Article

Brominated Flame Retardants in Antarctic Air in the Vicinity of Two All-Year Research Stations

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Abstract: Continuous atmospheric sampling was conducted between 2010–2015 at Casey station in Wilkes Land, Antarctica, and throughout 2013 at Troll Station in Dronning Maud Land, Antarctica. Sample extracts were analyzed for polybrominated diphenyl ethers (PBDEs), and the naturally converted brominated compound, 2,4,6-Tribromoanisole, to explore regional profiles. This represents the first report of seasonal resolution of PBDEs in the Antarctic atmosphere, and we describe conspicuous differences in the ambient atmospheric concentrations of brominated compounds observed between the two stations. Notably, levels of BDE-47 detected at Troll station were higher than those previously detected in the Antarctic or Southern Ocean region, with a maximum concentration of 7800 fg/m^3. Elevated levels of penta-formulation PBDE congeners at Troll coincided with local building activities and subsided in the months following completion of activities. The latter provides important information for managers of National Antarctic Programs for preventing the release of persistent, bioaccumulative, and toxic substances in Antarctica.

Keywords: Antarctica; persistent organic pollutants; brominated flame retardants; environmental transport; global chemical monitoring; chemical policy

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of organohalogen compounds used extensively as flame retardants in consumer products during the past 50 years [1]. Their environmental behavior of persistence and long-range dispersal, combined with their biological impact of bioaccumulation and toxicity, has led to the inclusion of all commercial PBDE formulations under Annex A of the Stockholm Convention on Persistent Organic Pollutants (POPs) [2]. The global ban of commercial penta- and octa-BDEs entered into force in 2009, although not until 2019 for deca-BDE [3].

PBDEs have been reported in Antarctic biota since 2004 [4–21], and in case studies of the Antarctic atmosphere since 2012 [22–27]. Unlike agrichemicals, such as organochlorine pesticides, the Antarctic occurrence of which can be attributed solely to long-range environmental transport (LRET), current and recently used POPs, such as PBDEs, are also finding their way to the remote Antarctic region via in situ usage [8–10]. Recent studies focusing on Antarctic research stations as emitters of PBDEs to the local environment have evidenced such emissions at: McMurdo station and Scott Base in the Ross Sea Region [10]; Casey Station in the East Antarctic sector [28]; and Julio Escudero and Gabriel de Castilla Stations [29] on the South Shetland Islands [29]. These findings in turn indicate that all polar research stations can be potential sources of these compounds to the local environment [8,10,28]. In the above-named studies, there were significant differences in both the levels and profiles of PBDEs detected within stations, and in the local surrounding area. Although station population capacity appears to be an indicator of absolute contaminant

levels, Hale et al. (2008) proposed that station contaminant profiles reflect the host nation of the station, and thereby national chemical legislation and national chemical usage patterns. Increasingly, as stations age and undergo renovation, profiles are also likely to reflect the chemical constituents of chosen building materials at the time of construction.

The published data concerning PBDEs in the Antarctic atmosphere reveals a number of limitations characteristic of POP research in the region, and which have previously been discussed in the literature [30,31]. Specifically, they have been derived from predominantly short, one-off sampling campaigns, with an evident strong spatial bias across the continent. Further, resulting data has been obtained by a variety of sampling approaches, and the targeted chemical structures of each study are also not uniform [31]. To our knowledge, there have been six case studies that have reported PBDEs in air masses of the Antarctic region. Associated sampling periods of these studies date back to 2001. Four of these studies originate from the Antarctic Peninsula region [23,24,26,27], whereas one originates from Dronning Maud Land [22], and one from the eastern Antarctic sector [25]. Four of the six studies implicated local emission sources for one or more of the congeners detected [24,26,27,32].

The Global Monitoring Plan (GMP) [33] was implemented to evaluate the effectiveness of the Stockholm Convention in meeting its goals. It seeks to do so through collection and analysis of comparable samples in UN regions, in order to understand temporal and spatial trends. Data are collected from the core matrices of ambient air, human breastmilk, and blood, in addition to surface water for water-soluble POPs. Although the human matrices monitored under the GMP are not applicable in Antarctica due to the absence of a subsisting human population, the detection of chemicals in the Antarctic atmosphere and surface waters can provide unique insight into hemispheric chemical usage patterns and the global reach of chemical emissions. As the most remote region on the planet, the Antarctic plays a special role under the GMP because it is to the greatest extent removed from manufacturing emissions. Detection of chemicals in Antarctica can therefore serve as direct and empirical evidence of chemical persistence and capacity for LRET, i.e., two of the four requisite criteria for categorization of a chemical as a POP [30]. Alternatively, detection may reveal local emissions, in breach of the Protocol on Environmental Protection to the Antarctic Treaty, which prevents the release of prohibited substances [34]. In both cases, monitoring plays a pivotal role in accelerated regulatory decision making and effective, evidence-led, chemical policy.

In support of the GMP, continuous atmospheric monitoring for POPs was implemented at Troll Station (Norway) and Casey Station (Australia) in Queen Maud Land and east Antarctica, respectively. Air extracts from the two programs were analyzed for PBDE to further investigate long-range hemispheric sources versus local emissions of these chemicals.

In addition to PBDEs, naturally occurring brominated compounds have been detected in the global environment, including Antarctica [8,35,36]. Many are structurally similar to problematic synthetic equivalents; hence, concerns have been raised with regard to their associated environmental and biological risks. 2,4,6-Tribromoanisole (TBA) is a fungal metabolite of brominated phenolic compounds often used as a fungicide or found as contaminants in pesticides. 2,4,6-tribromophenol, the chemical structure of which closely resembles PBDEs, was included in analysis for ancillary insight into the presence of, and regional differences in, levels of this organobromine compound.

