

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/8904656>

Passive Air Sampling of PCBs, PBDEs, and Organochlorine Pesticides Across Europe

ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · FEBRUARY 2004

Impact Factor: 5.33 · DOI: 10.1021/es034705n · Source: PubMed

CITATIONS

383

READS

251

5 AUTHORS, INCLUDING:



Foday Jaward

University of South Florida

28 PUBLICATIONS 1,473 CITATIONS

SEE PROFILE



Tom Harner

Environment Canada

203 PUBLICATIONS 11,373 CITATIONS

SEE PROFILE



Andrew James Sweetman

Lancaster University

76 PUBLICATIONS 4,216 CITATIONS

SEE PROFILE



Kevin C Jones

Lancaster University

668 PUBLICATIONS 29,325 CITATIONS

SEE PROFILE

Passive Air Sampling of PCBs, PBDEs, and Organochlorine Pesticides Across Europe

FODAY M. JAWARD,[†] NICK J. FARRAR,[†]
TOM HARNER,[‡]
ANDREW J. SWEETMAN,[†] AND
KEVIN C. JONES^{*,†}

Department of Environmental Science, Institute of Environmental and Natural Sciences, Lancaster University, Lancaster, LA1 4YQ, UK, and Meteorological Service of Canada, Environment Canada, 4905 Dufferin Street, Toronto, Ontario, Canada, M3H 5T4

This study presents concurrently sampled ambient air data for a range of persistent organic pollutants at the continental scale. This was achieved using a passive air sampling system, deploying polyurethane foam disks, which was prepared in one laboratory, sealed to prevent contamination, sent out by courier to volunteers participating in different countries, exposed for 6 weeks, collected, resealed, and returned to the laboratory for analysis. Europe was the study area—a region with a history of extensive POPs usage and emission and with marked national differences in population density, the degree of urbanization and industrial/agricultural development. Samplers were deployed at remote/rural/urban locations in 22 countries and analyzed for PCBs, a range of organochlorine pesticides (HCB, α -HCH, γ -HCH, ppDDT, ppDDE), and PBDEs. Calculated air concentrations were in line with those obtained by conventional active air sampling techniques. The geographical pattern of all compounds reflected suspected regional emission patterns and highlighted localized hotspots. PCB and PBDE levels varied by over 2 orders of magnitude; the highest values were detected in areas of high usage and were linked to urbanized areas. HCB was relatively uniformly distributed, reflecting its persistence and high degree of mixing in air. Higher γ -HCH, ppDDT, and ppDDE levels generally occurred in South and East Europe.

Introduction

Persistent organic pollutants (POPs) are stable in the environment, undergo long-range atmospheric transport (LRAT), and can bioaccumulate through food chains. This has focused international regulation on reducing emissions to air (1, 2) and risk assessment/modeling efforts on their ambient distribution (3). Research on POPs currently focuses on uncertainties over their ambient sources, atmospheric transport and fate, and air–surface exchange to improve understanding of the complex array of factors controlling air concentrations. These vary spatially and temporally and ultimately influence the global fate of POPs and their entry into food chains. Ideally, *simultaneous* measurements of air

concentrations in different locations are needed to assess the relative importance of sources, atmospheric processes, and the LRAT potential of POPs and to validate models. Such spatial mapping studies could be on a range of scales, from around potential point sources, across cities, or even nationally, regionally, and globally (4–9). However, such surveys at multiple sites are not feasible with conventional high-volume (active) air samplers, which are expensive and require power. Several interesting studies have therefore made use of ‘environmental media’, such as leaves and pine needles (4, 8, 10, 11), tree bark (12, 13), and butter (5), to map the spatial distribution of POPs on the assumption that their POPs concentrations broadly reflect ambient levels. However, there are often issues of sample comparability, exposure time, and potential confounding factors with such media, which can produce uncertainties in data interpretation.

There are therefore considerable incentives to develop passive air sampling techniques (14–17). These should be simple to use, cheap, versatile, and capable of being deployed in many locations concurrently. Passive samplers can be designed and calibrated to allow reliable estimates of air concentrations to be made or to allow semiquantitative comparisons of the levels and patterns of POPs. Several designs are possible and indeed desirable. For example, it would be useful to have samplers to integrate ambient concentrations over time scales as short as hours/days or as long as weeks/months/years. The shorter time scales facilitate studies of contaminant dispersal, fluxes, and transport processes and can provide data for dispersion/transport modeling. Longer time scales would allow source/sink regions to be identified and underlying trends in ambient levels to be investigated.

A range of different passive sampling devices has been utilized in the past few years. To date, most work on passive samplers has focused on integrating concentrations over weeks/months, using samplers with a high ‘capacity’ to retain POPs, such as semipermeable membrane devices (SPMDs) (14, 18–20), polyurethane foam (PUF) disks (15, 16), and XAD resins (21–23). These operate as ‘kinetic samplers’, where it is necessary to know the sampling/uptake rate, rather than as equilibrium samplers (24). PUF disks are particularly attractive samplers because they are cheap, easy to handle, and can be used to sample over periods of several weeks. PUF is the sampling medium routinely deployed in conventional (active) high-volume air samplers, and so there is also information already available about how POPs partition to it, its capacity, etc. (25). PUF disks of 14 cm diameter and 1.2 cm thickness have been tested as passive samplers previously; they sample POPs at a rate of a few cubic meters of air/day (16). With appropriate instrumental detection limits and low blanks, this allows detection of many classes of POPs, following exposure periods of weeks in ambient air. The sampling period used in this study was 6 weeks, so the PUF disk was still operating in the ‘kinetic’ phase (16), where uptake of gas-phase compounds occurs at the same rate for the range of target compounds and is practically independent of temperature.

In previous studies, we demonstrated the utility of passive samplers at the local scale (16, 19) and to conduct urban–rural (15) and latitudinal (6, 7) transects. However, in this study we wanted to demonstrate the feasibility of obtaining ambient data on a continental scale, thereby helping to shed light on large-scale source/sink/transport issues for these compounds. There are major differences between European countries in their production, usage, emission, and regulatory controls on POPs. It was hoped that this would provide an

* Corresponding author phone: +44 1524 593-972; fax: +44 1524 593-972; e-mail: k.c.jones@lancaster.ac.uk.

[†] Institute of Environmental and Natural Sciences.

[‡] Meteorological Service of Canada, Environment Canada.

