Spatial and temporal pattern of pesticides in the global atmosphere†

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As part of the Global Atmospheric Passive Sampling (GAPS) study, XAD-resin based passive samplers are being deployed for consecutive one-year periods at numerous sites on all seven continents to determine annually averaged concentrations of persistent organic pollutants. Concentrations of banned organochlorine pesticides as well as a number of current-use pesticides in samples from the first four years, roughly coinciding with 2005, 2006, 2007 and 2008, show distinct spatial and temporal patterns. Whereas organochlorine pesticides such as α- and γ-hexachlorocyclohexane, endosulfans, DDT and its metabolites, and chlordane-related compounds tend to be more prevalent in developing countries, especially in Asia, concentrations of current use pesticides such as trifluralin and chlorothalonil are often higher in Europe and North America. Based on 15 stations with four years of data, levels of hexachlorobenzene, hexachlorocyclohexanes and chlordanes decline in most world regions, which may reflect decreased usage in response to global restrictions. Levels of organochlorine pesticides in India, however, remain exceptionally high. Concentrations of α-endosulfan, chlorothalonil and trifluralin decrease in the European atmosphere during the sampling periods, indicating reduced usage. Consistently high α/γ-HCH ratios in air samples from high Northern latitudes confirm that re-volatilization from the Arctic Ocean is a significant source of α-HCH. The highest levels of α-HCH, however, occur in conjunction with high γ-HCH levels, suggesting that lindane use is now the major source of α-HCH to the global atmosphere. Although a wide variety of sampling site types aids in characterizing the entire global concentration variability of a pesticide, it also increases greatly the number of sites required for a robust regional differentiation.

Introduction

Global use of pesticides is estimated as approximately 11.2 billion kg annually, highlighting the immense amounts of toxic chemicals that are released into the global environment. In the past, organochlorine pesticides (OCPs) were used intensively around the world in agriculture and also to control vector-borne diseases. Because OCPs were found to persist in the environment and to bioaccumulate in food chains, many industrialized countries banned their use in the 1970s. Eventually, the Stockholm Convention on Persistent Organic Pollutants (POPs) led to world-wide bans and restrictions on many OCPs, initially aldrin, endrin, dieldrin, heptachlor, chlordane, mirex, toxaphene, DDT and hexachlorobenzene (HCB) and more recently on hexachlorocyclohexanes (HCHs). First detected in the atmosphere in the 1960s, the presence of OCPs in air today is a result of the volatilization from contaminated soil and water and of long range transport (LRT) from places where they are still being used, such as some developing countries. Detection in the atmosphere of remote regions where they have never been used shows that OCPs can travel hundreds of kilometres from source regions.

Pesticides less persistent than the OCPs are used in large quantities in many countries and are often referred to as current-use pesticides (CUPs). In particular, organophosphorus pesticides and carbamates are used in agriculture to control the emissions of POPs under the Stockholm Convention, this work provides valuable input for the efficient design of a global monitoring network: (1) statistically significant, inter-annual time trends in the atmospheric concentrations of POPs can be obtained from a small number of consecutive, year-long passive sampler deployments. (2) To allow for a meaningful comparison of trends in different regions, the types of sampling sites in those regions need to be similar. (3) If the number of sampling sites is to be kept small, the effectiveness of global restrictions is best observed through deployments in remote regions.

Environmental impact

As part of a pilot study to explore the feasibility of using passive air samplers to evaluate the effectiveness of global measures to control the emissions of POPs under the Stockholm Convention, this work provides valuable input for the efficient design of a global monitoring network: (1) statistically significant, inter-annual time trends in the atmospheric concentrations of POPs can be obtained from a small number of consecutive, year-long passive sampler deployments. (2) To allow for a meaningful comparison of trends in different regions, the types of sampling sites in those regions need to be similar. (3) If the number of sampling sites is to be kept small, the effectiveness of global restrictions is best observed through deployments in remote regions.