Here, we report the results of continuous atmospheric sampling, combined with targeted PBDE analysis, at two all-year research stations in Antarctica. Parallel sampling and analysis controls for inter-laboratory method variation and analyte repertoire comparison. Similarly, the extended monitoring period (one (Troll) to five (Casey) years) yields the first insight into the seasonal resolution of PBDEs in the Antarctic atmosphere. Finally, TBA is reported for the first time in the Antarctic atmosphere. We describe the dramatic differences in ambient atmospheric levels of PBDEs observed between the two stations. The latter provides important information for the Council of Managers of National Antarc-

tic Programs (COMNAPs) for local source identification, and thus mitigation of breaches of the Antarctic Treaty related to release of prohibited substances in Antarctica.

2. Materials and Methods

2.1. Site Descriptions

Casey Station is one of Australia's all-year Antarctic research stations. It is located on Wilkes Land in the Australian Antarctic Territory (66°16′56″S 110°31′32″E) (Figure 1). On a local scale, the station is situated on the Bailey Peninsula. A High Flow-Through Passive Air Sampler (HFTPAS) was installed at an upwind, "background" site across Newcomb Bay, at the abandoned Wilke's station, on the Clark Peninsula, approximately 3 km from Casey station [30].
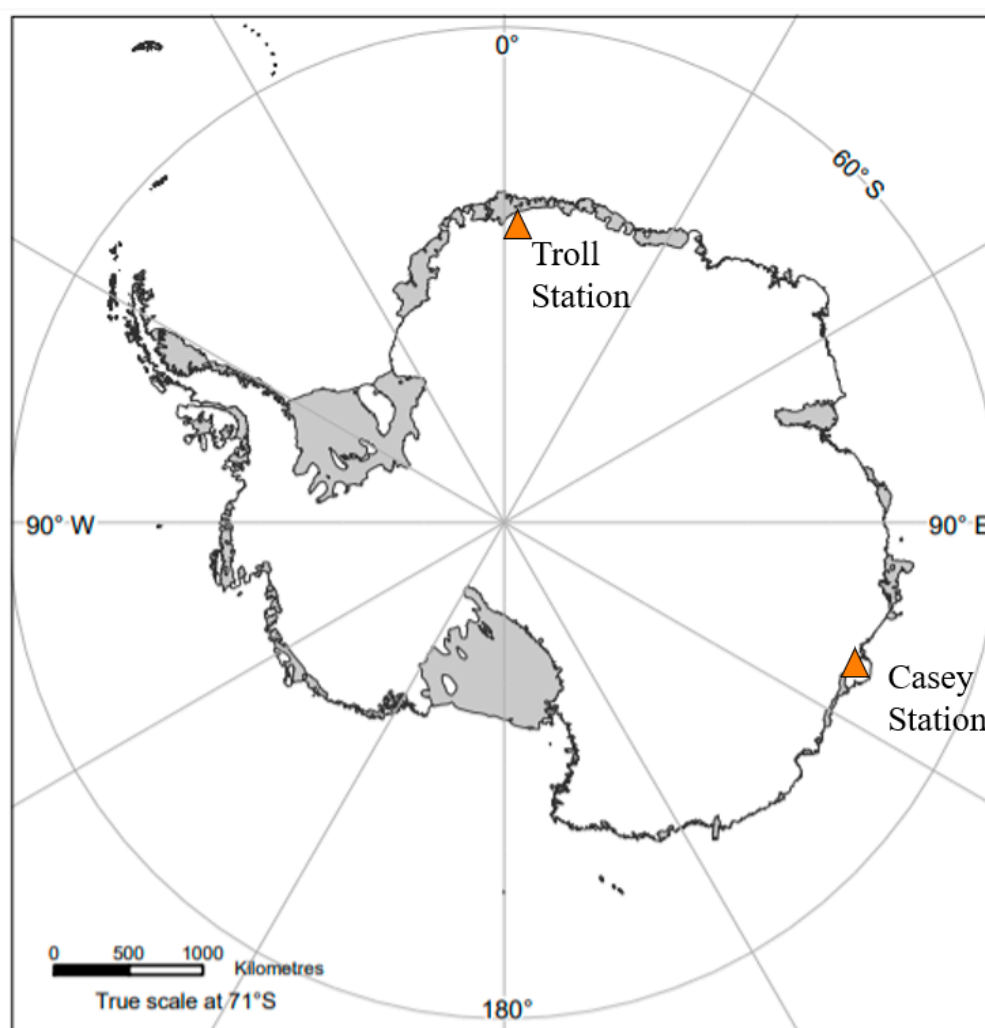

Figure 1. Antarctic air sampling locations in the current study.

The Norwegian Troll Atmospheric Observatory is located at 72°00′42″ S; 2°32′06″ E, in Dronning Maud Land, Antarctica (Figure 1). It is situated 235 km inland from the Antarctic coast and 1553 m above sea level. The South African SANAE IV station lies 190 km west–north–west of the observatory, and the German Neumeyer station lies 420 km to the east–north–east. Troll station is serviced by a blue-ice airfield on the Jutulsessen glacier, 7 km north of the main station.

