

Semivolatile Organic Contaminants in the Hawaiian Atmosphere

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Supporting Information

ABSTRACT: An air sampling campaign on the Island of Hawaii aimed to assess background concentrations of semivolatile organic compounds (SVOCs) over the Central Northern Pacific and to explore their distribution along an altitudinal transect. XAD-resin-based passive air samplers were deployed from May to September 2011 at six sites along a transect from the northeastern coast to the Mauna Loa Observatory and at three other island sites. By crossing the trade wind inversion, the transect comprised the marine boundary layer and free troposphere. At the two ends of the transect, flow-through samplers simultaneously sampled air at monthly resolution. Elevated levels of dieldrin, chlordane- and DDT-related pesticides, polycyclic aromatic hydrocarbons (PAHs), and polybrominated diphenyl ethers (PBDEs) at two urban sites indicated contributions from local sources. The composition of chlordane and DDT-related residues indicated recent emissions. PAHs concentrations that decline more rapidly with increasing elevation than those for PBDEs are consistent with faster atmospheric degradation of PAHs. SVOC levels on Mauna Loa were generally at the lower end of concentration ranges reported for remote sites, including the Arctic. However, in contrast to the Arctic, long-range atmospheric transport is deemed less important than human-induced material flow as the source of SVOCs to the island's atmosphere.



1. INTRODUCTION

Semivolatile organic chemicals (SVOCs) such as organochlorine pesticides, polybrominated diphenyl ethers (PBDEs), and polycyclic aromatic hydrocarbons (PAHs) constitute a potential hazard to environment and humans.^{1–4} Some SVOCs (e.g., PBDEs and pesticides) were produced intentionally, while others (e.g., PAHs) are generated from natural or anthropogenic processes such as combustion. Due to national and international regulations on some of the SVOCs, secondary emissions due to revolatilization are gaining importance relative to primary emissions to the atmosphere.⁵ Upon entering the atmosphere, SVOCs are prone to undergo long-range atmospheric transport (LRAT) to remote regions where local emissions are low. Global atmospheric transport of SVOCs mainly occurs in the free troposphere due to higher wind speeds and limited exchange with the earth's surface.^{6,7} As such, investigating the occurrence of SVOCs in the free troposphere is important for understanding LRAT of SVOCs to remote regions.⁷ Due to the difficulty of accessing sampling sites, much fewer measurements of SVOCs have been conducted in the free troposphere than in the planetary boundary layer. Such measurements were mainly conducted from aircraft^{8,9} or at high mountain sites,^{4,7,10} and most have been conducted over the continents. Only a few have focused on SVOCs in the free troposphere over the oceans by sampling high altitude sites on an island.⁷

Conventionally, SVOCs in air are sampled using high-volume active samplers (HVAASs)^{11,12} which can provide high temporal resolution and information on gas/particle partition-

ing.^{7,13,14} However, HVAASs require electricity and frequent operator visits and are difficult and expensive to deploy at multiple sites to study the spatial variations of SVOCs in the air of remote regions.¹³ To overcome these disadvantages, passive air samplers (PASs) are increasingly used to obtain time-integrated SVOC air concentrations in various types of environment.^{15–17} PASs are especially useful in providing high spatial resolution data to elucidate the fate of SVOCs in remote regions such as mountains.^{10,18–22} Although PASs have many advantages and have been widely used, passive sampling rates are potentially influenced by many factors. Understanding these factors is necessary in order to properly interpret and compare PAS-derived air concentrations. A few studies have investigated potentially influential factors such as wind, temperature, properties of the target chemicals, and sampler configuration.^{23–26}

While time-integrated sampling is an advantage of PASs, the sampling rates are generally low (<5 m³/d) so that PASs have to be deployed from several months to a year in order to allow for the detection of the accumulated chemicals. To overcome the limitation of low temporal resolution while keeping other advantages of PASs, a flow-through sampler (FTS) was developed to sample SVOCs in air.²⁷ The FTS consists of a horizontally oriented flow tube, which turns into the wind with

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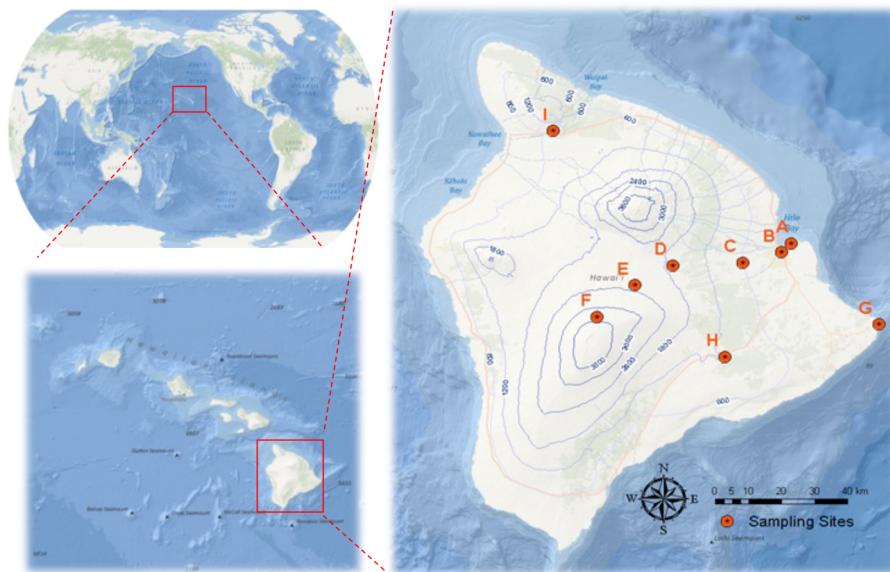


Figure 1. Locations of the sampling sites on the Island of Hawaii. (A–I) passive air samplers; (A, F) flow-through air samplers.

the help of vanes. It relies on the wind to pass air through a plug of polyurethane foam that serves as the sampling medium. Such a design can increase the sampling rate ($>15 \text{ m}^3/\text{d}$) and has proven useful for monitoring SVOCs in remote areas with a much higher temporal resolution than PAS.²⁸

In this study, an air sampling campaign using PASs and FTSSs was conducted on the Island of Hawaii with the aim of exploring the vertical variations of SVOCs from sea level to the top of the Mauna Loa volcano to assess the occurrence of several groups of SVOCs in the free troposphere over the central northern Pacific and compare their concentrations with those in the marine boundary layer.

2. MATERIALS AND METHODS

2.1. Sampling Sites. Located in the Central Northern Pacific, the archipelago of Hawaii is relatively easily accessed, despite being more than 3000 km from the nearest continent. The air sampling campaign was conducted on the Island of Hawaii (Figure 1), which is a volcanic island covering 10432 km².^{29,30} Less than 1.5 million people live within a 3000 km radius of the island, which itself has a population of 185000.²⁹ The elevation on the island rises by more than 3000 m over a horizontal distance of less than 60 km. Prevailing northeasterly trade wind bring marine air to the island. A persistent trade wind inversion caps the atmospheric planetary boundary layer at approximately 2000 m above sea level.³¹ These geographical features make the island an ideal place to study LRAT of SVOCs in the tropical region.

2.2. Sampling Campaign. Cylindrical PASs using XAD-resin filled mesh cylinders as the passive sampling medium were deployed to conduct time-integrated sampling at nine sites (labeled A–I in Figure 1) from May to September 2011. Six of these sites form a transect from the northeastern coast (Site A, elevation: 0 m) to the Mauna Loa Observatory (Site F, elevation: 3400 m) and extend from the planetary boundary layer (sites A–D) to the free troposphere (sites E and F). For comparison PASs were also deployed at sites on the east end of the island (G), in Volcano Village (H), and in the northeast of the island close to the village of Waimea (I). Two FTSSs with vortex sensors for wind speed measurements were deployed at

sites A and F to sample air at a monthly temporal resolution during the PAS deployment period. Detailed information on the location and elevation of the sampling sites is given in Table S1 of the Supporting Information (SI). At each of the sites (except A and H), three XAD-PASs (Figure S1) were deployed: a long one, a short one, and a short one with two XAD-resin filled mesh cylinders in one housing. Because they gave very similar results,³² they are treated as replicates. At each site, a temperature logger (ACR System Inc.) was mounted in a PAS housing to record the temperatures during the sampling period (Figure S2).

Pre-extracted XAD resin used in the PASs was cleaned by Soxhlet extractions with acetone for 24 h and with hexane for another 24 h. Polyurethane foam (PUF) plugs used in the FTSSs were cleaned up by tap water and deionized water, and then Soxhlet extracted with acetone for 24 h and with petroleum ether for another 24 h. XAD-resin filled mesh cylinders were sealed in precleaned metal tubes and PUF plugs were stored in precleaned airtight glass jars before being used in the field. Upon retrieval, each XAD-filled mesh cylinder and each PUF plug was separately placed in their original containers and stored in a freezer in Hilo, Hawaii, before being transported to a freezer in the lab in Toronto at the end of the sampling campaign. The samples from the FTSSs and from the PASs were extracted within one month and three months of retrieval, respectively.

