also observed.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) were intensively produced as brominated flame retardants (BFRs) over the last 30 years with global annual production estimated at 436,800 tons in 2005 (CEFIC, 2006). PBDEs were mainly produced at three different levels of bromination: penta-, octa- and deca-BDE mixtures (La Guardia et al., 2006). BDE-47 and BDE-99 contribute for over the 70% of the congeners in the penta-BDE mixtures, while in the octa-BDE, BDE-183 contributes for over the 40%. Finally in the deca-BDE mixtures, BDE-209 (the fully brominated congener) is almost the only component (Alaee et al., 2003). Since they are not chemically bound to the products, the use and the uncontrolled discharges of material containing PBDEs led to their environmental dispersion (Watanabe and Sakai, 2003) with potential toxic effects toward biocoenosis (Darnerud et al., 2001; Birnbaum and Staskal, 2004). PBDEs share similar molecular structure, chemical–physical and toxicological features with other persistent organic pollutants (POPs; Watanabe and Sakai, 2003). PBDEs are bioaccumulative in humans (Athanasiadou et al., 2008) and wildlife, with biomagnification phenomena of the tetra- to hexa-BDE congeners (de Wit et al., 2010). Although the long-range atmospheric transport (LRAT) of PBDEs is considered limited (Palm et al., 2002; Wania and Dugani, 2003), it is effective enough to travel over great distances by a series of volatilization/deposition hops (Gouin and Harner, 2003). Seasonally and diurnally fluctuating temperatures are able to alternatively enhance re-volatilization and deposition, allowing also low volatile molecules to travel for quite long distances under favorable wind conditions (Gouin and Harner, 2003). PBDE contamination in the Arctic environment indicates that these compounds reach this remote area by LRAT and local settlement emissions, with increasing concentration levels in both biotic and abiotic matrices (de Wit et al., 2006, 2010).

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Considering these evidences, in 2004 the Great Lakes Chemical Corporation (USA) voluntary stopped the production of penta- and octa-BDE formulations before official ban, while the European Union banned in 2005 the use of penta- and octa-BDE mixtures in electric and electronic devices (EU, 2005). Lastly, also the use of deca-BDE formulation has been banned since July 1st 2008 (European Court of Justice, 2008). In 2009, tetra- to hepta-BDEs contained in penta- and octa-BDE formulations were included in the Annex A of Stockholm Convention for Persistent Organic Pollutants (Stockholm Convention, 2009). Moreover, the UN ECE Convention recognized PBDEs as POPs on Long-Range Transboundary Air Pollution (UE ECE, 2010). Despite of international regulations, PBDEs are continuously found in humans and environment, including remote regions (de Wit et al., 2006; Hale et al., 2006) and mountain areas (Blais et al., 2006; Parolini et al., 2012a; Wang et al., 2009, 2012; Zheng et al., 2012). The majority of studies concerning PBDEs in environment, foodstuff and humans refers to the northern hemisphere (de Wit, 2002; Covaci et al., 2003; Gill et al., 2004; Hites, 2004), where it was concentrated the most part of their production, usage and dispersion (Hassanin et al., 2004). de Wit (2002) estimated that about 95% of the total amount of brominated flame retardants (BFRs) produced in USA, Europe, Middle East and Asia were distributed in North America, Far East and Europe. The southern hemisphere received less attention, even if many products containing BFRs (e.g. plastic, electronic equipment, textiles and building materials) were exported or discharged there. Notwithstanding, measurable PBDE concentrations were found in different environmental matrices sampled in countries from the southern hemisphere, such as Africa (Daso et al., 2012), South America (Pozo et al., 2004), Australia (Toms et al., 2007) and New Zealand (Harrad and Porter, 2007), as well as Antarctica (Hale et al., 2006). In Africa, Daso et al. (2012) measured PBDE levels in sewage sludge of wastewater treatment plant of Cape Town (South Africa) ranging between 13.1 and 652 ng/g dry weight, with BDE-47, -153, -183 and -209 as the prevalent congeners. Asante et al. (2010) reported PBDE concentrations in cow milk sampled in rural (0.047–2.8 ng/g lipid weight) and urban (0.47–11 ng/g lipid weight) sites from Ghana. Polder et al. (2008) showed PBDE contamination in bird eggs from South Africa ranging between 2.3 and 396 ng/g lipid weight, with the highest concentrations in the most industrialized area. Darnerud et al. (2011) found PBDE concentrations in breast milk from the northernmost province of South Africa between 0.70 and 6.3 ng g^{-1} lipid weight, not far from levels generally found in European studies. On the contrary, findings by Pozo et al. (2004, 2006) seem to suggest a low PBDE contamination of the southern hemisphere, since they found detectable PBDE levels just in air samples from Botswana and Argentina, while concentrations measured in Australia, Malaysia, Philippines, South Africa, Ghana, Bolivia, Chile, Colombia and Antarctica were negligible. This contrasting picture about PBDE contamination levels in the southern hemisphere needs more attention because of the possibility of consistent PBDE contamination transfer to the southern hemisphere by uncontrolled waste dumping coming from industrialized countries, especially in Africa. To date, background levels in the main biotic and abiotic matrices (e.g. soil) have not been established in many countries. In this paper we present the first PBDE background contamination data in African soils, referring to rural and natural sites from Mt. Meru area, Arusha district (Tanzania). Superficial soils were taken far away from any possible direct contamination source, along an altitudinal transect from 1535 m a.s.l. to the top of Mount Meru, the fifth highest mountain of Africa (4577 m a.s.l.). An altitudinal transect on this highest African mountain protected by a natural park was chosen in order to: a) establish the PBDE background contamination levels in a rural/natural remote area; b) evaluate the PBDE concentration in soils from very different biomes (agricultural fields, savannah, moist mountain forest, upper mountain forest, afroalpine prairies); and c) evaluate the PBDE altitudinal profile in an equatorial area.