2.2. Air Sampling

2.2.1. High Flow-Through Passive Air Sampler—Casey Station, East Antarctica

Atmospheric monitoring in the Australian Antarctic Territory was performed with a High Flow Through Passive Air Sampler (HFPAS) specifically developed for measuring trace contaminant levels encountered in remote regions (Figure S2) [31,37]. The sampling equipment has previously been outlined in detail [30,37]. In brief, the sampling unit consists of three polyurethane foam (PUF) plugs loaded into a cartridge in series and mounted in an aerodynamically shaped housing on a post with a rotatable joint. The sampler-housing unit is designed to automatically face into oncoming wind, thereby increasing airflow across the sampling media. This serves to increase the sampling rate compared to other non-powered passive air samplers, thus permitting remote sampling away from power sources/inhabited areas. The ambient wind speed is measured via an anemometer mounted on a post, at a similar height to the sampler, two meters from the sampler. At Casey station, each sampling set of cartridges included two PUF disk field blanks (one 7.62 cm and one 2.54 cm), in addition to the three PUF disks (two 7.62 cm and one 2.54 cm) that were used to make up the sampling train. Field blanks were handled in the same manner as the sample PUFs. Upon deployment and retrieval of the sample PUFs, the field blank jars were opened and the PUF disks removed and replaced using pre-cleaned tongs.

2.2.2. High-Volume Active Sampling—Troll Atmospheric Observatory, Queen Maud Land

Air samples from the Troll Atmospheric Observatory, Queen Maud Land, Antarctica were collected using a High Volume Active Air Sampler (HVAAS) (DHA-80, 5 DIGITEL, Hegenau, CH). Air samples were collected during 2013 on a weekly basis covering seven days per sample, drawing air at 15–25 m^3/h across a glass fiber filter (GFF) (particulate fractions) and two PUF plugs (gas phase fraction) (target volume of 2500–3500 m^3). Flow rates and sampling conditions were digitally monitored and documented.

2.3. Sample Preparation

Prior to deployment, the PUF disks for Casey station were scrubbed under hot water and pre-cleaned by soxhlet extraction for 24 h with petroleum benzene, followed by 24 h with acetone. PUF disks were dried in a dessicator under pure nitrogen flow and sealed in furnaced glass jars with Teflon-lined lids until sampling. All solvents, adsorbents, and gasses used were of the highest standard and selected for ultra-trace analysis. The PUF plugs for Troll station were pre-cleaned by soxhlet extraction for 24 h in toluene, 8 h in acetone, and 8 h in toluene, followed by drying in a dessicator. Glass-fiber filters were baked at 450 °C. Both media were wrapped in foil and sealed in airtight Ziplock bags.

Upon collection, the exposed sample media from both Troll and Casey stations were sealed in a gas-tight container for storage and transported to the Norwegian Institute for Air Research (NILU) for processing and quantification.

2.4. Sample Extraction and Analysis

All sample media (glass fiber filters, PUF plugs from the HVAAS and the HFTPAS) were soxhlet extracted for 8 h in hexane/diethylether (9:1) at NILU's laboratory. The glass fiber filter and PUF plugs from the HVAAS at Troll were extracted together and the concentrations from Troll represents the bulk concentrations of gas and particle phase. Prior to extraction, each sample was spiked with 10 ng of ^{13}C-labelled internal standard. The extract was cleaned by acid treatment and on a preconditioned silica column, topped with sodium sulphate. Once the solvent volume of the cleaned extract was concentrated down to 0.5 mL, 10 ng of tetrachloronaphthalene (TCN) was added as the recovery standard. Further concentration of the sample to ~100 μL was completed by applying a gentle stream of pure nitrogen gas.

The Casey and Troll air extracts were analyzed for seventeen PBDE congeners, namely; PBDE-28, -47, -49, -66, -71, -77, -85, -99, -100, -119, -138, -153, -154, -183, -196, -206, -209,

and for 2,4,6-Tribromoanisole (TBA). Compounds were separated using a Hewlett-Packard 6890N (2003–2006) high-resolution gas chromatography (HRGC) instrument with helium used as the gas carrier. Detection and quantification were performed using a Micromass AutoSpec (Micromass Waters, Manchester UK) high-resolution mass spectrometer (HRMS) with a resolution >10,000 running in electron impact mode (EI) and electron capture negative ion mode (ECNI).

2.5. Quality Assurance

To account for inherent PUF contamination or contamination that may have occurred during analysis and/or transportation, lab blanks and field blanks were included in the experimental protocol [38].

The following quantification conditions were fulfilled for all data presented: (i) The retention time of the native was within three seconds of the corresponding ^{13}C-labelled isomer; (ii) the isotope ratio of the two monitored masses was within +20% of the theoretical value; (iii) the signal/noise was >3/1 for quantification; (iv) the recovery of the added ^{13}C labelled internal standards was within 30% to 140%; (v) prior to each new series of samples, the blank values of the complete clean-up and quantification procedures were determined. Clean-up of samples only commenced when a sufficiently low blank value was obtained. At least once per year the laboratory participates in an international laboratory inter-calibration exercise.

The final reported chemical concentrations (fg/m^3) in Casey Station air samples were calculated by adding together the chemical masses extracted from the the individual sample PUF plugs of the sampling train, and subtracting the chemical masses extracted from twice the 7.63 cm field blank and that of the 2.54 cm field blank. Where levels in the blanks were below detection, the reported level of quantification (LOQ) was used. In 2014, all three of the PUF samples of the sampling train were extracted as one sample and all blank PUFs were extracted as a single sample. The final volume of air (m^3) for each sampling period was calculated by multiplying the average wind velocity (m/s), by the total sampling time (s), by the cross-sectional area of the flow through the sampler (m^2) and adjusting this for standard conditions [30]. On six occasions the instrument data logger failed to record wind data for the complete sampling period. On these occasions surrogate wind data obtained from the Bureau of Meteorology Casey Station observatory (30017) was applied for some or all of the sampling period. Finally, the total chemical mass was divided by the sampling volume to give the chemical concentration for each of the sampling periods.