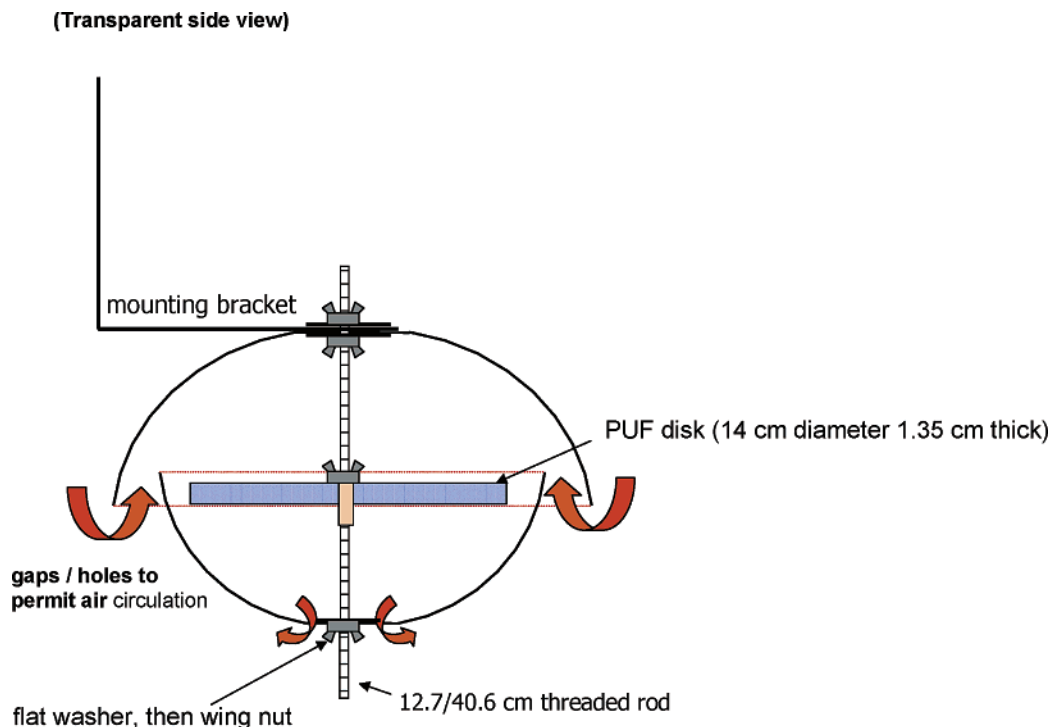


FIGURE 1. Schematic representation of the PUF disk sampling device.

interesting test area with which to demonstrate the feasibility of the large-scale deployment of passive sampling techniques. For the study to be most effective, it is clearly necessary to synchronize the start and finish dates of sample deployment. We therefore developed a sampling system that could be prepared in one laboratory, sealed to prevent contamination, sent out by courier to volunteers participating in different countries, exposed, collected, re-sealed, and returned to the laboratory to be analyzed there together with the same methods. This obviously provides scope for a relatively cheap but large-scale deployment exercise. An additional objective was to obtain ambient data in a form that could subsequently be used to test a European-scale multimedia model (26–28). The model utilizes information on air mass flows between different regions of Europe and can integrate air concentration data integrated over time scales of the order of weeks.

One of the benefits of such a study is in being able to make comparisons between compound classes which may have different properties or between compound classes which are relatively well-known/understood and those which are not. Data are therefore presented for polychlorinated biphenyls (PCBs), selected organochlorine (OC) pesticides, and polybrominated diphenyl ethers (PBDEs) obtained from the same sample deployment. These are all chemicals subject to LRAT, which have been measured in the atmosphere of remote regions, far from source areas (29–34). PCBs and OC pesticides have been subject to international regulations (2), while the patterns of production and use of PBDEs are changing rapidly; they have been little used in some countries, widely used in others, and recently restricted in others (35–37). They are being considered as ‘candidate POPs’ under the international protocol (1). Production, usage, and emission information (of variable quality) is available for these POPs in European and national inventories (e.g., refs 38–40).

PCBs, OC pesticides, and PBDEs enter the environment by different routes. PCBs are associated with industrialized countries and urban source areas (38, 39). Current atmospheric levels of PCBs in the environment are due to either primary anthropogenic emissions (e.g., intentional production and disposal or accidental releases of products or

materials containing PCBs), volatilization from environmental reservoirs (e.g., sea, soil), or incidental/unwanted formation of some congeners (e.g., in combustion processes) (38). OC pesticides are released into the atmosphere by spray drift, postapplication volatilization, and wind erosion of soil. These emissions are influenced by numerous physical and chemical factors (41–43). A substantial portion of hexachlorobenzene (HCB) measured in the atmosphere is thought to come from volatilization of ‘old’ (agricultural) HCB applied to soils in the past along with combustion and other poorly quantified sources (41). PBDEs have been extensively used in Europe and North America as flame retardants in various products, such as furnishing foam, plastics, textiles, wire and cable insulation, electrical and electronic connectors, etc. They reduce the risk of fire by interfering with the combustion of the polymeric materials (44–46). They presumably enter the environment by volatilization from these products (35).

This study reports the first attempt to monitor the distribution of PCBs, PBDEs, and OC pesticides in the European atmosphere using a passive sampler network.

Materials and Methods

Air Sampling, Extraction, and Analysis. The samplers have been described previously (16); they were deployed in sheltered chambers as shown in Figure 1. A precleaned and weighed PUF disk (14 cm diameter \times 1.35 cm thick; density 0.0213 g cm^{-3}) was suspended in the center of the two dishes between washers using solvent-rinsed tweezers. Samplers were then transferred to the sampling locations in airtight containers to avoid contamination during transit. Those deployed outside the United Kingdom were sent by courier. A total of 71 samplers were successfully deployed over a 6 week period (from June 15 to July 30, 2002) across 22 countries (see Figure 2). Local volunteers were given guidance on choice of deployment location; 25 were in urban locations and 46 in rural/remote locations as defined by the local volunteers. This definition is inevitably somewhat subjective. However, broad differences (e.g., between major cities/towns and rural areas) are clear. At the end of the deployment period, the samplers were retrieved by the volunteers, re-sealed in their