2. Materials and methods

2.1. Sampling method

All samples were collected on February 2011, at the end of the short dry season. For each sampling site three sub-samples of soil (litter was removed) were manually homogenized to reduce the intra-site variability. Samples were wrapped in a tinfoil and enclosed in plastic bags to avoid pollutant losses and frozen as soon as possible (−20 °C) until analyses. Information about sampling sites and total organic carbon of soils are reported in Table 1. More details on study area and sampling operations, as well as on distribution of vegetation, pedological categories and soil taxonomy, were reported by Guazzoni et al. (submitted for publication).

2.2. Reagents and standards

All solvents used were pesticide grade. Florisil (100–200 mesh) and anhydrous sodium sulfate were obtained from Fluka (Steinheim, Germany). The silica gel for column chromatography (70–230 mesh) was supplied by Sigma-Aldrich (Steinheim, Germany). A BDE-commonly occurring congener mixture (PBDE-COC) was purchased from AccuStandard (New Haven, CT, USA). The thirteen BDE congeners investigated in this study were as follows: BDE-17, 28, 71, 47, 66, 100, 99, 85, 154, 153, 138, 183 and 190. BDE congeners are numbered according to the International Union of Pure and Applied Chemistry (IUPAC) system originally designed for PCBs (Ballschmiter and Zell, 1980). The total PBDE (Σ_{13} PBDEs) concentrations in samples were calculated as the sum of these congeners. Two $^{13}C_{12}$-labeled mixtures (PBDE-MXA and PDE-MXB) composed of $^{13}C_{12}$-labeled BDE-47, 99 and 153 and BDE-28, 154 and 183, respectively, were purchased from AccuStandard (New Haven, CT, USA) and used as internal surrogate standards.

Table 1
Coordinates, altitude, vegetation type, total organic carbon and mean annual temperature of the sampling sites of Mt. Meru area.

Sample	Coordinates		Elevation	Vegetation	TOC	Temperature[a]
	Latitude	Longitude	(m a.s.l.)		(%)	(°C)
STZ1	−3,17011	36,76553	2351	Crops	9.51	14.1
STZ2	−3,16142	36,77402	2090	Crops	4.96	15.7
STZ 3	−3,15719	36,77856	1965	Crops	3.66	16.4
STZ 4	−3,14555	36,79373	2108	Pasture	5.76	15.5
STZ 5	−3,1412	36,79602	1891	Pasture	3.55	16.9
STZ 6	−3,13822	36,79796	1684	Pasture	2.52	18.1
STZ 7	−3,24796	36,83841	1756	Forest	10.87	17.7
STZ 8	−3,24294	36,82072	2018	Forest	8.07	16.1
STZ 9	−3,2327	36,81107	2279	Forest	16.79	14.5
STZ 9 bis	−3,22855	36,79936	2517	Forest	15.08	13.1
STZ 10	−3,22597	36,79362	2745	Forest	17.53	11.7
STZ 11	−3,22464	36,78636	3057	Forest	14.76	98
STZ 12	−3,22037	36,77978	3325	Shrubs	5.98	8.1
STZ 13	−3,2177	36,77259	3581	Shrubs	4.28	6.6
STZ 14	−3,24359	36,7498	4577	Rocks	1.50	0.5
STZ 15	−3,23347	36,74869	4263	Rocks	0.16	2.4
STZ 16	−3,22625	36,75475	4027	Rocks	0.18	3.8
STZ 17	−3,22154	36,76524	3838	Rocks	1.33	5.0
STZ 18	−3,2224	36,8578	1535	Shrubs	8.22	19.0
STZ 19	−3,13143	36,80411	1571	Shrubs	2.45	18.8
STZ 20	−3,12789	36,8115	1550	Crops	3.23	19.0

[a] Temperature of the sampling sites were calculated by a lapse rate of 0,61 °C per 100 m increase in altitude, using the relationship $y = 0.0061x + 28.407$ ($R^2 = 0.998$), where y is the temperature (°C) and x is the altitude (m a.s.l.). This relationship was obtained by the regression of several annual mean temperatures between 813 m a.s.l. and 5800 m a.s.l. recorded by meteorological stations on Mt. Kilimanjaro (OECD, 2003). Mt. Kilimanjaro is located not far from Mt. Meru and belongs to the same climatological region within Tanzania (Basalirwa et al., 1999).