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Insecticides and triazine herbicides are being used throughout the world.\textsuperscript{16,17} Eighty and thirty different CUPs have been detected in European rain and air samples, respectively.\textsuperscript{18} CUPs have also been detected in air samples from North and Central America.\textsuperscript{16,19–21} CUPs are not only found in the atmosphere of agricultural areas, but also in polar and mountain regions,\textsuperscript{7,22–24} suggesting that at least some of them can undergo LRT. Empirical and theoretical reasonings also support that whereas CUPs such as metolachlor and chlorpyrifos have a limited mobility, other CUPs, such as \textit{z}-endosulfan and dacthal, are subject to LRT.\textsuperscript{25}

Measuring pesticides in the atmosphere at the global scale would allow for a better understanding of their fate and sources as well as their transport over large distances. The Global Atmospheric Passive Sampling (GAPS) study, initiated in December 2004, is a multi-year project with the objective to prove the feasibility of monitoring POPs in the global atmosphere with the help of passive air samplers (PAS).\textsuperscript{26,27} Compared to conventional active samplers, PAS are inexpensive, simple to use, easily shipped, and require no power supply, making them powerful tools for studying large spatial scales.\textsuperscript{28} Indeed, several studies have employed PAS for monitoring POPs at the continental and regional scale. For example, the atmospheric distributions of POPs across North America have been investigated using XAD resin based PAS (XAD-PAS),\textsuperscript{28,29} whereas similar studies in Europe and East Asia relied on polyurethane foam disk based PAS (PUF-PAS).\textsuperscript{30,31} In order to determine spatial and temporal trends in the global air concentrations of POPs, GAPS relies on both types of PAS: whereas PUF-PAS are deployed for consecutive three-month period, thus providing seasonally resolved information, XAD-PAS are deployed for one year and yield annually averaged concentrations. Both types of PAS are co-located, which allows for a direct comparison of the two techniques under different climatic conditions.\textsuperscript{32} GAPS currently includes more than 55 sites around the world and between 33 and 46 of them use annually deployed XAD-PAS. Results from the PUF–PAS within GAPS have been described earlier.\textsuperscript{26,27} Here we report results for pesticides in the XAD-PAS deployed during the first four years of GAPS. To the best of our knowledge this is the first study to look at the distribution of CUPs on the global scale. Four years of data also allow a preliminary analysis of the time trends of pesticide concentrations in the global atmosphere since the Stockholm Convention on POPs came into force.

**Materials and methods**

**Sampling sites**

XAD-based PAS were deployed at 35, 34, 46 and 33 sites during each of the first four sampling years, respectively, which correspond roughly with the calendar years 2005 to 2008. Not every site participated every year, but there are 15 stations that did. GAPS sites are located in agricultural, background, polar, rural and urban areas (Fig. 1). Geographical coordinates and sampling periods for each site are reported in Table S1.\textsuperscript{†} GAPS is a low-budget pilot program relying on volunteers for sampler set-up and retrieval and the international postal and courier system for sampler transport to and from the sites. Operator training and site audits are restricted to written standard operating procedures.
procedures and regular e-mail exchanges. In particular during the first few years, GAPS was an evolving network and sites were added and removed to improve regional representativeness and to ensure long-term sustainability. As such, the site network during this phase was unsystematic, spatial coverage across the globe was non-uniform, and the distribution of sampling site types was also uneven. For example, there are no urban sampling sites in South America, Africa and Australia. These limitations in the sampling design need to be kept in mind when interpreting the results.

Passive air samplers

The XAD-PAS is comprised of a stainless steel mesh cylinder, filled with XAD-2 resin and suspended in a steel can with an open bottom. Contaminants in the vapour phase are taken up in the resin through diffusion. The XAD-PAS operates in the linear uptake region, i.e. semi-volatile organic compounds do not reach equilibrium between the XAD-2 resin and the atmospheric gas phase over extended time periods of more than one year.

This makes it suitable for the derivation of annually averaged gas phase concentration for POPs and most CUPs. The PAS, with written and illustrated instructions, were sent to contact people who installed the PAS. After one year of sampling, the samples were retrieved and mailed or couriered back to Canada, where they were stored frozen until extraction by Soxhlet. Extracts were analyzed for α- and γ-HCH, HCB, cis-(CC) and trans-chlordane (TC), trans-nonachlor (TN), heptachlor (HEPT), heptachlor exo-epoxide (HEPX), aldrin, dieldrin, endrin, p,p′-DDT, p,p′-DDD, p,p′-DDE, o,p′-DDD, o,p′-DDE, α- and β-endosulfan (α-ES, β-ES), endosulfan sulfate (ESS), trifluralin (TF), chlorothalonil (CT), dacthal (DT), and pendimethalin (PM) using gas chromatography negative chemical ionization mass spectrometry. Details on the analytical methods and the quality control measures, including blanks and recoveries, are given in the ESI†.