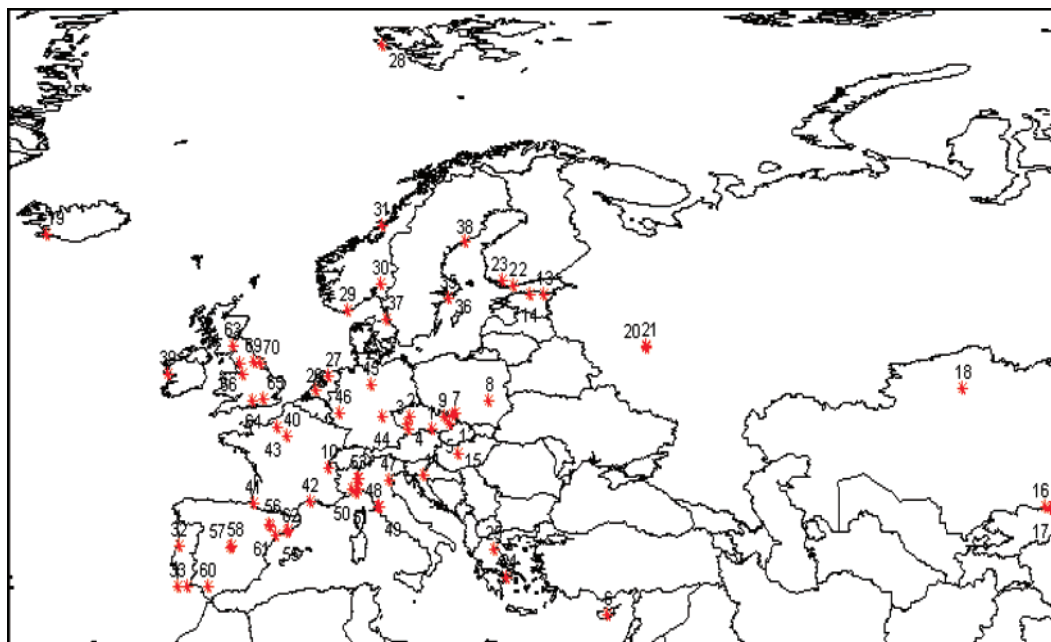


FIGURE 2. Map showing sampling sites.

original transport containers, and returned by courier to Lancaster University. On receipt in Lancaster, the disks were removed and stored in sealed, solvent-cleaned brown glass jars at -20°C until extraction.

The samplers were spiked with a range of $^{13}\text{C}_{12}$ -labeled PCB congeners ($^{13}\text{C}_{12}$ PCB 28, 52, 101, 138, 153, 180, 209) and three PCCD/F congeners ($^{13}\text{C}_{12}$ 1,2,3,4,6,7,8-HpCDF, 1,2,7,8-TCDF, and 1,3,6,8-TCDD) to monitor the extraction and cleanup procedures. They were extracted for 18 h with DCM in a Buchi extraction unit. The extract was rotary evaporated and transferred with hexane to a 15 mL amber vial. This was blown down under a gentle stream of nitrogen to about 0.5 mL and cleaned on a 9 mm i.d. chromatography column with 1 g of alumina (BDH neutral Alumina), 2 g of silica gel (Merck Silica 60), and 1 cm of baked sodium sulfate (all baked at 450°C overnight) and then passed through gel permeation chromatography (GPC) using 6 g of Biobeads SX 3. $^{13}\text{C}_{12}$ PCB 30 and two labeled PCB congeners, $^{13}\text{C}_{12}$ PCB 141 and $^{13}\text{C}_{12}$ PCB 208, were added to the sample prior to injection as internal standards. The samples were reduced to a final volume of 25 μL .

The samples were analyzed for PCBs and OC pesticides (except HCHs) by GC-MS on a Fisons MD800 operated in electron ionization mode using selected ion monitoring (18, 47). PBDEs and HCHs were analyzed separately with a Thermo Trace GC-MS operated in negative chemical ionization source in selected ion monitoring mode using ammonia as the reagent gas. GC temperature program and monitored ions are given elsewhere (44). A total of 29 PCB congeners (tri-PCB 18, 22, 28, 31; tetra-PCB 41/64, 44, 49, 52, 60/56, 70, 74; penta-PCB 87, 90/101, 95, 99, 110, 118, 123; hexa-PCB 138, 141, 149, 151, 153/132, 158; hepta-PCB 170, 174, 180, 183, 187), eight PBDE congeners (28, 47, 49, 75, 99, 100, 153, 154), and five OC pesticides (α -HCH, γ -HCH, HCB, ppDDE, ppDDT) regularly detected in samples were quantified using an internal standard method.

Quality Control/Quality Assurance (QA/QC). All analytical procedures were monitored using strict quality assurance and control measures. Laboratory and field blanks consisted of pre-extracted PUF disks extracted and analyzed in the same way as samples. Three field blanks sent to local volunteers in Germany, Spain, and the United Kingdom and six laboratory blanks were used. There was no difference between concentrations of analytes in the laboratory and

field blanks, indicating contamination was minimal during transport, storage, and analysis. Practical detection limits were 0.03–0.64 ng/sample for PCBs (depending on congener), 0.06–1.5 ng/sample for PBDEs, and 0.05–1.7 ng/sample for pesticides for the 6-week deployment period. Recoveries were 60–85% for PCBs and OC pesticides and 75–110% for PBDEs. Reported values are not recovery corrected. Method recoveries were determined by spiking six PUF disks with a working standard containing all analyzed PCB and PBDE congeners and pesticides. These PUF disks were extracted and cleaned in the same way as samples. Recoveries were found to be between 80% and 115%. Instrument efficiencies were monitored using quality control standards after every six samples run on the instrument. Peaks were only integrated where the signal-to-noise ratio was ≥ 3 ; otherwise, they were considered not detected. Mean recoveries of surrogates per sample were found to be $>75\%$ for all compounds.

Results and Discussion

Introductory Remarks. Table 1 presents a summary of the data arising from the study. Data on the detection limits (DL) and measured range in samples are given as nanograms of compound/sample.

Also shown is the percentage of samples above the detection limit ($\%>\text{DL}$), the ratio of the highest/lowest measured values (H/L ratio) calculated for those compounds that were routinely above the detection limits, and the estimated range of air concentrations (pg/m^3) (see below). Further details of sampling sites and compounds detected in individual samples are available in the Supporting Information (Table S1).

A number of compounds were detected in all the samples, namely, PCBs, γ -HCH, HCB, and ppDDT. The PBDEs were detected in about one-half of the samples. A longer exposure time would have ensured that a greater air volume was sampled and raised the frequency of their detection.

Observations on Comparisons between Compound Distributions. The variation in persistent contaminant concentrations in the atmosphere yields information which can be related to aspects of their sources-sinks and persistence (48). For example, the concentration of chlorofluorocarbons (CFCs) in the atmosphere is virtually the same around the world (49). Because of their high persistence and

TABLE 1. Summary Data for the Passive Air Sampling Program^a

compd.	DL	%>DL	measd range	H/L ratio ^b	air conc ^c
PCB-28	0.64	58	0.67–38		<5–230
PCB-52	0.03	100	0.20–36		1.6–210
PCB-90/101	0.03	100	0.35–21		2.8–120
PCB-118	0.03	100	0.12–15		0.9–90
PCB-138	0.03	100	0.19–15		1.5–90
PCB-153/132	0.03	100	0.24–18		1.9–110
PCB-180	0.03	94	0.03–4.1		<0.25–20
Σ ₂₉ PCB			2.5–280	>100	20–1700
α-HCH	1.72	57	1.7–17		<14–100
γ-HCH	0.13	100	1.1–65	60	9–390
HCB	0.13	99	1.4–8.9	6	11–50
pp-DDE	0.05	87	0.05–4.2		<0.4–25
pp-DDT	0.13	100	0.08–32	400	0.6–190
PBDE-28	0.06	82	0.06–4.5		<0.5–30
PBDE-47	0.95	55	0.97–13		<8–80
PBDE-49	0.06	30	0.07–2.0		<0.5–12
PBDE-75	0.06	54	0.07–0.58		<0.5–3
PBDE-99	1.47	45	1.6–21		<10–120
PBDE-100	0.29	41	0.31–3.5		<2–20
PBDE-153	0.09	55	0.09–2.4		<0.7–15
PBDE-154	0.10	44	0.10–1.5		<0.8–10
Σ ₈ PBDE			0.06–43	>700	0.5–250