2.6. Sampling Schedule

Continuous sampling was conducted at Casey Station between December 2009 and November 2014. Twenty-six cartridge sample-sets were obtained during this period, each set representing sampling periods from 4 to 17 weeks (average 6.3 weeks) (Table S1).

The 39 weekly samples from the Troll station in February-November 2013 were combined into ten monthly mean concentrations and one annual mean concentration. Troll sample IDs, sampling period, and captured wind volumes are presented in Table S2.

2.7. Statistics

A simple linear regression (R^2) was performed on homologue groups to evaluate atmospheric concentrations relative to temperature. Similarly, Pearson's correlation coefficients were calculated for breakthrough of key congeners in each of the HFTPS samples, relative to temperature, average wind speed, and total air volume captured.

The cosine theta similarity metric (Cosθ) [39] was employed to compare the similarity of BDE congener profiles from the two stations. This metric calculates the cosine of the angle between two multivariate vectors.

The cosθ metric is calculated from the formula for a Euclidean dot product of two vectors according to:

$$\cos\theta = \frac{\sum\limits_{k=1}^{n}(x_{ak}.x_{sk})}{\sqrt{\sum\limits_{k=1}^{n}x_{ak}^2}.\sqrt{\sum\limits_{k=1}^{n}x_{sk}^2}}$$

where x_{ak} is the concentration (fg/m^3) of congener k in Casey Station air samples, x_{sk} is the concentration of the same congener in Troll station air samples, and n is the number of BDE congeners analyzed. Values of cosθ can range from 0.0 to 1.0, with 1.0 representing a perfect match, and 0.0 indicating perpendicular vectors and no similarity between the congener profiles [40]. This approach has been used previously to quantify the similarity of PCB congener profiles in sediment and air [40–42].

3. Results and Discussion

3.1. Brominated Compounds in Antarctic Air

Sixteen PBDE congeners were detected in the Antarctic atmosphere throughout the monitoring period. The only BDE congener not detected in any sample was BDE-138, and as such BDE-138 is not mentioned in further discussion. At Casey station, all congeners, except for BDE-138, were detected, although only congeners BDE-28, -47, -49, -66, -99, -100, -153, -154, -206, and -209 were detected in >50% of samples. At Troll station, all congeners, except both BDE-119 and -138, were detected. Only BDE-28, -47, -49, -66, -99, and -100 were detected in >50% of samples. At Casey station, congeners BDE-71, -77, and -119 were detected in <10% of samples. For Troll station, this list further included BDE-85, -153, -183, and -196. BDE-206 and -209 were detected in 60% and 63% of samples at Casey Station, and 37% and 47% of samples at Troll Station. Despite these differences, the profiles of both stations showed a high degree of similarity, as indicated by a Cosθ value of 0.830.

Σ_{17}PBDEs at Casey ranged from <0.035 to 1700 fg/m^3 (average of 130 fg/m^3). Σ_{17}PBDEs at Troll station ranged from 25.0 to 19,000 fg/m^3 (average of 2000 fg/m^3), revealing a marked difference in overall concentrations. If we exclude BDE-209 from ΣPBDEs, because BDE-209 is commonly associated with analytical challenges and thereby a larger analytical variability, the ranges and average Σ_{16}PBDE concentrations at Casey and Troll were 0.035–580 fg/m^3 (48 fg/m^3) and 25–9500 fg/m^3 (1100 fg/m^3), respectively.

TBA was measured and detected for the first time in Antarctic air and was found to be a ubiquitous contaminant in the air profiles of both stations, with a range of 30–27,000 fg/m^3 at Troll and 8.6–860 fg/m^3 at Casey. At both stations, TBA and BDE-209 contributed the two highest mean concentrations of 110 and 140 fg/m^3, and 27,000 and 2100 fg/m^3, at Casey and Troll stations, respectively. Summary statistics are presented in Table 1, full sample data are presented in Tables S3 and S4, and annual station average concentrations are presented in Table 2 alongside recent atmospheric measurements at the Canadian Arctic Station, Alert [43].

Table 1. Summary statistics for brominated compounds in Antarctic air in the vicinity of Casey and Troll Stations, where the mean concentration (fg/m^3) is obtained only from samples in which compounds were detected at >LOQ. The % Detection is the percentage of samples that were >LOQ, and non-detect (ND) denotes concentrations <LOQ.

	Casey			**Troll**		
Compound	**Mean (±SD)**	**Range**	**% Detection**	**Mean (±SD)**	**Range**	**% Detection**
TBA	110 (190)	<LOQ-856	90	7100 (1100)	30–27000	100
BDE-28	0.38 (0.54)	<LOQ-2.6	77	29 (46)	1.0–190	100
BDE-47	4.9 (7.3)	<LOQ-29	87	760 (1500)	23–7800	100
BDE-49 *	0.27 (0.49)	<LOQ-2.2	69	25 (44)	<LOQ-190	92