2.3. Sample Extraction. Prior to extraction, each sample was spiked with 100 μL of isotope-labeled standards. Identities and concentrations of those standards are listed in Table S2. The XAD-resin was extracted by accelerated solvent extraction (Dionex ASE-350) using 33 or 66 mL cells for the short and long mesh cylinders, respectively. The ASE conditions followed methods previously optimized in our laboratory:^{26,33} solvent 50:50 hexane/acetone; temperature 75 °C; pressure 1500 psi; static time 5 min; static cycles 3; flush volume 100%; purge time 240 s. The PUF plugs were Soxhlet extracted with petroleum ether for 24 h. After extraction, each extract was rotoevaporated to ~2 mL and filtered through ~1 g of anhydrous sodium sulfate packed in a disposable Pasteur pipet to remove moisture. The eluent was solvent exchanged to

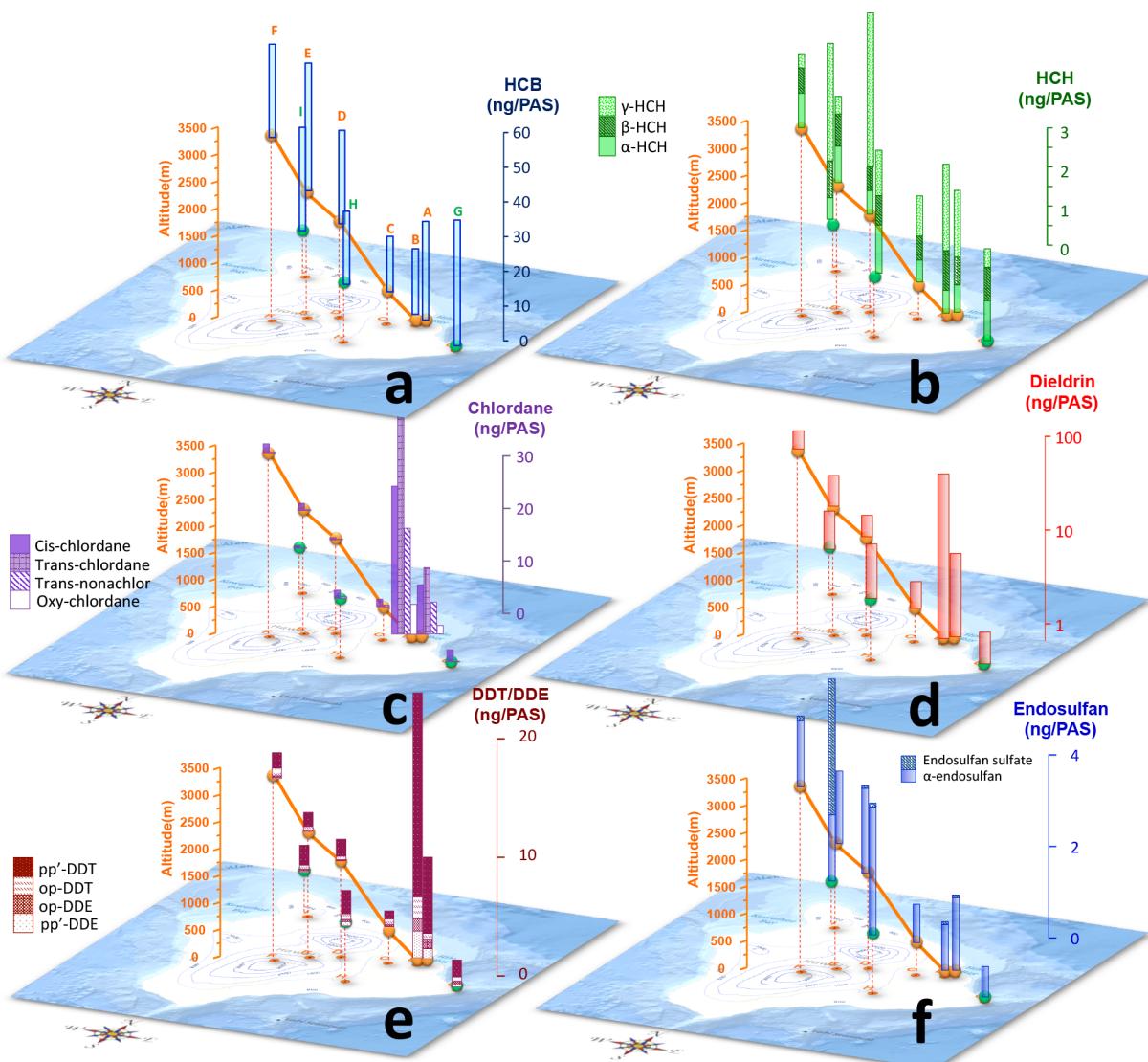


Figure 2. Spatial distributions of (a) hexachlorobenzene (HCB), (b) hexachlorocyclohexanes (HCHs), (c) chlordanes, (d) dieldrin, (e) dichlorodiphenyltrichloroethane (DDT), and (f) endosulfan derived by passive air samplers (PASs, 20 cm-long XAD filled mesh cylinder as the sampling medium) on the Island of Hawaii. Dash lines indicate the altitude of the sampling sites.

isoctane, blown down with high purity nitrogen, transferred to a vial, and further reduced to 0.5 mL. To the vial, 10 μ L of 10 ng/ μ L mirex and 20 μ L of 1 ng/ μ L each of BDE-75, 116, 205 (not present in air) were added to quantify the recovery of surrogates.

2.4. Sample Analysis. Selected PAHs, PBDEs, and pesticides were analyzed using an Agilent 7890A gas chromatograph coupled to an Agilent 7000A triple quadrupole mass spectrometer with electron-impact ion source. Instrumental settings and parameters for analysis of the three groups of compounds are listed in Table S3. All compounds were detected using multiple reaction monitoring mode with helium (2.25 mL/min) as the quench gas and nitrogen (1.5 mL/min) as the collision gas. The precursor ions, product ions, and collision energies selected for multiple reaction monitoring of PAHs, PBDEs, and pesticides are listed in Tables S4–6.

2.5. Quality Assurance. Sampling and analysis followed routine QA/QC practice. We quantified field blanks, analytical procedure blanks, and recoveries of isotope-labeled spikes added prior sample extraction. Ratios of quantifier and qualifier

ions had to be within 30% of the expected value to confirm the target peaks from the chromatogram.

Eight field blanks of the XAD-filled mesh cylinder were collected. Ten field blanks (one for each site every month) were originally planned for the FTSSs during the whole sampling campaign. However, two glass jars broke while being transported to the lab, so the number of field blanks for the FTSSs was reduced to eight. Field blanks of the sampling media were exposed to air at the sampling sites for 1 min and stored and transported the same way as the samples until analysis. Of the chemicals analyzed, only fluorene and phenanthrene were detected in the field blanks for the FTSSs. The blank levels (1–10 ng/sample) were <5% for 90% of the samples and <10% for all the samples. The reported data were thus not blank corrected. The relative standard deviation between triplicates was $36 \pm 34\%$. Recoveries of isotope-labeled standards were 61–120% for PAHs (except for the front section of the FTS in August at site A, which had consistently higher PAH recoveries of 124–134%), 63–121% for PBDEs, and 73–108% for pesticides. Recovery of the analytes was accounted for by using

the isotope-labeled standards as internal standards for the calibration.

Volumes of air sampled by the FTSs were calculated from measured wind speed using a previously derived relationship. Breakthrough of HCBs, HCHs, and PAHs with less than 4 rings occurred for FTSs, which was adjusted based on frontal chromatography theory and a relationship with chemical property, wind speed, and temperature as described in Xiao et al.²⁷

2.6. Air Mass Back Trajectory Analysis. The origin of air masses arriving at sampling sites A and F were assessed via back trajectories calculated using the hybrid single-particle Lagrangian integrated trajectory (HYSPIT) model.³⁴ Based on the Global Data Assimilation System (GDAS) 1 degree latitude longitude meteorological data set, 14 d back trajectories for air masses arriving at 50 m above ground of the two sites were calculated every 6 h for the entire sampling period. The point densities of end points of the trajectories were derived and mapped using the spatial analysis tool of ArcGIS 10.0.

3. RESULTS

3.1. Concentrations in Passive Air Samples. The concentrations of SVOCs in the PASs in ng/PAS are listed in Table S7. The same data as bars are superimposed on a map of Hawaii for the organochlorine pesticides in Figure 2, for four PAHs in Figure 3a, and for the two PBDE congeners 47 and 99

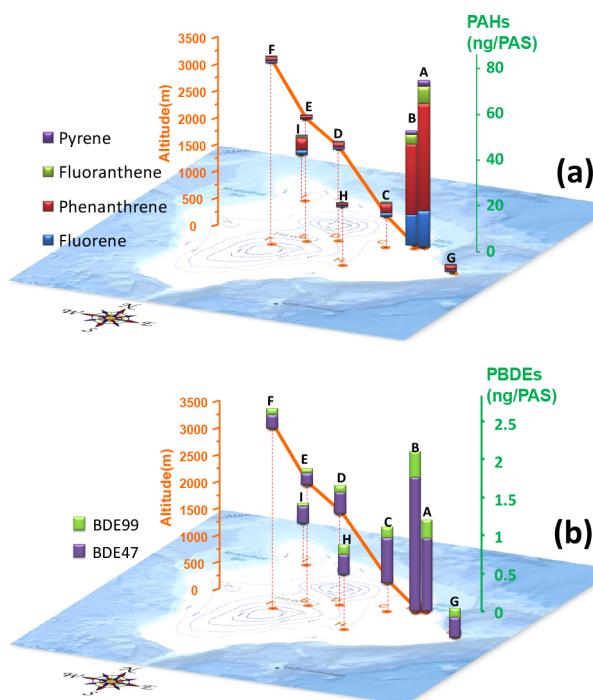


Figure 3. Spatial distributions of (a) polycyclic aromatic hydrocarbons (PAHs) and (b) polybrominated diphenyl ethers (PBDEs) sampled by passive air samplers (20 cm long XAD filled mesh cylinder) on the Island of Hawaii. Dash lines indicate the altitude of the sampling sites.

in Figure 3b. Concentrations are not converted into volumetric air concentrations because (i) the use of sampling rates inevitably introduces uncertainty and (ii) the main purpose of the PAS deployment is the delineation of spatial distribution pattern. The uniformity of the quantified amounts of HCB, a compound with a very long atmospheric residence time and

therefore uniform hemispheric background concentrations, indicates that meteorological factors such as temperature and wind speed did not introduce large differences in sampling rates along the PAS transect, and it is thus valid to derive spatial pattern from data in units of ng/PAS.^{35,36} Following previous practice, we only report concentrations for PAHs of intermediate volatility.^{37–39} More volatile PAHs tend to approach equilibrium with the PAS sorbent during the deployment period, whereas less volatile PAHs tend to be primarily particle bound in the atmosphere. Similarly, we only report concentrations for the PBDE congeners that occur mostly in the atmospheric gas phase.