^a Data on the detection limits (DL) and measured range in samples is given as ng/sample. Also shown is the ratio of the highest/lowest measured samples (H/L ratio), the percentage of samples above the detection limit (%>DL), and the estimated range of air concentrations (pg/m³). ^bThis ratio has only been calculated for compounds where ~100% of samples gave detectable levels. ^c Derived as described in the text. < values utilize the %<DL data.

volatility, they have become extremely well mixed in the air. Other chemicals may show marked source-sink gradients, resulting in substantial differences in air concentrations between locations. Differences between locations also shed light on the relative transport potential of compounds. The dataset obtained here demonstrates contrasting behavior for different POPs. For example, the Σ₂₉PCBs and Σ₈PBDEs show differences of over 2 orders of magnitude between the highest and lowest locations. The highest values are in urban centers of high past/present use, while the lowest values are from remote parts of Europe. This is powerful evidence that there are continuing primary emissions of these compound classes,

presumably mainly from past/ongoing use in buildings (6). In contrast, the distribution of HCB through the European atmosphere is very consistent, only varying by a factor of ~6 between the samples (see Table 1). HCB is much more volatile than PCBs and PBDEs and very stable in the atmosphere (50). As a result, it is predicted to have an atmospheric characteristic travel distance (CTD) of ~100 000 km (50), about 2 orders of magnitude greater than that of PCBs (50) and PBDEs (37).

Comparing Derived Air Concentrations with Measured Concentrations. When the PUF disks are deployed in the sampling chambers (Figure 1), they give typical sampling rates of ca. 3–4 m³ air per day (16). Hence, a 6-week deployment 'samples' ca. 130–170 m³. The ambient concentrations (pg/m³) represented by the measured ng/sampler values were therefore derived and are shown in Table 1. In summary, this indicates that European Σ₂₉PCB concentrations broadly lie in the range of tens to a few thousand pg/m³, perhaps typically being in the low hundreds of pg/m³. This is exactly in line with data obtained with conventional high-volume air samplers. Some of the United Kingdom's air monitoring stations where PCB data are obtained were used to deploy samplers for this study. The data were consistent with expectations. For example, inner city sample sites, such as London and Manchester, are typically 1000–2000 pg Σ₂₉PCB/m³, while those at semirural United Kingdom sites are a few hundred pg/m³ (51). HCB (10s pg/m³) and HCH (tens to hundreds of pg/m³) values of the survey are also very consistent with measured results from other studies (43, 52, 53). On the basis of work by Bailey (41, 54), average ambient HCB concentrations in the northern hemisphere atmosphere of ca. 50 pg/m³ are expected, for example. Table 1 suggests Σ₈PBDE values in the range ~0.1–10s pg/m³. PBDEs have been reported for the remote west coast of Ireland at ca. 0.1–5 pg/m³ and in rural/semirural England up to tens of pg/m³ (55).

In summary, the data presented so far give confidence that the samplers are capable of reflecting the spatial variations and absolute values of these POPs in the European atmosphere. It is therefore appropriate to examine the spatial patterns in more detail.

General Comments on Spatial Trends. A wide range of sample sites was utilized. Remote/background locations included sites at Mace Head (western Ireland), Iceland, and

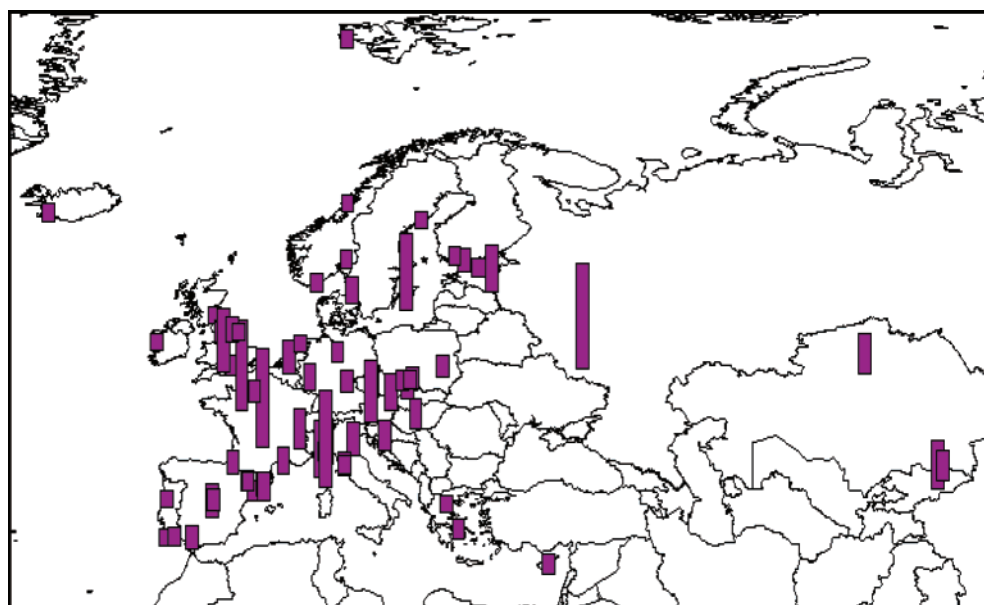


FIGURE 3. Spatial distribution of PCB (ng/sample—June 15 to July 30, 2002). Note: the bars center on the sample site in all the figures. Key: Largest bar = 280 ng/sample (site 21).