Table 1. *Cont.*

Compound	Casey			Troll		
	Mean (±SD)	Range	% Detection	Mean (±SD)	Range	% Detection
BDE-66	2.4 (6.6)	<LOQ-3.4	76	21 (31)	−120	76
BDE-71 *	0.13	<LOQ-0.13	4	58 (64)	<LOQ-130	8
BDE-77	0.16 (0.06)	<LOQ-0.2)	7	43	<LOQ-43	3
BDE-85	0.25 (0.33)	<LOQ-0.89	27	3	<LOQ-4	3
BDE-99	2.1 (2.4)	<LOQ-7.8	87	160 (220)	<LOQ-990	76
BDE-100	0.67 (0.68)	<LOQ-2.3	63	62 (92)	<LOQ-390	82
BDE-119	0.32	<LOQ-0.32	4	ND	<LOQ	0
BDE-138	ND	<LOQ	0	ND	<LOQ	0
BDE-153	0.19 (0.18)	<LOQ-0.65	53	18 (13)	<LOQ-30	8
BDE-154	0.16 (0.18)	<LOQ-0.67	57	15 (10)	<LOQ-34	16
BDE-183	0.57 (0.6)	<LOQ-1.3	47	15 (8)	<LOQ-24	8
BDE-196	32 (60)	<LOQ-170	33	300	<LOQ-300	3
BDE-206	46 (120)	<LOQ-480	63	210 (290)	<LOQ-1200	37
BDE-209 **	140 (280)	<LOQ-1100	63	2100 (2300)	<LOQ-9200	47

* Summary statistics based upon 2012–2014 data in which these congeners were independently quantified. ** Data associated with uncertainties.

Table 2. Annual average brominated compound concentrations (fg/m^3) at Casey and Troll Stations, presented alongside recent measurements from the Arctic. Casey and Troll station annual mean concentrations were obtained only from samples >LOQ. Non-detect (ND) denotes concentrations < LOQ and "-" denotes an analyte not targeted.

	Casey 2010	Casey 2011	Casey 2012	Casey 2013	Casey 2014	Troll 2013	Alert 2002–2004 [43]
TBA	62.0	41.0	35.0	170.0	180.0	7100	
BDE-28	1.1	0.033	0.28	0.28	0.10	29.0	180.0
∑Tri-BDE	1.1	0.033	0.28	0.28	0.10	29.0	180.0
BDE-47	19.00	0.89	2.0	2.8	2.4	760	2500.0
BDE-49	1.0	0.04	0.22	0.42	0.057	25.0	160.0
BDE-66	13.0	ND	0.51	0.95	0.081	21.0	100.0
BDE-71	In 2010 and 2011, congeners 49 and 71 were co-quantified.	ND	0.13	ND	ND	58.0	-
BDE-77	ND	ND	0.11	0.2	ND	ND	-
∑Tetra-BDE	33.0	0.93	3.0	4.4	2.5	860.0	2800.0
BDE-85	0.29	0.026	0.04	0.17	0.89	ND	120.0
BDE-99	4.2	0.91	2.2	1.6	1.4	160.0	2400.0
BDE-100	1.5	0.17	0.32	0.71	0.47	62.0	450.0
BDE-119	ND	ND	ND	0.32	ND	ND	-
∑PentaBDE	6.0	1.1	2.6	2.8	2.8	220	3000.0
BDE-138	ND	ND	ND	ND	ND	ND	50.0
BDE-153	0.56	0.17	0.2	0.14	ND	18.0	170.0
BDE-154	0.37	0.066	0.13	0.20	ND	15.0	170.0
∑HexaBDE	0.93	0.236	0.33	0.34	ND	33.0	390.0
BDE-183	0.59	0.39	0.23	0.83	0.31	15.0	150.0
∑HeptaBDE	0.59	0.39	0.23	0.83	0.31	15.0	150.0
BDE-196	8.7	1.4	1.64	89.0	ND	300.0	-
∑OctaBDE	8.7	1.4	1.64	89.0	ND	300.0	-
BDE-206	37.0	12.0	5.3	140.0	1.3	210.0	-
∑NonaBDE	37.0	12.0	5.3	140.0	1.3	210.0	-
BDE-209	120.0	60.0	41.0	440.0	9.7	2100.0	1600.0
∑DecaBDE	120.0	60.0	41.0	440.0	9.7	2100.0	1600.0

3.2. Regional Differences

The concentrations of PBDEs in air samples from Troll station throughout 2013 were on average 70 times higher than those observed in Casey air samples during the same time period. The differences were most pronounced for tri-and tetra-BDEs (e.g., BDE-47 being 270 times greater), but comparable for nona-BDE-206. Despite comparatively elevated ambient PBDE air concentrations at Troll station compared to Casey station, recent measurements in the Canadian Arctic remained, on average, eight times higher than at Troll for comparable congeners [44].

Dickhut et al. (2012) [24] performed high volume air sampling for PBDEs at three Antarctic locations during four austral summer seasons, between 2001 and 2005. The measured average ambient concentrations of key BDE congeners at these locations, together with Troll and Casey levels, are presented in Table 3. From these comparisons, it is evident that the measured concentrations of tri- and tetra-BDE congeners (BDE-28, -47, -66) at Troll station, are the highest concentrations measured in Antarctic air to date, and even higher than those detected in Marguerite Bay in 2001 following a laboratory fire at Rothera station in spring 2001 (Table 3. By contrast, BDE-100 and -209 concentrations at Troll were not the highest in this comparison (third and second highest of the five stations, respectively).

Table 3. Comparison of selected average PBDE congeners in Antarctic air in the vicinity of active research stations (fg/m^3).