Results and discussion

Pesticides in the global atmosphere

The concentrations of pesticides in the XAD-PAS from the first four years of the GAPS project are reported in units of nanograms of compound per PAS in Tables S2 and S3 †. XAD-PAS were not deployed in duplicates in this study, however, Shen et al. 28,29 Daly et al. 20,24 Hayward et al. 33 and Gouin et al. 31 deployed the same samplers in duplicates and observed good reproducibility for legacy OCPs and CUPs. The sequestered amounts can be converted to volumetric air concentrations by division with the product of the deployment period (generally 365 days) and the sampling rate determined previously for the XAD-PAS. 15,21 The focus here is on spatial and temporal trends that can be evaluated without that conversion, thereby avoiding the additional uncertainty that it introduces. The sampling period was generally close to one year, so that normalization to the deployment period was not deemed necessary. The data are summarized in box-and-whisker plots (Fig. 2). Since the median is less sensitive than the mean to high levels at a few sites, the pesticides are arranged from the highest to the lowest median concentration. HCB has by far the highest median value of all the analytes, whereas α-endosulfan has a higher average because of higher maximum concentrations. Although there are minor differences in the sequence during the four sampling years, the next most abundant pesticides in the global atmosphere are α- and γ-HCH, CT, and TF. Air samples contained lower levels of DT, ESS and the chlordanes (TC, CC and TN).

The size of both boxes and whiskers in Fig. 2 is a measure of the variability of the global concentrations of a pesticide. Unusually high concentrations at a few of the sampling sites will cause the mean to fall above the box, i.e. the interquartile range. On the other hand, a small box and a mean falling within the interquartile range indicate a more uniform global distribution of a pesticide. A more detailed picture of the concentration distribution for HCB, γ-HCH and α-ES can be obtained from a frequency histogram (Fig. S4 †). Whereas generally the arithmetic mean is above the 75th percentile, this is not the case for HCB in 2005, 2006 and 2008, for PM in 2006, for TC in 2007 and for α-HCH and DT in 2008. In general, DT, HCB, and the chlordane-related compounds appear to have a relatively small box and a mean falling within the interquartile range, indicative of more uniform air concentrations and the absence of exceptionally high levels at some sites. Indeed, the air concentrations for HCB are log-normally distributed (Fig. S4 †). Similar distribution patterns were observed for HCB on a continental scale, 29,30 and are likely due to the exceptionally long atmospheric lifetime of HCB in the atmosphere. 34

Fig. 2 Box-and-whisker plot of the concentrations of the pesticides detected most often in the global atmosphere (HCB: hexachlorobenzene, ES: endosulfan, HCH: hexachlorocyclohexane, PM: pendimethalin, CT: chlorothalonil, TF: trifluralin, ESS: endosulfan sulfate, DT: dacthal, CC: cis-chlordane, TN: trans-nonachlor, TC: trans-chlordane). Four entries for each pesticide represent the data for the first four years of GAPS. The boxes represent the interquartile range, containing 50% of the data. The upper and the lower edges of the box indicate the 75th and 25th percentile, respectively. The ends of the vertical lines indicate the 1 and 99 percentile and outliers that are greater than 1.5 times the interquartile range are represented by a cross. Median and arithmetic mean are designated by the horizontal bar in the box and a square, respectively.

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magnitude from a low of 0.3 ng PAS\(^{-1}\) at Cape Grim, Australia to a high of 800 ng PAS\(^{-1}\) in Delhi, India.