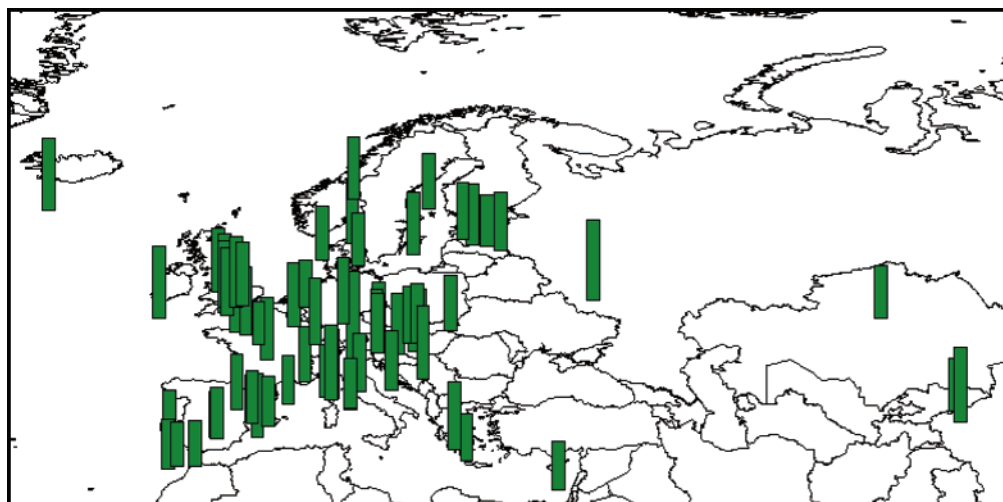


FIGURE 4. Spatial distribution of HCB (ng/sample—June 15 to July 30, 2002). Note: the bars center on the sample site in all the figures. Key: Largest bar = 8.9 ng/sample (site 44).

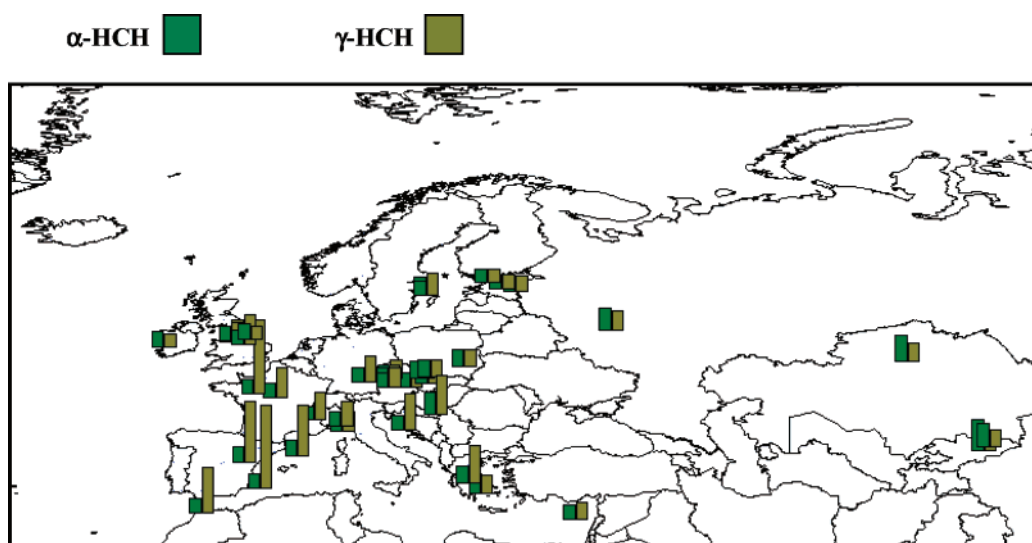


FIGURE 5. Spatial distribution of α - and γ -HCH (ng/sample—June 15 to July 30, 2002). Note: the bars center on the sample site in all the figures. Key: Largest bar α -HCH = 17 ng/sample (site 16). Largest bar γ -HCH = 65 ng/sample (site 61).

Svalbard (Norway) (sites 39, 19, and 28, respectively). Additionally, low concentrations were often detected in samples from the southwest of the European region, Portugal, and southwest Spain (sites 32, 33, and 60). These areas experience relatively clean air coming off the Atlantic Ocean. In contrast, a number of samplers were deployed in major urban centers, notably London, Manchester, Paris, Madrid, Barcelona, Stockholm, Milan, and Moscow (site numbers 65, 68, 40, 57, 62, 36, 54, and 21, respectively).

PCBs. The spatial variation in PCBs is shown in Figure 3, where the length of the bars is proportional to the ng PCB/sampler. The full dataset is Table S1. As expected, the predominant gradient was between urban–rural–remote locations. The lowest levels were measured in rural/remote sites, such as in Ireland, Norway, Cyprus, Greece, Portugal, and Sweden. The highest levels occurred at urban sites in Russia, France, Italy, Sweden, the United Kingdom, and Eastern Europe (Croatia, Hungary, Estonia). Europe is the area of the world where PCB usage has been most concentrated (38, 39). It is interesting that Eastern European levels are among the highest. Manufacture and use is believed to have continued in Eastern Europe after bans were imposed in some western European countries (38, 39). As noted earlier, the urban–rural gradient in PCB concentrations extends over at least 2 orders of magnitude, emphasizing that diffusive

atmospheric emissions from urban locations continue to contaminate the regional atmosphere, over 30 years after international restrictions on usage were first introduced.

HCB. Bailey (41) assembled information from a variety of sources to give a picture of global HCB emissions in the mid-1990s. He suggested that no single overwhelming source dominated, but rather emissions resulted from (largely past) pesticide applications, manufacturing, and combustion. Pacyna et al. (40) focused on European emissions, concluding that emissions had reduced from a total of ~ 200 t/year in 1970 to ~ 40 t/year in 1993. They estimated that by the mid-1990s, the greatest contributors to the European inventory were Russia, Spain, the Ukraine, France, and Germany.

As noted earlier, HCB levels throughout the survey were very consistent (Table 1), reflective of the atmospheric persistence of HCB. Ambient levels are declining (40) as primary sources have reduced and may be being maintained by emissions from its former use as a fungicide. As the sources of HCB are diffuse and its volatility is relatively high, it is perhaps not surprising that the ambient levels revealed by this study are very consistent (see Figure 4). Slightly elevated concentrations at individual sites are probably due to local sources. For example, the highest value was obtained at a location in rural Germany (site 44) where local agricultural usage of HCB in glasshouses has been high.

ppDDE



ppDDT

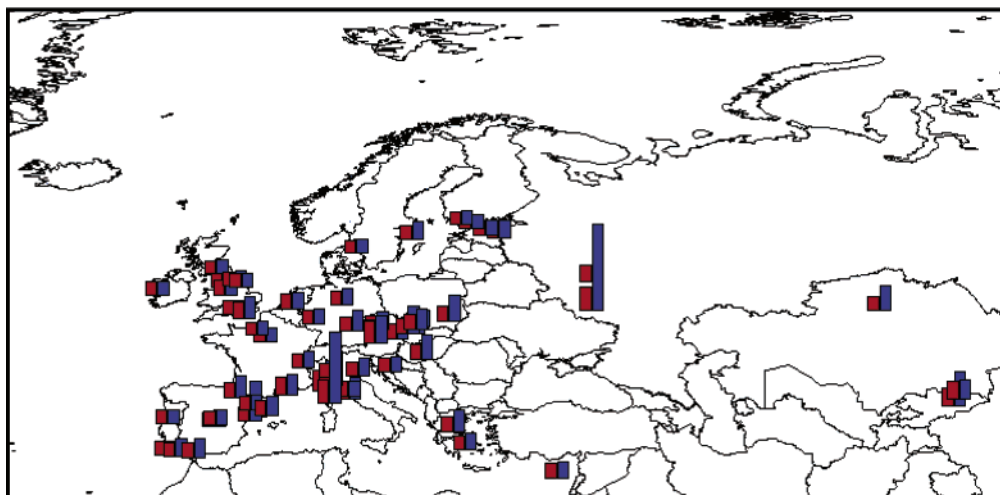


FIGURE 6. Spatial distribution of ppDDE and ppDDT (ng/sample—June 15 to July 30, 2002). Note: the bars center on the sample site in all the figures. Key: Largest bar ppDDE = 4.2 ng/sample (site 21). Largest bar ppDDT = 32 ng/sample (site 21).