	Casey (2010–2014)	Troll (2013)	Terra Nova Bay (2003–2005) [24]	Palmer Station (2002) [24]	Marguerite Bay (2001) [24]
BDE-47	4.8	760	218	305	430
BDE-99	2.0	160	155	285	260
BDE-100	0.67	62.0	60.0	60	110
BDE-209	140	2100	355	765	103,000

The higher levels observed at Troll station compared to Casey station may be attributed to the closer proximity of the Troll air monitoring observatory to the main station (200 m) compared to the Casey station monitoring site from the main station buildings (3 km). Further, the presence of an ice run-way/flight traffic just 7 km from Troll station remains a plausible source of contamination. Finally, the elevated concentrations of the tri- and tetra-BDEs at Troll station, which are the main constituents of the commercial penta-formulation, may be related to construction of a new sampling container in the vicinity of the Troll Observatory in February-March 2013. Although the original Troll and Casey stations were erected in 1990 and 1988, respectively, local emissions of penta-BDE may originate from re-emission from land disturbance, or from materials/products present during construction. This latter possibility is supported by the significant drop in tri-and tetra-BDEs throughout 2013 at Troll station (Figure 2). This observation highlights the constraints of short-term, case-study air sampling in the region in accurately determining background levels, and underscores the need of longitudinal monitoring for the determination of robust temporal trends.
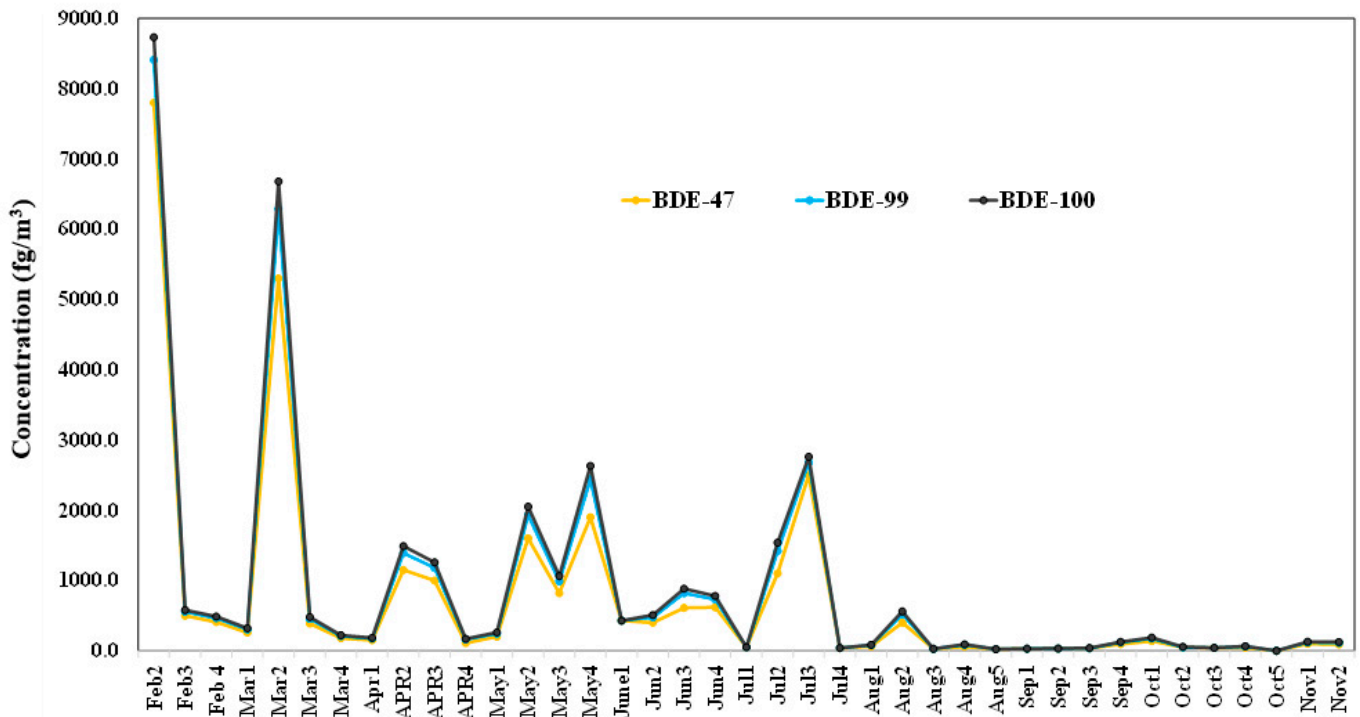
Figure 2. Levels of key penta-formulation congeners detected at Troll station throughout 2013.

Although interpretation of deca-BDE-209 results require caution due to associated analytical challenges, e.g., frequent analytical contamination by this congener, it is interesting to note the dominance of this and other highly brominated congeners in samples in which they were quantified. Penta-formulations containing BDE-47, -99, and -100 were listed under the Stockholm Convention in 2009. The deca-BDE formulation was used as a replacement for octa- and penta-BDEs until its inclusion under Annex A in 2019 [3]. We may expect the impact of this global chemical policy action to be reflec\ted in residential and environmental levels, and in the homologue profiles of the different stations (Figure 3).
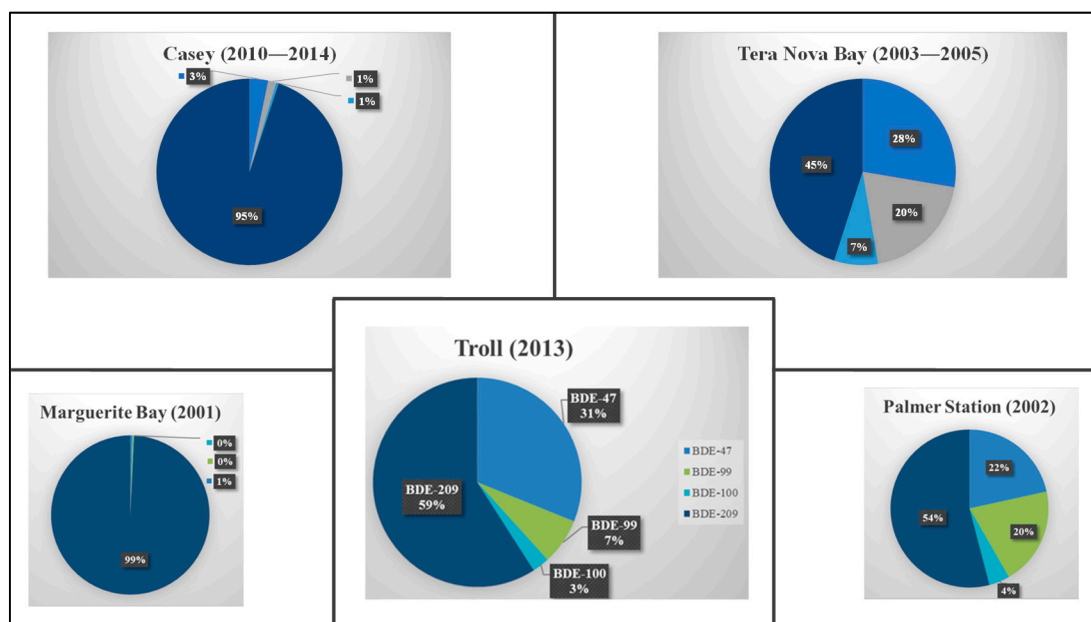
Figure 3. Relative congener homologue contributions to the respective station air profiles.