Dieldrin, HEPT, HEPX and DDT and its metabolites are not included in Fig. 2 because they were only detected in a few samples and their concentrations were low (Table S3\(^\dagger\)). Aldrin was not detected in any of the samples. Air samples from Tudor Hill, Bermuda, Manila, the Philippines, Paris, France, Darwin, Australia, and Teide, Canary Island, had high levels of dieldrin, whereas HEPT and HEPX were highest in samples from Asia. The levels of DDT-related substances in air samples from developed countries were much lower than in some developing countries (Table S3\(^\dagger\)), whereas DDTH and HEPT were highest in samples from Asia.

The highest concentration was recorded for air samples from India, where the use of DDT for agricultural purposes was banned in 1989, but where 10 000 tonnes continue to be used annually for controlling vector borne diseases.\(^{37}\) Zhang \textit{et al.}\(^{36}\) also found high levels of DDT-related compounds in air samples from India. Not only DDT, HEPT, and HEPX were recorded at the highest concentration in samples from Asia, but the levels of HCHs and \(\alpha\)-ES were also higher in those air samples than at any other sites in the world. India is a major producer of ES and more than 10\% of its total insecticide use is attributable to this compound alone.\(^{37}\)

**Differences in the abundance of pesticides in different regions**

Large scale differences in the pesticide levels around the world can be deciphered by comparing the concentrations of selected pesticides in air samples from different world regions (Fig. 3). The small number of sites limits the number of regions that can be contrasted: the grouping “North America” includes all sites in North and Central America, whereas the “South” comprises all sites in South America, Africa, and Australia (Fig. 1). When comparing regions it should be cautioned that they differ with respect to the assembly of site types, \textit{e.g.} some regions have more urban sites, whereas others have more agricultural sites (Fig. 1). For example, the grouping “South” does not include a single urban sampling site. Four entries for each pesticide and region represent the data for the first four years of GAPS. For North America, a fifth entry represents data reported by Shen \textit{et al.}\(^{28,29}\) for 2000/1. When comparing years one should keep in mind that the assembly of sites is not always the same during different years. The OCPs \(\alpha\)-HCH, \(\gamma\)-HCH, TC and CC show a similar pattern, in that the median concentrations are higher in samples from Asia than in those from other regions. The levels of HCHs in Asia appear to be lower in the fourth sampling year because the sites in India with exceptionally high values were no longer sampled in 2008. The distribution pattern for the CUPs CT, TF, DT and \(\alpha\)-ES suggests that their use varies throughout the world, with some of them applied heavily in Asia and the South and others used predominantly in Europe and North America.

**Hexachlorocyclohexanes.** HCHs in the samples from Asia have a large interquartile range, suggestive of a high concentration variability (Fig. 3). Samples taken in the vicinity of Delhi had the highest concentrations of both isomers (Fig. S1-1\(\dagger\)), reflecting widespread usage of HCH-based pesticides in India. As much as 36 000 tonnes of technical HCH were used annually in the 1980s.\(^{36}\) After banning technical HCH in 1997, India relied heavily on lindane,\(^{40}\) with about 6000 tonnes used annually since 1991.\(^{36}\) Concentrations of HCHs vary in the samples from North America and the South, but not to the same extent as in the Asian samples (Fig. 3). During the first three years the HCHs were much lower in North America and the South than in Asia. The large whiskers of the box plot for \(\alpha\)-HCH in the South are due to higher levels in DeAar, South Africa, and Cairo, Egypt (Fig. S1-1\(\dagger\)), even though \(\gamma\)-HCH was not particularly high. A similar pattern with higher levels of \(\alpha\)-HCH than \(\gamma\)-HCH was also found in Izmir, Turkey, and Dhulikhel, Nepal (Fig. S1-1\(\dagger\)). This indicates \(\alpha\)-HCH sources to the atmosphere, either from usage of technical HCH or the evaporation from obsolete stockpiles.
In contrast to the great variability of HCH levels in the atmosphere over Asia, very small boxes in Fig. 3 indicate that the \(\alpha\)-HCH concentrations display little variability across Europe, consistent both with the uniform pattern observed by Jaward et al.\(^{19}\) and a lack of sources on this continent. \(\gamma\)-HCH, on the other hand, is not uniformly distributed in the European atmosphere. The large whiskers of its box plot are caused by high levels of \(\gamma\)-HCH in samples from Paris, which are among the highest in the world (Fig. S1-1†). Officially, lindane was used in France only until 1998,\(^{41}\) but there may still be use of remaining stocks. In addition to Paris, Tapanti in Costa Rica and Delhi and Coimbatore in India, Kuwait City, and Veracruz in Mexico had high levels of \(\gamma\)-HCH (Fig. S1-1†) accompanied by \(\alpha\)-HCH levels above the global median. Since the technical HCH mixture is not likely to be used in these places any longer, this may suggest that lindane use will also lead to some contamination of the atmosphere with \(\alpha\)-HCH, presumably because of the presence of small amounts of \(\alpha\)-HCH in the formulation.\(^{42}\)