3.2. Concentrations in Flow-Through Samples. The average and standard deviation of the concentrations of SVOCs in pg/m^3 measured with the FTS at sites A and F are displayed in Figure 4; the data are listed in Table S8. The temporal variability in the concentrations of most SVOCs at the two sites was minor in general. This small month-to-month variability in air mass contamination is consistent with a very stable air mass origin during the five months of sampling. Based on the end point density of 14 d back trajectories (Figure S3), the air always originated from above the Pacific Ocean to the NE of Hawaii. A discussion on larger deviations in the concentrations of PAHs and PBDEs during selected months is included in the SI. The ratio of the FTS concentrations measured at sites A and F, which is displayed in Figure 4b, shows a wide range from a minimum close to unity for compounds such as HCB and α -HCH to a maximum of 3 orders of magnitude for *trans*-chlordane.

Concentrations of SVOCs measured by the FTS and expressed in volumetric units (pg/m^3) are compared with those measured in remote locations in other parts of the world in Table S9. Data were retrieved from the Global POPs Monitoring Plan Database⁴⁰ if they were measured in 2012 or within a time window of ± 2 years (2010–2014), if 2012 data were not available. Only concentrations based on more than two measurements were included. Besides data from polar regions where quite a few monitoring campaigns have been conducted to study the LRAT of SVOCs,^{41,42} we compared data from remote locations in tropical/subtropical regions. Being located in the free troposphere above the trade wind inversion layer, the Mauna Loa sampling site (F) in particular should reflect background concentrations over the Central North Pacific Ocean.

Mean and median concentrations of all the SVOCs measured at Mauna Loa in this study were within the range of concentrations measured in other remote locations (Table S9). Median concentrations of HCB and α -HCH at Mauna Loa were comparable with those in Hedo, Japan, and higher than at most other sites except Stórhöfði, Iceland, and Tam Dao, Vietnam, which had 2.6 and 1.8 times higher HCB and 2.5 and 1.1 times higher α -HCH. The median concentration of β -HCH was higher than that of all other sites, although the maximum was four times lower than that at Zeppelinfjell, Norway. γ -HCH in Mauna Loa had median concentrations comparable to those at Alert, Canada, and lower than those at other sites. The maximum difference was found with Stórhöfði, Iceland, where median concentration was 30 times higher. Although elevated levels of *cis*- and *trans*-chlordane and *trans*-nonachlor were found in Hilo, their median concentrations at Mauna Loa were lower than those at other sites, suggesting their presence on the mountain is due to LRAT. α -endosulfan had higher concentrations at Mauna Loa than at Alert and lower

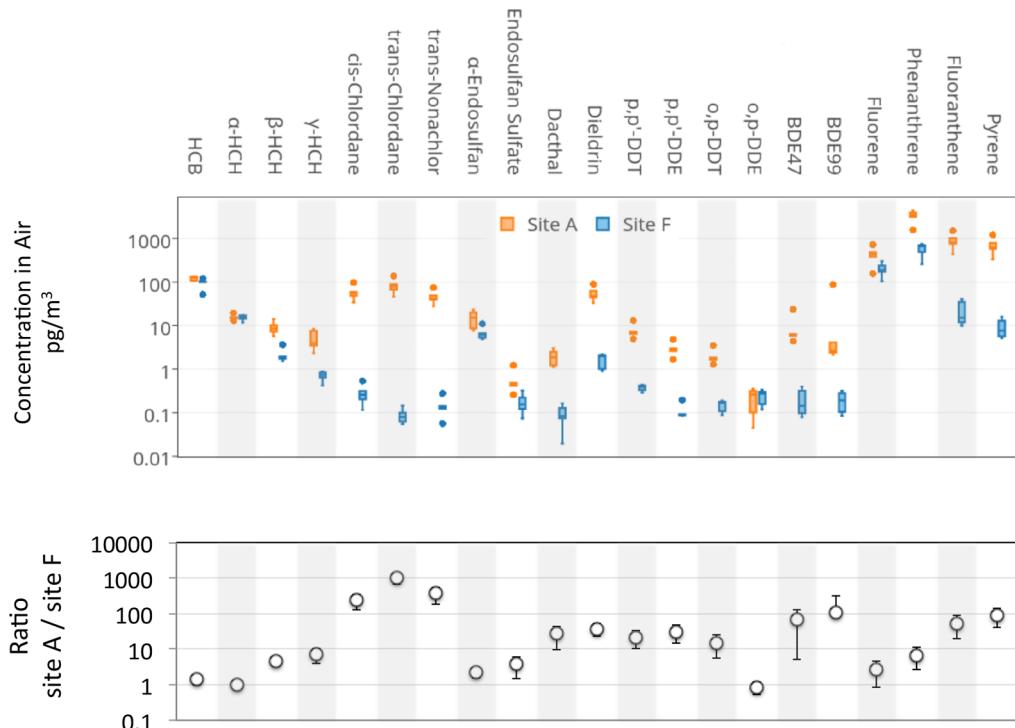


Figure 4. Average and standard deviation of five monthly concentrations of selected SVOCs in the atmosphere of site A (sea level, Hilo) and F (Mauna Loa) in units of pg/m³ as measured by a flow-through sampler in the time period May to September 2011. The bottom panel shows the ratio of the concentration at the two sites.

concentrations than at Mt. Kenya, Kenya and Koumakondo, Togo. Median and maximum concentrations of dieldrin at Mauna Loa were higher than at most sites except Mt. Kenya and Koumakonda, which had two times higher concentrations. Median concentration of *p,p'*-DDT at Mauna Loa was higher than at most polar remote sites by over a factor of 5 except at Pallas, Finland, which had 3 times higher median *p,p'*-DDT. The median concentration of *p,p'*-DDT at Mauna Loa was 30–96%, lower than at other tropical remote sites. The median concentrations of BDE-47 and –99 at Mauna Loa were 90% and 70% lower than at Alert, 60% and 10% lower than at Koumakonda, but 2 and 4 times higher than at Mt. Kenya.

4. DISCUSSION

4.1. The Influence of Local Sources. For the majority of the quantified SVOCs, including a number of organochlorine pesticides (dieldrin, DDT-related substances, chlordane-related substances), the PAHs, and the PBDEs, elevated concentrations were recorded in the PAS deployed at sites A and B. Site B is in a residential area within the town of Hilo (ca. 40000 inhabitants), whereas site A is ~4 km to the east of site B at the northeastern coast of the island. The largest difference of more than 1 order of magnitude between the Hilo sites (A and B) and those elsewhere on the island (C to I) occurred for chlordanes, *p,p'*-DDT, and PAHs. The difference is approximately 1 order of magnitude for dieldrin, whereas it is only a factor of 2 to four for the PBDEs and dacthal. Two chlordane-related substances (*trans*-nonachlor, oxychlordane) were only detected above the detection limit at sites A and B. For most of these SVOCs, site B has higher levels than site A, which is at the coast and is influenced by air masses arriving from the sea in addition to air that is blowing seaward from the town. Only for the PAHs are the levels at site A higher than at site B.

The higher levels of the pesticides (chlordane, dieldrin, DDT-related compounds) at sites A and B can be explained by their past use in the Hilo area. Specifically, chlordane, dieldrin, and DDT were all used for termite control in Hawaii in the past.⁴³ They were commonly applied directly to soil beneath buildings or beneath slab foundations and around the foundation perimeter for new construction. Chlordane, in particular, was the most common termiticide used in Hawaii, its usage exceeding that of other termiticides by at least a factor of 2.⁴³ Despite regulation, chlordane, dieldrin, and *p,p'*-DDT still show over one orders magnitude higher concentrations than dacthal, which is a current-use organochlorine herbicide. Similarly, dacthal has elevated concentrations at site A and B (2–3 times higher than other sites), indicative of its urban uses.

The composition of chlordane and DDT residues in air are indicative of relatively recent usage. A high abundance of *p,p'*-DDT relative to *p,p'*-DDE is typically associated with a fresh source of DDT to the atmosphere.⁴⁴ The *p,p'*-DDT/*p,p'*-DDE ratios at sites A and B were 3, while at sites H and I where both *p,p'*-DDT and *p,p'*-DDE were detected, the ratios were around 1.0 and 0.8. These ratios are even higher than those recorded in Mexico and Central America, where recent usage of DDT in agriculture was suspected.⁴⁴ The *trans*-/*cis*-chlordane ratio (*t/c*-C-ratio) at sites A and B was 1.34 and 1.50 while at other sites it was below 0.5. This ratio is commonly used to distinguish aged and new emission of chlordane. In the technical chlordane mixture, the *t/c*-C-ratio is 1.17.⁴⁵ Accounting for the slightly higher volatility of *trans*-chlordane,⁴⁶ the *t/c*-C-ratio can be over 1.5 in the atmosphere of source areas.^{44,47,48} *trans*-Chlordane is more likely to degrade through photodegradation in the air than its *cis*-counterpart,⁴⁷ causing the *t/c*-C-ratio to be lower after LRAT. The USEPA banned all uses of chlordane in 1983 except to control termites and banned all uses in 1988.⁴⁹

Dieldrin was used for termite control in Hawaii until 1987.⁴³ DDT was banned in the United States in 1972.