3.3. Breakthrough Considerations at Casey Station

The elevated levels of PBDEs, in addition to the naturally occurring TBA, at Troll compared to Casey station, flag the possibility that the air volumes sampled with the HFTPAS at Casey may have resulted in breakthrough. Breakthrough occurs when the sampling media becomes saturated with an analyte before the sampling period is finished, thus the calculated ambient chemical concentrations are lower than they should be. Analysis of the last PUF in the HFTPAS sampling train found that it contained on average 19% of the bulk analyte mass, ranging from an average of 8% for BDE-154 to an average of 34% for BDE-100. The back PUF (size adjusted), represents one third of the sampling media, so an analyte proportion of 33% or greater suggests that complete saturation of the media has occurred. BDE-28, -47, -49, -99, and -100 approached this threshold, indicating that Casey station measures for these analytes should be considered an under-estimate of ambient concentrations (Table S5), and consequently the differences to Troll station an overestimation.

There was little apparent relationship between the level of breakthrough of key compounds (TBA, BDE-28, -47, -49, -100, -153, -154, -206, and -209) and temperature, with the exception of BDE-153 ($r = 0.52$). All other key compounds were found to have r values ranging from low negative values to 0.19. Similarly, the captured wind volume showed little correlation with the level of breakthrough. Indeed, negative relationships were observed for TBA, BDE-47, -100, -154, -206, and -209. The only apparent positive relationship was observed for BDE-49 ($r = 0.4$). Wind speeds were likewise found not to impact the level of breakthrough ($r = 0.009$ to 0.20). Deployment duration impacted breakthrough of the lightest key congeners (BDE- 47, -49, -100) in a negative manner ($r = -35, -0.42, -0.26$, respectively). This is a counterintuitive relationship and may suggest that saturation occurs quickly, and these trace levels are easily influenced by minor fluctuations.

3.4. Seasonal Trends

The Casey station dataset offers the first multi-year data regarding ambient PBDE air concentrations in Antarctica. Lighter PBDE congeners may be expected to be more prone to temperature dependent volatilization due to their lower vapor pressure. This may lead to an increase in atmospheric levels with higher summer temperatures as previously shown for legacy POPs [30]. As Casey station measurements for the lighter BDE-congeners were impacted by breakthrough, further interpretation of such trends was, however, not performed. Larger congeners (hepta-, octa-, nona- and deca-) showed no significant relationship with either temperature, season, or wind speed, although correlations may have been obscured by, e.g., temporarily elevated measurements during 2013 (Figure 4).
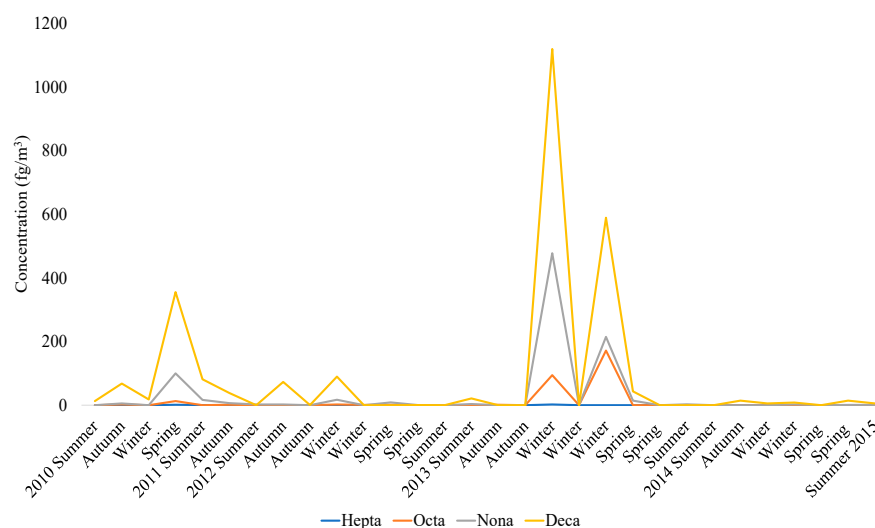

Figure 4. Levels of higher brominated PBDEs according season and year.