The \(\alpha/\gamma\)-HCH ratios in almost all air samples are lower than in the technical mixture (Fig. 4), consistent with insignificant worldwide use of technical HCH and with lindane being the primary source of HCH contamination to the atmosphere. Only in samples from polar regions is the mean of the \(\alpha/\gamma\)-ratio close to or even higher than that in the technical mixture, \(i.e.\) those samples have an unusually high relative abundance of the \(\alpha\)-isomer. Among the background sites, Whistler, Ucluelet, Lasqueti Island, Canada and Dysea, USA, all located on the Pacific coast of North America, Stôráhóði, Iceland, Fraserdale, Sable Island, and Little Fox Lake, Canada, Point Reyes, California, USA and Mauna Loa Observatory, Hawaii, USA had relatively high \(\alpha/\gamma\)-HCH ratios. Re-volatilization of \(\alpha\)-HCH from cold water bodies, such as the Arctic Ocean, the Atlantic and the Northern Pacific, can account for these observations.\(^{41,28}\) It is noteworthy that only the \(\alpha/\gamma\)-HCH ratios were unusually high in the Arctic, but not the absolute \(\alpha\)-HCH levels. Air samples from polar regions had relatively low levels of \(\alpha\)-HCH, but the \(\gamma\)-HCH levels were even lower (Fig. S1-1†). Even though it clearly is a source of \(\alpha\)-HCH to the high latitude atmosphere, evaporation from cold water bodies cannot be its only source to the global atmosphere. The highest \(\alpha\)-HCH levels worldwide are actually observed at the same sites that also have high concentrations of \(\gamma\)-HCH (such as India) (Fig. S1-1†). The \(\alpha/\gamma\)-HCH ratios have decreased in air samples from urban, agricultural and rural areas but the opposite trend was observed in air samples from background and polar areas, indicating the \(\gamma\)-HCH levels are continuing to decrease at a faster rate compared to \(\alpha\)-HCH.

Chlordanes. The atmospheric concentrations of chlordanes are generally very low around the world (Fig. 3 and S1-2†), yet the length of the whiskers for TC and CC in Fig. 3 indicates that levels vary greatly across Asia, North America and the South. Indeed, a few sites in Southern Asia, Northern Australia and the Southeastern United States had higher levels of TC and CC than places elsewhere (Fig. S1-2†). The urban site in Manila in the Philippines contained the highest concentrations of TC, CC and TN during years one and two. This site was no longer sampled in 2007 and 2008, but was replaced by a background site in the Philippines. An urban site in Sydney, Florida, USA, a site newly added in 2007, contained the highest total chlordane levels during years three and four. Similar to \(\alpha\)-HCH, the concentrations of TC and CC do not vary greatly across Europe (Table S2†), although higher concentrations are recorded in Spain and France (Table S2†). Chlordane is no longer used in North America and Europe and the TC/CC ratio is higher in some samples from these continents than in the technical mixture, suggesting that evaporation from soils, that are contaminated due to its former use as a termiticide, is most likely the source to the atmosphere in those regions. Lower TC/CC ratios in some samples from the two continents than in the technical grade indicate that old source of chlordanes are present in the atmosphere and also that TC was lost from the atmosphere at a faster rate than CC.\(^{43}\)

The TC/CC ratio in the technical chlordane mixtures is approximately 1.17 (dashed line in Fig. 4).\(^{44}\) This value can be exceeded in the atmosphere of source areas, because TC has a higher vapor pressure than CC.\(^{45}\) TC is lost faster than CC from the atmosphere because it is more susceptible to photodegradation.\(^{43}\) Chlordane that has undergone atmospheric processing has therefore a lower TC/CC ratio than freshly evaporated chlordane. This has been used to distinguish between aged and new sources of chlordane.\(^{29,43}\) Consistent with this, the mean TC/CC ratios in air samples from agricultural, rural, urban areas were greater than 1.17, but those in samples from polar and background regions were generally lower, suggesting that these areas had received chlordane that aged while being atmospherically transported from somewhere else.