The greatly elevated air concentrations of chlordanes, DDTs, and dieldrin in the urban area, in combination with the high *p,p'*-DDT/*p,p'*-DDE, and *t/c*-C-ratios suggests that even 30 years after their ban, there appear to be fresh sources of these organochlorine pesticides in the Hilo area. This does not necessarily indicate recent uses of those pesticides. It is possible that the "freshness" of the pesticide signatures is due to slower degradation when used for termite control under house foundation or under carpets than when applied to agricultural soils, where microbial activity is stronger. This hypothesis is supported by a mean *p,p'*-DDT/DDE ratios of 2 in 35 indoor air samples and 3 in 48 indoor dust samples taken in 2002 from Arizona where pesticides such as DDT were also used for termite control.⁵⁰ Based on geometric mean concentrations of pesticides in carpet dust of Detroit, Iowa City, Los Angeles, and Seattle measured in 1999–2001,⁵¹ ratios of *p,p'*-DDT/DDE and *trans-/cis*-chlordane were 3.2–5.3 and 1.7–1.8, respectively, which is even higher than the ratios from this study. We therefore infer that most of the pesticides measured in outdoor air in Hilo are of household origin.

The spatial pattern for γ -HCH was different from that of any other SVOCs. The value at site G (Cape Kumukahi) was 1 order of magnitude lower than at site D, which is half way up Mauna Loa. Waimea (site I), a small town with a population of ~10000²⁹ at an elevation of ~800 m above sea level, and Hilo (sites A and B) also had above average γ -HCH levels. Higher concentrations of γ -HCH may be associated with historical use of lindane as a termiticide for wood preservation.^{52,53} Relatively low α -/ γ -HCH ratios between 0.2 to 2.4, which are much lower than the ratio of 4–7 in the technical HCH mixture, are also indicative of lindane use.⁵⁴

The highest PAH concentrations were found at sampling site A (Figure 3a). Although the population density around site A is lower than that around site B, Hilo Airport is ~1000 m to the south, a freight cargo port with petroleum refining facilities is ~500 m to the west, and a beach park is ~200 m to the northeast of site A. Both airport and seaport are sources of PAHs^{55,56} and thus the proximity of these facilities could explain the ~50% higher PAHs levels at site A than at site B. Besides sites A and B, sites C and I also had slightly higher levels than the other sampling sites, presumably due to the proximity to Hilo and Waimea, respectively. Overall, the distribution of PAHs across the island indicates that local sources close to the sampling sites are the main contributor to the variability in the measured PAH levels and that sites D to H reflect the background levels of PAHs on the island.

The highest BDE-47 and 99 levels were observed at the Hilo site B (Figure 3b) in agreement with other studies indicating that urban areas have strong sources of PBDEs.^{15,57} At site A, PBDE levels were ~40% lower. At site G, another coastal site farthest east on the island, PBDE levels were ~30% of that at site A, which suggests that PBDEs measured at site A are mainly attributable to local sources. The low PBDE levels at sites E and F likely represent hemispheric background conditions.

4.2. Well-Mixed Tropical Troposphere. A number of compounds, namely HCB, α -HCH, and α -endosulfan, have very similar concentrations in the FTS deployed at sea level and on Mauna Loa and display a rather uniform concentration along the PAS transect and at the three additional sites. In other words, these compounds have essentially uniform concen-

trations across the island's atmosphere. This suggests that they have no local sources that are sufficiently large to impact air concentrations and have atmospheric residence times sufficiently long to become well mixed across the entire height of the troposphere.

The lack of local sources of HCB and α -HCH is consistent with what is known about the history of their use in the USA. HCB has not been deliberately produced in the USA since the 1970s, and after 1984, there has been no registered use of HCB as a pesticide.⁵⁸ Technical HCH, which has been the main source of α -HCH, was banned from use in the United States in the 1970s, although use in Asian countries continued into the mid-1980s and 1990.^{59,60} While use of some organochlorine pesticides dating back several decades appears to impact air concentration to the present day (section 4.1), this is not the case for HCB and α -HCH. This is likely related to the much higher volatility of these SVOCs, which facilitates their dispersal from past areas of application.

Because of the local influence of Hilo for substances other than HCB, α -HCH, and endosulfan-I, the FTS measurements at site A cannot serve to represent the background contamination of the marine boundary layer. Accordingly, the ratios of the FTS concentrations at sites A and F (Figure 4) cannot be used to assess the relative contamination of the free troposphere and marine boundary layer. On the other hand, sampling site G on Cape Kumukahi in the farthest East of the island with few human inhabitants within a 5 km radius appears to be hardly influenced by local sources. Interestingly, the ratio of the concentrations in the PAS at sites G (Cape Kumukahi) and F (Mauna Loa) is remarkably close to one for most of the analytes (Table S7). Only for the two PBDEs and dacthal do the concentrations at sea level exceed those on the mountain top by more than a factor of 2. Most of the SVOCs have similar levels in the marine boundary layer and the free troposphere. In particular, there is no evidence of strong concentration differences across the tropical inversion layer. This suggests that far from continents most of the SVOC can become well mixed throughout the troposphere, which agrees with a previous study showing a large proportion of pollutants emitted into the boundary layer is transported to the free troposphere in a short time via advection and turbulent mixing during long-range atmospheric transport.⁶¹

4.3. Spatial Concentration Gradients of PAHs and PBDEs. If we assume that sources of PAHs and PBDEs outside of the Hilo area are negligible, we can interpret the rate of PAS concentration decline along the A to F transect in terms of relative LRAT potential. The rates of decline were lower for PBDEs than for PAHs (Figure S4). Concentrations of SVOCs in air decrease with distance from sources due to dilution, dry and wet deposition, and degradation.⁶² The effect of dilution is identical for different chemicals. Because BDE-47 and 99 have higher octanol/air and lower air/water partition coefficients than the three- and four-ring PAHs we quantified, the deposition rates for the PBDEs should be higher than for the PAHs. Therefore, if deposition were to control the rate of concentration decrease, levels of PBDEs would decrease faster than those of the PAHs along the transect. Because this was not the case, we postulate that the faster decline in the PAH concentration is due to their faster atmospheric degradation. This is supported by the AOPWin (v1.92)⁶³ estimated atmospheric half-lives due to reaction with the hydroxyl radical (Figure S5), which are ~1 d for the PAHs and >15 d for the PBDEs. Atmospheric degradation half-lives of the PAHs are

within a factor of 6 which is insufficient to cause significant differences in the decreasing trend between sites A and F ([Figure S4](#)).

4.4. Origin of SVOCs in Hawaii: Long-Range Atmospheric Transport vs Local Sources. Source contributions were investigated using principal component analysis on SVOCs detected at all sites. On the score plot ([Figure S6](#)), the two urban sites A and B were separated from the others confirming that chemical sources in this area affect the SVOC composition over the island. The first principal component, with higher contributions from PAHs and the pesticides used for termite control, explains 56% of the data variance and can be attributed to those urban sources. The second component with high contribution by HCB, HCH, and endosulfan, which explains 21% of the data variance, can be attributed to LRAT. The back trajectory analysis ([Figure S3](#)) suggests these pesticides originate primarily from the west coast of North America.

From the spatial distributions of pesticides, PAHs, and PBDEs on the Island of Hawaii, we conclude that these SVOCs largely originate locally. This is in contrast to polar regions, which SVOCs mainly reach by LRAT from continental source regions. Despite studies showing local sources of SVOCs, e.g., from research stations,⁶⁴ the population density and anthropogenic activities in polar regions are still much less than on the Island of Hawaii. While PAHs are emitted from combustion sources, PBDEs emissions are, in the absence of production facilities, mainly associated with consumer products, to which the chemicals had been added as a flame retardant. Five years after the ban on penta-BDEs,⁶⁵ elevated penta-BDE concentrations can still be observed in air close to the urban area of the island, indicative of emissions from consumer products and the long lifetime of PBDEs in those products. As, to our knowledge, no PBDEs have been produced on the island, the PBDE stock on the island is mainly associated with material flows associated with human activities. Such chemical transport via material flow to a “remote” island could be a more important process than the transport of chemical in the natural environment and deserves attention during environmental impact assessments of chemicals in such ecosystems.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.est.7b03841](https://doi.org/10.1021/acs.est.7b03841).

Tables and figures with details on sampling sites, sampler configuration, and analytical method; tables with concentrations measured in PAS and FTS; figures with results of the air trajectory analysis and PCA; table comparing data with those reported for other locations; figure with concentration decline with distance from site A; discussion of the monthly variations in PAHs and PBDEs concentrations ([PDF](#))

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Notes

The authors declare no competing financial interest.

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Supporting Information for

Semi-volatile organic contaminants in the Hawaiian atmosphere

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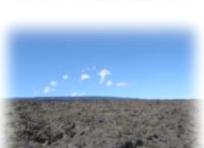
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Table S1. Geographic coordinates and elevations of the sampling sites

SiteCode	Latitude	Longitude	Elevation (m)	Scene
A	19°43'53.38"N	155°2'51.89"W	0	
B	19°42'28.67"N	155° 4'29.04"W	11	
C	19°40'49.88"N	155°10'48.00"W	587	
D	19°40'23.00"N	155°22'12.00"W	1699	
E	19°37'15.42"N	155°28'25.20"W	2240	
F	19°32'9.03"N	155°34'30.97"W	3400	
G	19°30'58.22"N	154°48'38.83"W	2	
H	19°25'46.36"N	155°13'41.46"W	1123	
I	20° 1'53.58"N	155°41'42.72"W	784	

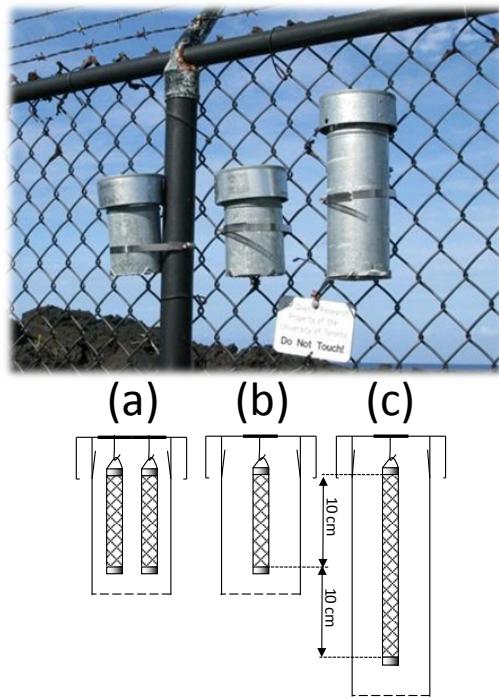


Figure S1. Illustration of the three passive air sampler configurations used in this study