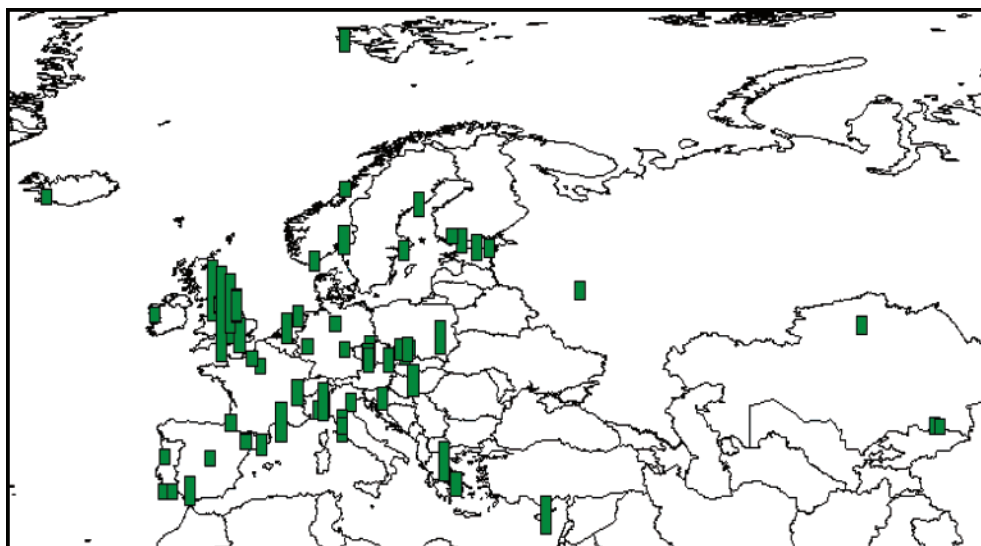


FIGURE 7. Spatial distribution of PBDE (ng/sample—June 15 to July 30, 2002). Note: the bars center on the sample site in all the figures. Key: Largest bar = 43 ng/sample (site 68).

Other studies in Europe, using latitudinally deployed SPMDs as long-term air samplers exposed for 2 years, found higher HCB concentrations in colder, northerly latitudes (56, 57). In other words, HCB can undergo 'cold condensation' onto solid phases from the atmospheric gas phase. In contrast, Hellstrom (58) studied pine needles sampled across Europe in the late 1980s. There was no evidence of increasing HCB concentrations northwards and evidence that the needles had not reached equilibrium with the air prior to sampling (59). It should be noted that there is no indication from Figure 4 of a latitudinal increase in HCB on the samplers in this study. These observations may support the contention that the samplers were still operating in the (kinetic) uptake phase (17), which is not influenced by temperature, and had not attained air-sampler equilibrium after 6 weeks of exposure. Theoretical predictions, from knowledge of compound K_{OA} suggest that HCB would be beginning to approach equilibrium after this exposure time (16). Alternatively, the lack of condensation may be a function of the season of sampling: deployment was in June/July, when temperatures across Europe may be more uniform than in winter.

HCHs. Figure 5 presents the spatial distribution data for α -HCH and γ -HCH. A greater proportion of nondetect values occurred for the α isomer (see Table 1), and measured concentrations ranged between 1.7 and 17 ng/sample. The distribution of α -HCH was reasonably homogeneous, although some of the higher values were observed in samples from eastern locations (samples sites 16 and 17 in Kazakhstan; 8, 9, and 12 in Poland; 15 in Hungary; 13 in Estonia; and 20 and 21 in Russia). Most nondetect values were in the northerly latitudes. The use of the technical mixture reduced substantially in much of Europe during the 1970s (53). Li et al. (60) assumed there was no usage worldwide of technical HCH in 2000. The ongoing distribution of α -HCH shown by Figure 5 probably reflects diffuse emissions from past usage in Europe (61, 62) and limited ongoing usage in some parts of the continent, for example, Russia. Values of γ -HCH show greater variability (see Figure 5). Highest concentrations occurred in the south and east of Europe, notably Spain, parts of France, Italy, and the Balkans region. Some ongoing usage of lindane continues on vegetable and tomato crops in these countries (11, 53, 63). In Hellstrom's (58) study with

pine needles sampled in the late 1980s, the highest γ -HCH concentrations were also observed in the southernmost part of the transect.

ppDDT and ppDDE. The spatial distribution of ppDDT and its stable metabolic breakdown product, ppDDE, are shown in Figure 6. Most European usage of ppDDT occurred in Eastern Europe, Spain, Italy, and France (64). Various countries introduced bans and restrictions on ppDDT usage through the 1970–80s (40).

ppDDT was routinely detected in the samples and showed a very wide range in concentrations—ca. 400-fold—between the highest and lowest values (see Table 1). This was influenced by a couple of very high ‘outlier’ samples. The highest levels were recorded in Russia and Italy. In both cases, low ppDDE/ppDDT ratios were measured, suggestive of a fresh ppDDT signal. The elevated Russian sample could be due to limited local usage of old stocks of ppDDT, despite the restrictions on its use (52). The high Italian sample was obtained in the north, near Milan. ppDDT has been produced in a factory in that area as a precursor of dicofol (64). It exerts a strong signal on ambient residues in the surrounding area, which is likely reflected in this sample (site number 54). As expected, the lowest values were in the north and west of Europe (Figure 6).

PBDEs. Figure 7 presents the spatial distribution data for the Σ_8 PBDEs. PBDE production and use has been a relatively recent phenomenon, with the resultant environmental emissions peaking much later than for the organochlorine substances discussed earlier (35–37). It is therefore not surprising that there should be a large ‘gradient’ between samples collected in source regions and remote regions; as noted in Table 1, the ratio of highest/lowest sample is ~700. An overriding feature of Figure 7 is the focus of the most elevated samples in the United Kingdom. The United Kingdom has a history of PBDE production and has been a major user of PBDE-based flame retardants, owing to particularly stringent fire regulations (35–37, 55). The United Kingdom is clearly a regional source area for PBDEs to the European atmosphere. In contrast, levels reaching Europe from the west (i.e., over the Atlantic) are low (see Figure 7).