![Fig. 4 Box-and-whisker plot of \(\alpha/\gamma\)-HCH, TC/CC and \(\alpha/\beta\)-endosulfan ratios in air samples from different types of sites. Also given is the composition of technical HCH (gray band), technical chlordane (dotted line) and technical endosulfan (solid line). Multiple entries for each type of site represent the data for the different years of the GAPS study.](image-url)
Endosulfan. The dominant CUP in Asia and the South is ES, with particularly high levels in samples from India, Ghana and Korea (Fig. S1-3†). Finding high levels of ES in samples from these regions is consistent with its heavy use for agricultural purposes in developing countries. The mean $\alpha$-ES concentration in samples from North America lies far above the 75th percentile, resulting from a few sites (Tlalpuca and Veracruz, Mexico, and Sydney, Florida, USA) having high levels. $\beta$-ES and the metabolite ESS were also detected in most samples at levels lower than $\alpha$-ES. The measured relative abundance of $\alpha$-ES is almost always higher than the ratio of 2.3 in the technical endosulfan mixture (Fig. 4). In particular, the average $\alpha/\beta$-ES ratio is higher in samples from background sites, suggesting that during atmospheric transport $\beta$-ES is being preferentially lost. Only in air samples from Sydney, Florida, USA, Pomlewo, Poland, Paris, France, Accra, Ghana, Abdaly and Kuwait City, Kuwait, Coimbatore and Delhi, India was the isomeric ratio of ES close to the technical mixture, which indicates ongoing application of ES. Others also found $\alpha/\beta$-ES ratios close to that of the technical mixture in Indian air samples. 46

Other CUPs. Similar to ES, pendimethalin (PM) is a pesticide prevalent in the atmosphere over Asia, but unlike ES, it appears to not be used extensively around the world (its concentrations are not included in the box plots since it was detected in only a few samples). Hotspots for PM are the sites in Korea and the Czech Republic (Fig. S1-4†). The distribution pattern of trifluralin (TF), chlorothalonil (CT) and dacthal (DT) is strikingly different from that of $\alpha$-ES and PM, as these CUPs are found in higher levels in Europe and North America than in Asia and the South (Fig. 3 and Table S2†). Even though TF is a candidate for listing as a POP under the UNECE LRTP convention45 and its use is banned in some European countries, it is the most abundant CUP in the European atmosphere (especially at French and Czech sites), whereas it is present only at very low levels elsewhere (Fig. S1-4†). Chlorothalonil (CT) is the most abundant CUP in the North American atmosphere, with particularly high levels in samples from Mexico and Florida, USA. CT is also abundant in Europe, again in samples from the Czech Republic and France (Fig. S1-4†). High levels of CT are also found in samples from Korea. Relative to other CUPs, the air concentrations of dacthal (DT) are very low (Table S2†). It is more abundant in the atmosphere of North America and Europe than elsewhere but only at a few sites (e.g. Toronto, Paris). 271 tonnes of dacthal are used on crops in the USA per year whereas Canadian use is less than 1% of that of the USA. 47 A decreasing trend is observed for dacthal in the global atmosphere (Table S2†).

As limited as the GAPS network is, it succeeded in revealing large scale distributions patterns of pesticides in the global atmosphere. In general, the CUPs CT, DT and TF tended to have higher levels in North America and Europe while the CUPs ES and PM were found in higher levels in air samples from Asia and the South. Levels of OCPs are particularly high in Asia. The levels in air reflect that developing countries such as India, Ghana, Nepal, and the Philippines are continuing the use of OCPs, while the use of at least some of the quantified CUPs is more prevalent in the more developed countries. Sampling sites in India and France were hotspots for OCPs and for most of the detected CUPs, respectively.