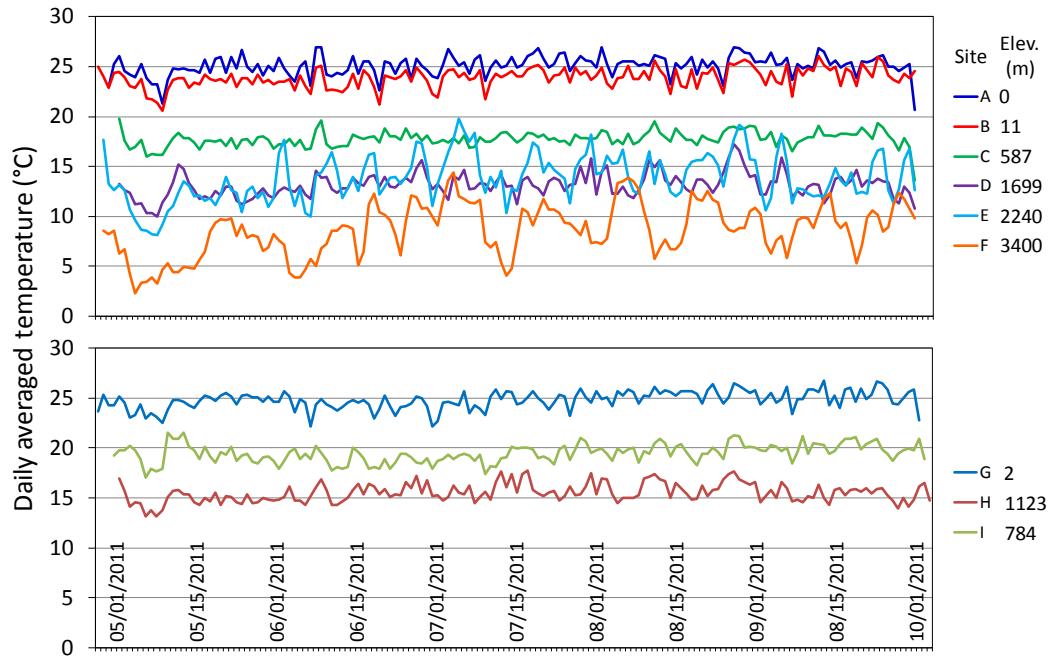


Figure S2. Daily averaged temperature profiles at the sampling sites.

Table S2. Information on the 100 μ L surrogate standards spiked prior to sample extractions

Chemical	Concentration (ng/uL)	Chemical	Concentration (ng/uL)
^{13}C 12 BDE28	0.2	D10 Acenaphthene	0.25
^{13}C 12 BDE47	0.19	D8 Acenaphthylene	0.25
^{13}C 12 BDE153	0.19	D10 Anthracene	0.25
^{13}C 12 BDE209	0.84	D12 Benz[a]anthracene	0.25
		D12 Benzo[b]fluoranthene	0.25
^{13}C 12 PCB77	0.2	D12 Benzo[k]fluoranthene	0.25
^{13}C 12 PCB101	0.2	D12 Benzo[g,h,i]perylene	0.25
^{13}C 12 PCB141	0.2	D12 Benzo[a]pyrene	0.25
^{13}C 12 PCB178	0.2	D12 Chrysene	0.25
		D14 Dibenz[a,h]anthracene	0.25
D4 endosulfan	0.25	D10 Fluoranthene	0.25
^{13}C 6 HCB	0.25	D10 Fluorene	0.25
^{13}C 6 aHCH	0.25	D12 Indeno[1,2,3-cd]pyrene	0.25
^{13}C 6 gHCH	0.25	D8 Naphthalene	0.25
^{13}C 4 dieldrin	0.25	D10 Phenathrene	0.25
^{13}C 10 trans chlordane	0.25	D10 Pyrene	0.25
^{13}C 12 4,4 DDT	0.25		

Table S3. Instrument parameters for the analyses of PAHs, PBDEs and pesticides

Compound	Injection Volume (μL)	Injection mode	Injector temperature ($^{\circ}\text{C}$)	GC column	Carrier gas	GC temperature program	Injector temperature ($^{\circ}\text{C}$)	Ion source temperature ($^{\circ}\text{C}$)	Quadrupole temperature ($^{\circ}\text{C}$)
PAHs	1.0	Pulsed splitless	250	J&W HP-5MS (30m \times 250 μm ID \times 0.25 μm film thickness)	helium (1.2 mL/min)	90 $^{\circ}\text{C}$ for 1 min, to 250 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$, to 300 $^{\circ}\text{C}$ at 5 $^{\circ}\text{C}\cdot\text{min}^{-1}$, and held for 3 min	250	230	150
PBDEs	2.0	Pulsed splitless	285	J&W HP-5MS column (15m \times 250 μm ID \times 0.25 μm film thickness)	helium (1.2 mL/min)	100 $^{\circ}\text{C}$, to 185 $^{\circ}\text{C}$ at 25 $^{\circ}\text{C}\cdot\text{min}^{-1}$, to 275 $^{\circ}\text{C}$ at 15 $^{\circ}\text{C}\cdot\text{min}^{-1}$, to 315 $^{\circ}\text{C}$ at 45 $^{\circ}\text{C}\cdot\text{min}^{-1}$, and held for 6 min	300	230	150
pesticides	1.0	Pulsed Splitless	250	J&W HP-5MS (30m \times 250 μm ID \times 0.25 μm film thickness)	helium (1.2 mL/min)	70 $^{\circ}\text{C}$ for 1 min then 50 $^{\circ}\text{C}/\text{min}$ to 150 $^{\circ}\text{C}$ for 0 min then 6 $^{\circ}\text{C}/\text{min}$ to 200 $^{\circ}\text{C}$ for 3 min then 10 $^{\circ}\text{C}/\text{min}$ to 300 $^{\circ}\text{C}$ for 0 min	250	230	150

Table S4. Precursor ions, product ions and collision energies for the multiple reaction monitoring mode for PAH analysis

Chemical	Precursor Ion	Product Ion	Collision Energy	Chemical	Precursor Ion	Product Ion	Collision Energy
Fluo	166.0	165.0	30	D10-Fluo	176.0	174.0	30
Phe	178.0	152.0	20	D10-Phe	188.0	160.0	34
Ant	178.0	152.0	20	D10-Ant	188.0	184.0	34
Flu	202.0	201.0	30	D10-Flu	212.0	210.0	30
Pyr	202.0	201.0	30	D10-Pyr	212.0	210.0	30
Chry	228.0	226.0	38	D12-Chry	240.0	236.0	38
BaA	228.0	226.0	38	D12-BaA	240.0	236.0	38
BbF	252.0	250.0	42	D12-BbF	264.0	260.0	42
BkF	252.0	250.0	42	D12-BkF	264.0	260.0	42
BeP	252.0	250.0	42				
BaP	252.0	250.0	42	D12-BaP	264.0	260.3	42
IP	276.0	274.0	42	D12-IP	288.0	284.0	42
DBA	278.0	276.0	38	D14-DBA	292.0	284.0	40
BghiP	276.0	274.0	30	D12-BghiP	288.0	284.0	38
Mirex	274.0	274.0	0				

Fluo: fluorene; Phe: phenanthrene; Ant: anthracene; Flu: fluoranthene; Pyr: pyrene; Chry: chrysene; BaA: benzo(a)pyrene; BbF: benzo(b)fluoranthene; BkF: benzo(k)fluoranthene; BeP: benzo(e)pyrene; BaP: benzo(a)pyrene; IP: Indeno(1,2,3-c,d)pyrene; DBA: Dibenzo(a,b)anthracene; BghiP: Benzo(g,h,i)perylene

Table S5. Precursor ions, product ions and collision energies for the multiple reaction monitoring mode for PBDE analysis

Chemical	Precursor Ion	Product Ion	Collision Energy	Chemical	Precursor Ion	Product Ion	Collision Energy
BDE-17	247.9	139.0	30	¹³ C-BDE-28	259.9	150.1	30
BDE-28	247.9	139.0	30	¹³ C-BDE-47	497.7	337.9	25
BDE-47	485.7	325.8	55	¹³ C-BDE153	655.7	495.7	25
BDE-66	325.9	138.0	55	¹³ C-BDE209	811.4	651.1	55
BDE-71	325.9	138.0	55				
BDE-100	565.7	405.7	55	BDE-75	325.9	138.0	55
BDE-99	565.7	405.7	55	BDE-116	403.7	137.1	25
BDE-138	643.6	483.6	25	BDE-205	801.5	641.6	25
BDE-153	643.6	483.6	25				
BDE-154	643.6	483.6	25				
BDE-181	561.6	454.6	30				
BDE-183	561.6	454.6	30				
BDE-190	561.6	454.6	30				
BDE-209	799.7	639.6	55				

Table S6. Precursor ions, product ions and collision energies for the multiple reaction monitoring mode for pesticides analysis