Other high values were detected in urban centers in mainland Europe—samples from Milan, Bilthoven (Netherlands), Geneva, Athens, and Seville, for example. Lower levels were detected in the samples from France and Germany. Nondetectable/very low values occurred in the remote/background sites, especially in Iceland, Ireland (Mace Head), Norway, and Sweden. Values in Eastern Europe were generally low. As expected from previous studies, PBDE-47 and -99 were the dominant contributors to the pattern, contributing ca. 75% to the Σ_8 PBDE. These are the dominant congeners in the Bromkal 70-5DE commercial product, where they constitute ~70–80% of the mixture (46, 65).

Compound Overview. In general, the geographical pattern of all the compounds studied reflected the suspected regional emission patterns. The samples also highlighted localized hotspots; great care therefore needs to be taken over the choice of site locations. The study demonstrates that it is possible to map local, regional, and global sources of POPs using passive air samplers. Reconnaissance studies of this nature can provide information on trends and identify sources regions. The trends of PCBs and PBDEs are linked to urbanized source areas. The levels of α -HCH and HCB were relatively uniform throughout Europe, while the levels of γ -HCH and the ppDDT and ppDDE were higher in southern and eastern locations. Predicted concentrations of compounds reported in this study are comparable to concentrations reported by other authors, indicating that quantitative data, suitable for modeling purposes, can be obtained.

Acknowledgments

We are grateful to the UK Department of the Environment, Food and Rural Affairs (DEFRA) Air Quality Division for financial support. We thank numerous colleagues and friends who helped in deploying the sampling devices: colleagues at Lancaster University, especially Dr. Gareth Thomas, Dr. Robert Lee, Dr. Rainer Lohmann, and Mrs. Victoria Burnett for their analytical support and meaningful consultations and Costas Prevedouros for assistance with data handling. Anonymous referees provided helpful comments. F.M.J. is grateful to the Commonwealth Commission for Ph.D. funding.

Supporting Information Available

Further details of sampling sites and compounds detected in individual samples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) UNECE Protocol on Persistent Organic Pollutants under the 1979 Convention on Long-Range Transboundary Air Pollution; United Nations Economic Commission for Europe: 1998 (ECE/EB.Air/60).
- (2) UNEP Preparation of an Internationally Legally Binding Instrument for Implementing International Action on Certain Persistent Organic Pollutants; United Nations Environment Programme: 1998; UNEP/POPs/Inc.1/6.
- (3) Klecka, G.; et al. *Evaluation of persistence and long-range transport of organic chemicals in the environment*; SETAC Special Publication Series; SETAC: Pensacola, FL, 2000.
- (4) Calamari, D.; Tremolada, P.; Di Guardo, A.; Vighi, M. *Environ. Sci. Technol.* **1994**, *28*, 429–434.
- (5) Kalantzi, O. I.; Alcock, R. E.; Johnston, P. A.; Santillo, D.; Stringer, R. L.; Thomas, G. O.; Jones, K. C. *Environ. Sci. Technol.* **2001**, *35*, 1013–1018.
- (6) Meijer, S. N.; Ockenden, W. A.; Steinnes, E.; Corrigan, B. P.; Jones, K. C. *Environ. Sci. Technol.* **2003**, *37*, 454–461.
- (7) Ockenden, W. A.; Sweetman, A.; Prest, H. F.; Steinnes, E.; Jones, K. C. *Environ. Sci. Technol.* **1998**, *32*, 2795–2803.
- (8) Tremolada, P.; Burnett, V.; Calamari, D.; Jones, K. C. *Environ. Sci. Technol.* **1996**, *30*, 3570–3577.
- (9) Jones, K. C.; Barber, J. L. Sample matrices, site selection and sampling techniques, Proceedings of the UNEP Workshop to Develop a Global POPs Monitoring Programme to Support the Effectiveness Evaluation of the Stockholm Convention; UNEP: Geneva, 2003; pp 185–199.
- (10) Tremolada, P.; Burnett, V.; Calamari, D.; Jones, K. C. *Chemosphere* **1996**, *32*, 2189–2203.
- (11) Villa, S.; Finizio, A.; Diaz, R. D.; Vighi, M. *Water Air Soil Pollut.* **2003**, *146*, 335–349.
- (12) Simonich, S. L.; Hites, R. A. *Science* **1995**, *269*, 1851–1854.
- (13) Simonich, S. L.; Hites, R. A. *Environ. Sci. Technol.* **1997**, *31*, 999–1003.
- (14) Ockenden, W. A.; Jaward, F. M.; Jones, K. C. *Sci. World* **2001**, *1*, 557–575.
- (15) Harner, T.; Ikononou, M.; Shoeib, M.; Stern, G.; Diamond, M. *Organohalogen Compd.* **2002**, *57*, 33–36.
- (16) Shoeib, M.; Harner, T. *Environ. Sci. Technol.* **2002**, *36*, 4142–4151.
- (17) Harner, T.; Farrar, N. J.; Shoeib, M.; Jones, K. C.; Gobas, F. A. P. C. *Environ. Sci. Technol.* **2003**, *37*, 2486–2493.
- (18) Ockenden, W. A.; Prest, H. F.; Thomas, G. O.; Sweetman, A.; Jones, K. C. *Environ. Sci. Technol.* **1998**, *32*, 1538–1543.
- (19) Lohmann, R.; Corrigan, B.; Howsam, M.; Jones, K. C.; Ockenden, W. *Environ. Sci. Technol.* **2001**, *35*, 2576–2582.
- (20) Wennrich, L.; Popp, P.; Hafner, C. J. *Environ. Monit.* **2002**, *4*, 371–376.
- (21) Billings, W. N.; Bidleman, T. F. *Environ. Sci. Technol.* **1980**, *14*, 679–683.
- (22) Billings, W. N.; Bidleman, T. F. *Atmos. Environ.* **1983**, *17*, 383–391.
- (23) Wania, F.; Shen, L.; Lei, Y. D.; Teixeira, C.; Muir, D. C. G. *Environ. Sci. Technol.* **2003**, *37*, 1352–1359.
- (24) Mayer, P.; Tolls, J.; Hermens, J. L. M.; Mackay, D. *Environ. Sci. Technol.* **2003**, 3A–9A.
- (25) Patton, G. W.; Walla, M. D.; Bidleman, T. F.; Barrie, L. A. J. *Geophys. Res.—Atmos.* **1991**, *96*, 10867–10877.