Interestingly, seasonal analysis of Troll data revealed a strong winter peak in TBA concentrations (Figure 5). This pattern corresponds to that previously found in Norwegian air [35]. Although authors of this previous study could not explain the pattern, they emphasized the prerequisites of both the precursor of 2,4,6-TBA, namely bromophenols, and the airborne fungi or bacteria responsible for biotransformation of bromophenols to TBA.
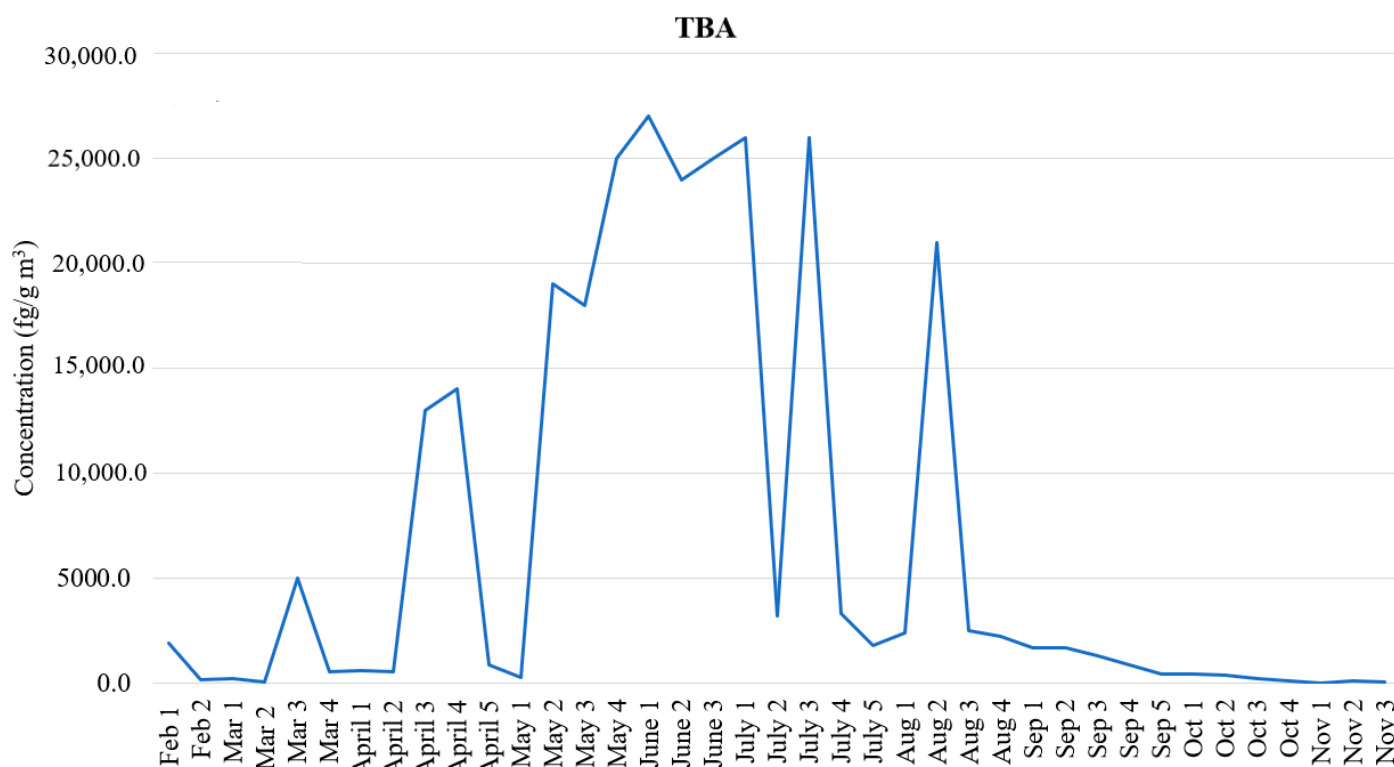

Figure 5. TBA levels at Troll station throughout 2013.

4. Conclusions

Levels of BDE-47 detected at Troll station were higher than those previously detected in the Antarctic or Southern Ocean region [24,42], and in the range of those previously detected in ambient air in Southern Taiwan [45] and the Bay of Bengal [46]. Levels of BDE-99, -100, and -209 corresponded well with measurements made previously in the Antarctic in the vicinity of active research stations. Although on-station PBDE sources at both Casey and Troll station remain unidentified, and indeed are likely to be numerous and varied, the atmospheric PBDE levels observed in the vicinity of these active stations emphasize the growing importance of local sources for Antarctic chemical contamination, and represent important quality assurance data for untangling local versus long-range contaminant sources in long-term monitoring studies in the region.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/atmos12060668/s1. Figure S1. Trollhaugen atmospheric monitoring observatory, Figure S2. Photograph of the HFTPAS (rights) and anemometer plus logger unit (left) installed at Casey Station, Table S1. Casey Station sample-sets (A-I1) together with corresponding sampling periods and Sample volume. '-' denotes sample sets in the series for which Brominated compound measure-ments are not available, Table S2. 2013 Troll Station samples together with corresponding sampling periods and captured wind volume, Table S3. Casey Station chemical concentrations by sample set (2 sig. figures). Values are travel blank corrected (LOQ). Concentrations are presented in fg/m3 to two significant figures. 'ND' denotes non-detected values. In 2010 congeners BDE-49 and BDE-71 were co-quantified (*), Table S4. Troll Station chemical concentrations by sample set. Concentrations are presented in

fg/m3 to two significant figures. 'ND' denotes non-detected values, Table S5. Average percent (%) of analyte mass held within the last (3 of 3) PUF in the sampling train (size adjusted), where ~33% indicates complete saturation of media for the analyte.

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