Chemical	Precursor Ion	Product Ion	Collision Energy	Chemical	Precursor Ion	Product Ion	Collision Energy
Trifluralin	306.1	264.0	5	Chlorpyrifos	196.9	168.9	15
Phorate	231.0	174.9	10	Dacthal	300.9	222.9	25
α -HCH	181.0	145.0	15	Trans-Chlordane	372.9	265.9	20
HCB	283.9	248.8	25	Endosulfan I	240.9	205.9	15
Dazomet	161.9	89.1	5	Cis-Chlordane	372.9	265.9	40
Dimethoate	124.8	78.8	5	trans-Nonachlor	408.8	301.8	30
Carbofuran	163.9	149.1	10	Dieldrin	262.9	192.9	40
β -HCH	181.0	145.0	15	Endosulfan II	195.0	159.0	10
γ -HCH	181.0	145.0	15	Endosulfan Sulfate	271.9	236.9	20
Quintozene (PCNB)	236.9	118.9	25				
Diazinon	179.1	137.2	20				
Disulfoton	88.1	60.0	5				
δ -HCH	181.0	145.0	15	α -HCH- ¹³ C6	224.9	152.0	20
Chlorthalonil	265.9	133.0	40	HCB- ¹³ C6	289.9	254.9	20
Metribuzin	197.9	82.0	10	γ -HCH- ¹³ C6	229.9	155.7	20
Malathion	173.1	99.0	15	Trans-Chlordane- ¹³ C10	384.9	276.0	20
Aldrin	262.9	192.9	40	Dieldrin- ¹³ C12	269.8	199.7	30

Table S7. Amount of target chemicals (ng/sampler, average \pm standard deviation^a) accumulated in passive air samplers

Compound	Site								
	A	B	C	D	E	F	G	H	I
HCB	38.42	25.47 \pm 0.71	16.14 \pm 3.61	28.63 \pm 5.08	31.52 \pm 17.18	33.52 \pm 2.55	29.43 \pm 17.44	47.39 \pm 3.71	28.85 \pm 7.94
α-HCH	0.73	0.70 \pm 0.10	0.50 \pm 0.08	0.75 \pm 0.12	0.85 \pm 0.10	1.00 \pm 0.07	0.90 \pm 0.46	1.28 \pm 0.20	0.63 \pm 0.04
β-HCH	0.70	1.01 \pm 0.41	0.77 \pm 0.10	0.75 \pm 0.20	0.72 \pm 0.16	0.73 \pm 0.19	1.02 \pm 0.34	0.79 \pm 0.17	0.90 \pm 0.03
γ-HCH	1.73	1.84 \pm 0.62	1.12 \pm 1.34	4.31 \pm 7.24	0.40 \pm 0.56	0.48 \pm 0.59	0.36 \pm 0.35	1.34 \pm 1.38	2.94 \pm 1.93
cis-Chlordane	9.41	27.02 \pm 1.00	1.20 \pm 0.33	0.96 \pm 0.39	0.68 \pm 0.84	0.60 \pm 0.73	0.83 \pm 1.08	1.15 \pm 1.00	1.52 \pm 0.59
trans-Chlordane	12.59	40.41 \pm 1.48	0.35 \pm 0.05	0.19 \pm 0.04	0.17 \pm 0.03	0.01 \pm 0.01	0.09 \pm 0.01	0.08 \pm 0.02	0.33 \pm 0.05
trans-Nonachlor	5.90	19.13 \pm 0.91	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
oxy-Chlordane	1.16	3.66 \pm 0.60	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
α-Endosulfan	2.20	1.00 \pm 0.10	0.79 \pm 0.15	1.78 \pm 0.09	1.39 \pm 0.24	1.27 \pm 0.19	1.08 \pm 0.36	2.89 \pm 0.48	0.68 \pm 0.18
Endosulfan sulfate	0.11	0.06 \pm 0.05	<0.05	0.12 \pm 0.01	<0.05	0.23 \pm 0.14	<0.05	0.14 \pm 0.02	3.00 \pm 0.31
Dacthal	0.31	0.19 \pm 0.01	0.09 \pm 0.01	0.12 \pm 0.02	0.12 \pm 0.08	0.05 \pm 0.02	0.17 \pm 0.14	0.23 \pm 0.05	0.07 \pm 0.01
Dieldrin	7.75	54.43 \pm 3.11	3.40 \pm 1.03	3.21 \pm 1.23	2.95 \pm 0.74	3.11 \pm 1.05	3.14 \pm 0.39	3.15 \pm 0.70	3.81 \pm 0.29
p,p-DDT	1.02	9.25 \pm 0.89	<0.2	<0.2	<0.2	<0.2	<0.2	0.21 \pm 0.04	0.31 \pm 0.03
o,p-DDT	<0.2	1.65 \pm 0.10	<0.2	<0.2	<0.2	<0.2	<0.2		
p,p-DDE	0.30	2.76 \pm 0.19	0.20 \pm 0.05	0.37 \pm 0.19	<0.2	<0.2	<0.2	0.20 \pm 0.02	0.35 \pm 0.05
o,p-DDE	<0.2	0.18 \pm 0.03	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
BDE47	0.96	1.72 \pm 0.22	0.41 \pm 0.27	0.43 \pm 0.23	0.38 \pm 0.20	0.16 \pm 0.06	0.40 \pm 0.51	0.42 \pm 0.22	0.22 \pm 0.07
BDE99	0.24	0.31 \pm 0.04	0.13 \pm 0.08	0.14 \pm 0.11	0.09 \pm 0.04	0.06 \pm 0.03	0.17 \pm 0.21	0.16 \pm 0.09	0.04 \pm 0.02
Fluorene	14.73	15.88 \pm 0.53	1.84 \pm 0.33	1.54 \pm 0.49	0.37 \pm 0.08	0.70 \pm 0.27	0.74 \pm 0.21	1.60 \pm 0.74	2.75 \pm 0.51
Phenanthrene	43.20	35.75 \pm 1.74	3.68 \pm 0.66	3.59 \pm 1.11	0.78 \pm 0.55	1.37 \pm 0.71	1.28 \pm 0.61	3.38 \pm 1.61	6.19 \pm 1.49
Fluoranthene	6.80	4.60 \pm 0.35	0.46 \pm 0.05	0.28 \pm 0.05	0.10 \pm 0.01	0.12 \pm 0.05	0.18 \pm 0.07	0.21 \pm 0.07	0.98 \pm 0.06
Pyrene	2.60	1.77 \pm 0.18	0.23 \pm 0.03	0.21 \pm 0.06	0.08 \pm 0.03	0.13 \pm 0.05	0.18 \pm 0.06	0.15 \pm 0.06	0.61 \pm 0.05

a. chemical amounts in 10 cm long XAD filled mesh cylinders were multiplied by 2 to calculate the average values and standard deviations, which are equivalent to amount of chemicals accumulated in 20 cm long XAD filled mesh cylinders

Table S8. Maximum, median and minimum concentrations^a (pg/m³) of chemicals measured by flow-through samplers at sites A and F

Chemicals	Site A			Site F		
	Min	Median	Max	Min	Median	Max
HCB	106.12	131.22	135.12	51.66	102.60	120.66
α-HCH	13.10	14.81	19.54	11.77	15.52	17.23
β-HCH	5.65	8.59	14.27	1.53	1.77	3.65
γ-HCH	2.33	4.00	8.39	0.42	0.74	0.88
cis-Chlordane	33.66	56.52	97.11	0.12	0.26	0.54
trans-Chlordane	46.10	79.17	137.51	0.06	0.08	0.15
trans-Nonachlor	27.52	40.69	74.56	0.06	0.14	0.28
α-Endosulfan	7.66	15.12	23.10	4.86	6.18	10.92
Endosulfan Sulfate	0.26	0.48	1.22	0.07	0.15	0.32
Dacthal	1.12	1.86	3.05	0.02	0.08	0.16
Dieleadrin	33.00	46.74	88.80	0.91	2.03	2.18
p,p-DDT	4.9	6.7	13.2	0.3	0.4	0.4
p,p-DDE	1.7	2.7	4.9	0.1	0.1	0.2
o,p-DDT	1.3	1.8	3.5	0.1	0.2	0.2
o,p-DDE	0.04	0.3	0.4	0.1	0.3	0.3
BDE47	4.37	6.02	23.61	0.08	0.14	0.39
BDE99	2.12	2.63	87.57	0.08	0.19	0.32
Fluorene	155.66	435.20	718.37	103.16	188.21	301.93
Phenanthrene	1562.07	3367.33	4348.88	257.79	695.61	751.18
Fluoranthene	437.09	771.05	1496.94	9.90	15.10	40.75
Pyrene	329.38	615.07	1208.33	5.12	7.63	15.98