- (26) MacLeod, M.; Woodfine, D. G.; Mackay, D.; McKone, T.; Bennet, D.; Maddalena, R. *Environ. Sci. Pollut. Res.* **2001**, *8*, 156–163.
- (27) Woodfine, D. G.; MacLeod, M.; Mackay, D.; Brimacombe, J. R. *Environ. Sci. Pollut. Res.* **2001**, *8*, 164–172.
- (28) Prevedouros, K.; MacLeod, M.; Jones, K. C.; Sweetman, A. J. *Environ. Pollut.* 2004, in press.
- (29) Fuoco, R.; Colombini, M. P.; Ceccarini, A.; Abete, C. *Microchem. J.* **1996**, *54*, 384–390.
- (30) Bidleman, T. F.; Jantunen, L. M.; Falconer, R. L.; Barrie, L. A. *Geophys. Res. Lett.* **1995**, *22*, 219–222.
- (31) Bidleman, T. F.; Walla, M. D.; Roura, R.; Carr, E.; Schmidt, S. *Mar. Pollut. Bull.* **1993**, *26*, 258–262.
- (32) Larsson, P.; Jarnmark, C.; Sodergren, A. *Mar. Pollut. Bull.* **1992**, *25*, 281–287.
- (33) ter Schure, A. F. H.; Larsson, P. *Atmos. Environ.* **2002**, *36*, 4015–4022.
- (34) Oehme, M.; Haugen, J.-E.; Kallenborn, R.; Schlabach, M. *Organohalogen Compd.* **1994**, *20*, 523–528.
- (35) Alcock, R. E.; Sweetman, A. J.; Prevedouros, K.; Jones, K. C. *Environ. Int.* **2003**, *29*, 691–698.
- (36) Alae, M.; Arias, P.; Sjodin, A.; Bergman, A. *Environ. Int.* **2003**, *29*, 683–689.
- (37) Gouin, T.; Harner, T. *Environ. Int.* **2003**, *29*, 717–724.
- (38) Breivik, K.; Sweetman, A.; Pacyna, J. M.; Jones, K. C. *Sci. Total Environ.* **2002**, *290*, 199–224.
- (39) Breivik, K.; Sweetman, A.; Pacyna, J. M.; Jones, K. C. *Sci. Total Environ.* **2002**, *290*, 181–198.
- (40) Pacyna, J. M.; Breivik, K.; Munch, J.; Fudala, J. *Atmos. Environ.* **2003**, *37*, S119–S131.
- (41) Bailey, R. E. *Chemosphere* **2001**, *43*, 167–182.
- (42) Bidleman, T. F. *Water Air Soil Pollut.* **1999**, *115*, 115–166.
- (43) Walker, K.; Vallero, D. A.; Lewis, R. G. *Environ. Sci. Technol.* **1999**, *33*, 4373–4378.
- (44) Gouin, T.; Thomas, G. O.; Cousins, I.; Barber, J.; Mackay, D.; Jones, K. C. *Environ. Sci. Technol.* **2002**, *36*, 1426–1434.
- (45) Rahman, F.; Langford, K. H.; Scrimshaw, M. D.; Lester, J. N. *Sci. Total Environ.* **2001**, *275*, 1–17.
- (46) Sjodin, A.; Jakobsson, E.; Kierkegaard, A.; Marsh, G.; Sellstrom, U. *J. Chromatogr., A* **1998**, *822*, 83–89.
- (47) Thomas, G. O.; Sweetman, A. J.; Parker, C. A.; Kreibich, H.; Jones, K. C. *Chemosphere* **1998**, *36*, 2447–2459.
- (48) Junge, C. E. *Tellus* **1974**, *26*, 477–488.
- (49) Stanley, L. J.; Hites, R. A. Chlorinated Organic Contaminants in the Atmosphere. In *Organic Contaminants in the Environment: Environmental Pathways and Effects*; Jones, K. C., Ed.; Elsevier Applied Science Publishers: London and New York, 1991; pp 1–338.
- (50) Beyer, A.; Mackay, D.; Matthies, M.; Wania, F.; Webster, E. *Environ. Sci. Technol.* **2000**, *34*, 699–703.
- (51) Halsall, C. J.; Lee, R. G. M.; Coleman, P. J.; Burnett, V.; Harding-Jones, P.; Jones, K. C. *Environ. Sci. Technol.* **1995**, *29*, 2368–2376.
- (52) Iwata, H.; Tanabe, S.; Ueda, K.; Tatsukawa, R. *Environ. Sci. Technol.* **1995**, *29*, 792–801.
- (53) Li, Y. F.; McMillan, A.; Scholtz, M. T. *Environ. Sci. Technol.* **1996**, *30*, 3525–3533.
- (54) Bailey, R. E. *Hexachlorobenzene Concentration Trends in the Great Lakes*, 2nd ed.; Report prepared for the HCB/BaP Working Group of the Great Lakes Binational Toxics Strategy; Environmental Chemistry Consultants: Midland, MI, 2001; pp 1–29.
- (55) Lee, R. G. M.; Thomas, G. O.; Jones, K. C. *Organohalogen Compd.* **2002**, *58*, 193–196.
- (56) Ockenden, W. A.; Breivik, K.; Meijer, S. N.; Steinnes, E.; Sweetman, A. J.; Jones, K. C. *Environ. Pollut.* **2003**, *121*, 75–80.
- (57) Meijer, S. N.; Ockenden, W. A.; Sweetman, A.; Breivik, K.; Grimalt, J. O.; Jones, K. C. *Environ. Sci. Technol.* **2003**, *37*, 667–672.
- (58) Hellstrom, A. Uptake of Airborne Organic Pollutants in Pine Needles: Geographical and Seasonal Variations. Ph.D. Thesis, Swedish University of Agricultural Sciences, Uppsala, Sweden, 2003.
- (59) Kylin, H.; Sjodin, A. *Environ. Sci. Technol.* **2003**, *37*, 2350–2355.
- (60) Li, Y. F.; Scholtz, M. T.; Van Heyst, B. J. *Environ. Sci. Technol.* **2003**, *37*, 3493–3498.
- (61) Breivik, K.; Pacyna, J. M.; Munch, J. *Sci. Total Environ.* **1999**, *239*, 151–163.
- (62) Breivik, K.; Wania, F. *Environ. Sci. Technol.* **2002**, *36*, 1024–1032.
- (63) Van Jaarsveld, J. A.; Van Pul, W. A. J.; Leeuw, F. A. A. M. D. *Atmos. Environ.* **1996**, *31*, 1011–1024.
- (64) Di Guardo, A.; Zaccara, S.; Cerabolini, B.; Acciarri, M.; Terzaghi, G.; Calamari, D. *Chemosphere* **2003**, *52*, 789–797.
- (65) Sundstrom, G.; Hutzinger, O. *Chemosphere* **1976**, *5*, 187–190.

Received for review July 3, 2003. Revised manuscript received September 17, 2003. Accepted October 7, 2003.

ES034705N