a. Based on five monthly concentrations

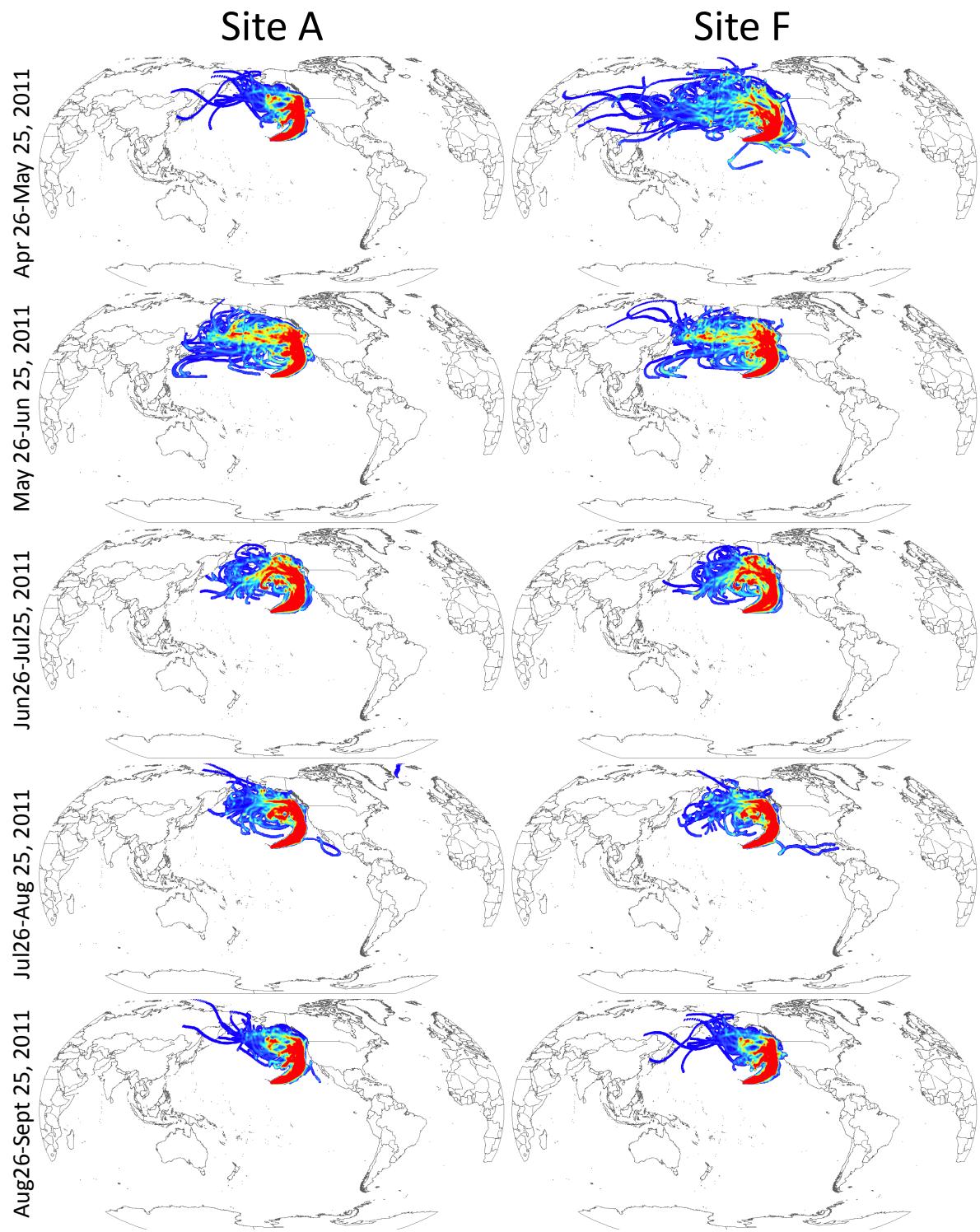


Figure S3. Endpoint density of trajectories arriving at site A and F during the five sampling months based on 14 d back trajectory calculated using HYSPLIT model at every 6 h interval.

Table S9. Concentrations (mean/median [min, max]) of semivolatile organic compounds in pg/m³ measured on Mauna Loa in this study compared with those reported for other polar (>60°N) and tropical (<30°N) remote locations in the northern hemisphere

Chemicals	Mauna Loa, HI USA (this study) 2012	Alert, Canada 2011, 2012	Zeppelinfjell, Norway 2010	Andoya, Norway 2011	Pallas, Finland 2012	Storhofdi, Iceland 2011	Hedo, Japan 2012	Tam Dao, Viet Nam 2010, 2012	Mt. Kenya, Kenya 2010	Koumakonda , Togo 2010
HCB	95/103 [52, 121]	43/43 [15, 64]	81/82 [73, 87]	25/22 [16, 41]	70/73 [33, 100]	268/ 271 [119, 367]	108/105 [75, 177]	207/ 190 [73, 358]	22/23 [18, 27]	
α-HCH	15/16 [12, 17]	5.3/5.4 [1.9, 9.4]	7.6/7.0 [5.0, 10]	4.6/ 4.6 [3.8, 5.6]	8.9 /8.0 [2.5, 17.1]	44/ 40 [35, 59]	15/ 17 [6.0, 22]	20 /18 [6.4, 36]	4.9 /4.8 [3.5, 6.4]	
β-HCH	2.1/1.8 [1.5, 3.7]	0.018/0.018 [0.017, 0.021]	4.2/0.09 [0.070, 14]	n/a	1.19/ 0.86 [0.50, 2.5]	1.05/ 1.02 [1.0, 1.1]	0.8 /0.7 [0.3, 1.2]	1.2/ 1.2 [0.8, 1.5]	0.35/ 0.17 [0.041, 1.0]	
γ-HCH	0.7/0.7 [0.4, 0.9]	0.73/0.69 [0.37, 1.20]	1.0/1.0 [0.70, 1.3]	1.1/ 1.1 [0.6, 1.7]	3.7/ 2.7 [1.4, 7.9]	22/ 21 [17, 27]	2.60/ 2.90 [0.90, 3.80]	6.9/ 8.5 [2.3, 9.9]	2.66 /2.90 [0.83, 4.00]	
cis-Chlordane	0.29/0.26 [0.12, 0.54]	0.34/0.33 [0.16, 0.59]	0.49/0.47 [0.34, 0.64]	0.49/ 0.48 [0.45, 0.56]		0.57/ 0.53 [0.34, 0.85]	2.85/ 2.65 [0.60, 5.30]	0.9 /1.0 [0.5, 1.3]	1.94 /1.97 [1.72, 2.12]	2.1/2.1 [2.1, 2.1]
trans-Chlordane	0.09/0.08 [0.06, 0.15]	0.16/0.15 [0.04, 0.30]	0.18/0.17 [0.06, 0.33]	0.21/ 0.23 [0.08, 0.31]		0.18/ 0.19 [0.12, 0.23]	3.08/ 2.75 [0.60, 6.40]	0.82/ 0.62 [0.45, 1.40]	1.47 /1.49 [1.30, 1.60]	1.6/1.6 [1.6, 1.6]
trans-Nonachlor	0.15/0.14 [0.06, 0.28]	0.39/0.34 [0.20, 0.74]	0.39/0.39 [0.28, 0.52]	0.43/0.44 [0.35, 0.50]		0.31/ 0.30 [0.22, 0.45]	2.62 /2.45 [0.60, 4.90]	0.47/ 0.32 [0.32, 0.77]		
α-Endosulfan	6.8/6.2 [4.9, 11]	1.1/1.0 [0.29, 2.1]							23.3 /22.7 [8.6, 39.3]	37.8/ 38.2 [14.5, 60.4]
Dieldrin	1.6/2.0 [0.91, 2.2]	0.42/0.42 [0.19, 0.68]				0.62/ 0.62 [0.35, 0.98]	0.99/ 0.88 [0.30, 1.90]	0.46/ 0.47 [0.27, 0.65]	3.5 /3.5 [3.1, 3.8]	3.8/ 3.8 [3.7, 3.8]
p,p-DDT	0.39/0.37 [0.29, 0.44]	0.097/0.084 [0.029, 0.32]	0.067/0.073 [0.014, 0.12]	0.066/ 0.063 [0.035, 0.11]	1.2 /1.3 [0.3, 1.7]	0.059/ 0.059 [0.050, 0.068]	0.55/ 0.55 [0.20, 1.10]	6.6/ 4.0 [3.7, 12]	1.2 /1.2 [0.8, 1.7]	11.6/ 12.2 [4.5, 17.5]
p,p-DDE	0.37/0.09 [0.08, 0.20]	0.32/0.33 [0.10, 0.66]	4.1/4.2 [2.0, 6.4]	0.42/ 0.36 [0.14, 0.86]	1.2 /1.3 [0.7, 1.7]	18.4/ 13.3 [4.6, 38.9]	1.23/ 0.95 [0.42, 4.10]	7.0/ 5.9 [5.9, 9.2]	1.6/1.4 [1.3, 2.2]	13.9 /14.1 [5.6, 21.8]
o,p-DDT	0.11/0.17 [0.09, 0.19]	0.12/0.10 [0.028, 0.43]	0.14/ 0.17 [0.010, 0.23]	0.13/ 0.13 [0.07, 0.20]	0.83/ 0.84 [0.27, 1.37]	0.59/ 0.090 [0.089, 2.0]	0.56/ 0.42 [0.26, 1.40]	3.7/ 2.9 [2.6, 5.6]	1.8/ 1.8 [1.2, 2.5]	4.5/ 4.5 [2.4, 6.7]
o,p-DDE	0.15/0.28 [0.12, 0.34]	0.085/0.064 [0.022, 0.26]	0.058/0.050 [0.011, 0.14]	0.06/ 0.05 [0.01, 0.10]			0.22/ 0.14 [0.08, 0.88]	0.9 /0.9 [0.7, 1.0]		
BDE47	0.24/0.14 [0.08, 0.39]	3.1/1.2 [0.28, 20]							0.07/ 0.07 [0.05, 0.11]	0.39/ 0.34 [0.28, 0.60]
BDE99	0.21/0.19 [0.08, 0.32]	1.5/0.62 [0.25, 7.3]							0.052/ 0.047 [0.023, 0.092]	0.230/ 0.214 [0.18, 0.31]

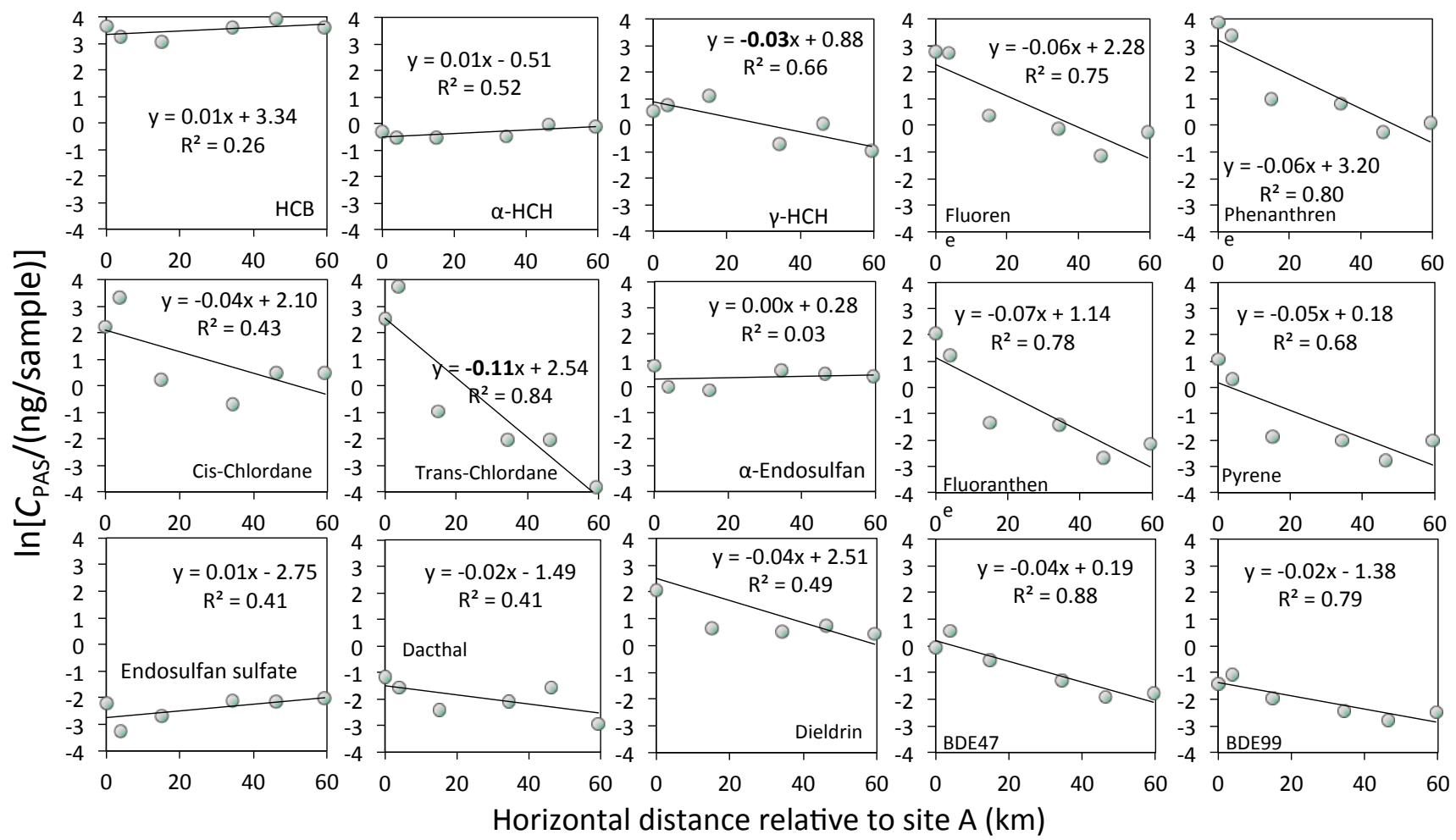


Figure S4. Trend of frequently detected SVOCs in air along the transect A to F.

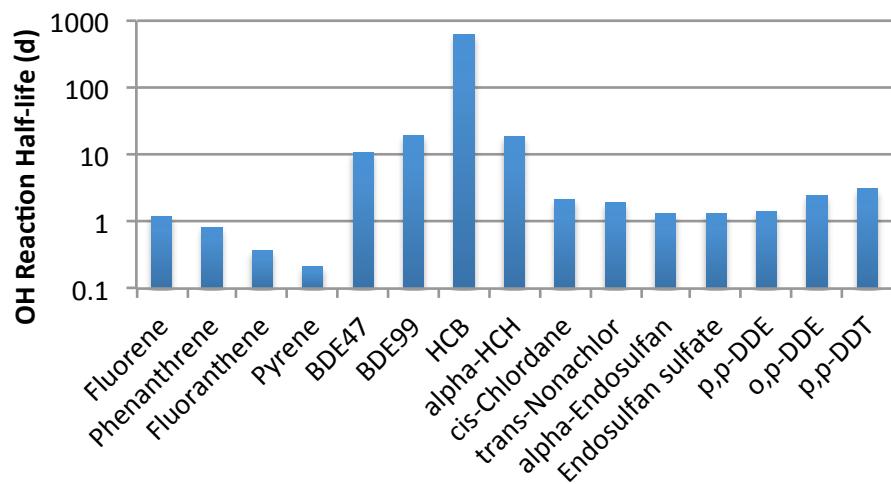


Figure S5. AOPWin (v1.92) estimated half-lives of reactions with hydroxyl radicals in the atmosphere.

Section 1: Monthly Variations of PAHs and PBDEs

Concentrations of the four PAHs 14luorine, phenanthrene, fluoranthene, pyrene at site A were ~50-70% lower in August than during the other sampling months. At site F, the PAH concentrations in August and September were ~3 fold of those in May to July. Differences in air mass origin are minor (Figure S4) and therefore cannot explain these variations. Elevated PAHs in August and September at site F were therefore presumably due to local sources.

BDE-47 and 99 concentrations showed little variations at site A from May to August, but in September levels were ~ 5 and 30 times higher. Again we cannot attribute this to the origin of the air mass. In the September sample, BDE-99 was higher than BDE-47 while in previous months, BDE-47 was dominant. This could indicate a different source of PBDEs to the September sample. Since flow through samples were not replicated, we cannot exclude the possibility of that specific sample having become contaminated during the transport to/from the field, although the field blanks indicate little sample contamination. The monthly variation of PBDEs at site F was different: concentrations of BDE-47 and 99 in May and August were ~4 times higher than in June and July and ~2 times higher than in September. It is interesting to compare the relative abundance of BDE-47 and 99 at the two sites. At site A, except for the September sample, concentrations of BDE47 are higher than BDE99 while at site F, the two congeners have about equal abundance. This is consistent with a higher estimated atmospheric transport potential for BDE-47 compared to 99.¹ Note that no such change between sites A and F is apparent in the PAs, because they mainly sample the gas phase while FTSSs sample both gas and particle phase SVOCs from air.

¹ Wania, F.; Dugani, C. B. Assessing the long-range transport potential of polybrominated diphenyl ethers: a comparison of four multimedia models. *Environ. Toxicol. Chem.* **2003**, *22*, 1252-1261.

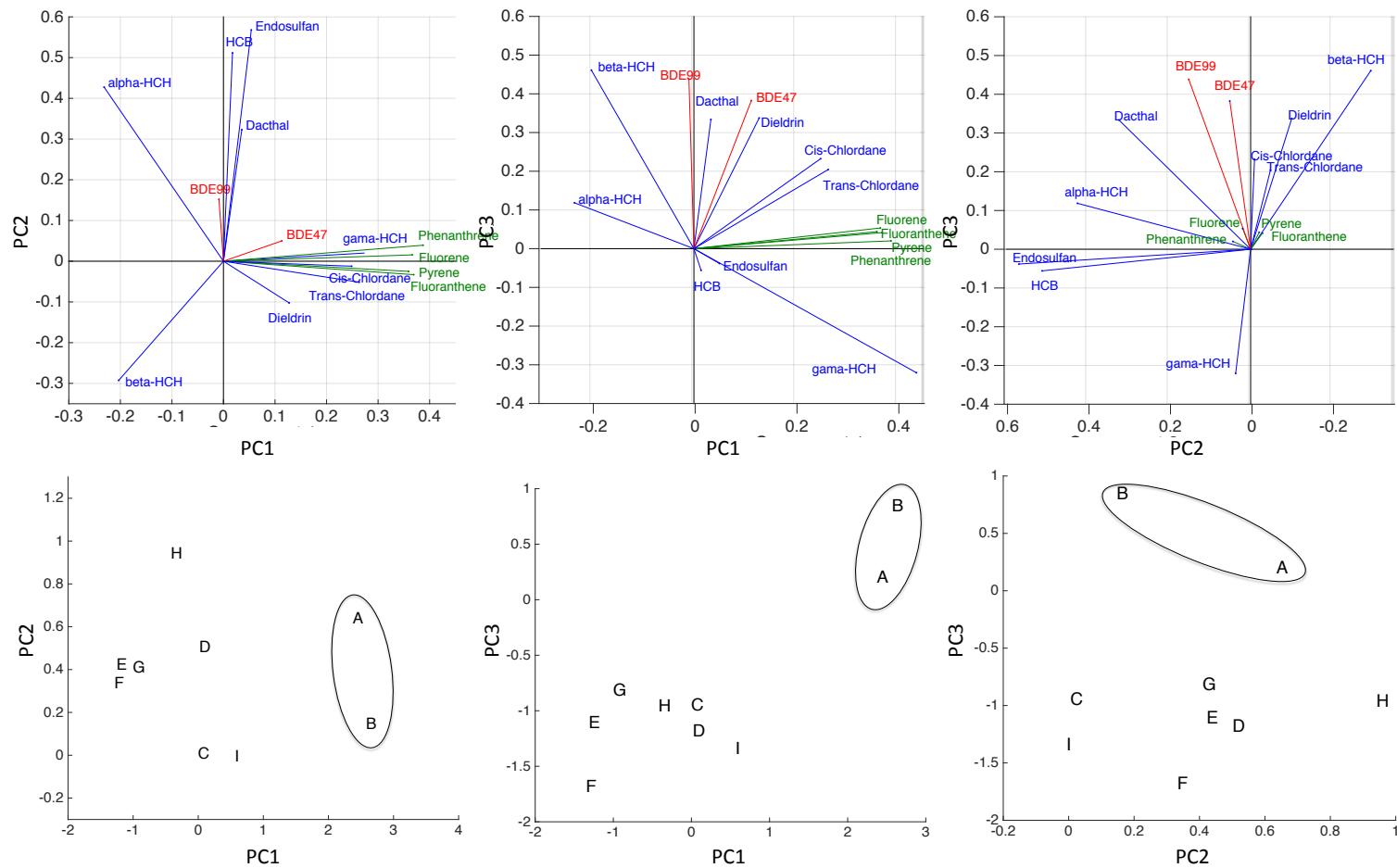


Figure S6. Principal component analysis (upper panels: loading plots; lower panels: score plot) on the composition profile SVOCs detected in all sampling sites. PC1-3 explain 56%, 21%, and 10% of the data variance.