Can we gain information on time trends from monitoring networks such as the GAPS?

The global monitoring program’s main purpose is to serve in the evaluation of the effectiveness of the Stockholm Convention, i.e. it will seek observational evidence that the concentrations of regulated POPs are decreasing globally and provide information for assessing their regional and global transport. The levels observed over this 4-year period can be used to establish a “baseline” upon which future changes in concentration can be compared. They may also be used to test whether evidence of decreasing concentrations can be obtained from a global monitoring program based on PAS. A comparison of the levels measured during the first four years of GAPS, as aggregated in Fig. 3, may be deceiving, because the number and type of sampling sites that are used in the drafting of the box-and-whisker plots are changing from year to year. A single site with an unusually high concentration which is dropped or added during a sampling year, can strongly influence the observed time trend. We therefore produced another version of the plot (Fig. S2†) that only considers the 15 sampling sites (4 each in North America and Europe, 6 in the South and 1 in Asia) that were operational during all four years. Fig. S3† graphs the time trends observed at each of these 15 sites. For some of the pesticides, declining levels were observed from 2005 to 2008. This is the case for total chlordane, $\gamma$-HCH and $\alpha$-HCH in all three regions. Randomized block ANOVA was performed to test differences in the concentrations of HCHs, HCB, $\alpha$-endosulfan and total chlordanes among the 4 years sampling (2005 to 2008) in North America (Bragg’s Lake, Toronto, Tudor Hill, Tapanti), the South (Arauca, Indaiatuba, Cape Grim, Darwin, Kalahari, DeAar), and Europe (Koetice, Storhöfö, Malin Head, Paris). The results are reported in Table S4†. The levels of $\alpha$-HCH, $\gamma$-HCH and total chlordane in North America, $\gamma$-HCH and HCB in the South, $\alpha$-HCH, HCB and total chlordane in Europe differ significantly among the four years of sampling ($p < 0.05$, Table S4†), implying significant declines (Fig. S2†). Regression analysis was also performed between the levels of $\alpha$-HCH, $\gamma$-HCH, total chlordane, and $\alpha$-endosulfan at 15 sites and sampling year (from 2005 to 2008). The concentrations of $\alpha$-HCH, $\gamma$-HCH and total chlordane are significantly negatively correlated ($p < 0.05$, Table S5†) at 5 out of 10 sites (Table S5†), indicating a significant decrease during the 4 years of sampling. The CUPs, including ES, do not display clear trends over the four years of sampling (Fig. S2†), except that the levels of $\alpha$-ES and CT are decreasing in the European atmosphere. Interestingly, the levels of HCB have declined, while pesticides believed to contain HCB as a by-product, such as DT and CT, experienced stable or even increasing levels. This may suggest that the contamination of CUPs with HCB either has been reduced or is not an important source for HCB to the atmosphere. Although based upon only four years of continuous sampling at 15 sites worldwide, our data indicate that the levels of several banned OCPs are declining around the world. This may be seen as an indication that the ban and/or restrictions on OCPs imposed by national jurisdictions and in some cases globally through the Stockholm Convention are effective in reducing the emissions of those substances to the global atmosphere. One may question whether it is justified to infer time trends from a few years of data obtained by PAS, considering (i) the much larger
number of HiVol air samples that is generally believed necessary
to derive significant inter-annual air concentration time
trends, and (ii) the uncertainties in the sampling rate of PAS,
which is substantially higher than for HiVol samples. Long term
air monitoring of POPs using HiVol samplers sometimes relies
on episodically taken samples, i.e. air is not sampled continu-
osly but only in “snapshots”. When such data are applied in the
derivation of long term time trends, it is assumed that the levels
during the sampling periods are representative of the long term
average concentrations. Because of the large short term vari-
ability in the concentration of most pesticides, this assumption
is valid only if a large number of air samples is averaged. PAS,
on the other hand, sample continuously and thus directly yield the
long term average concentrations that are required for the
identification of inter-annual trends. Consequently, it is
conceivable that a much smaller number of samples, and likely
even a smaller number of years, is required to discern time trends
with PAS than with episodic HiVol sampling. Interestingly, the
greatest weakness of PAS, namely the semi-quantitative nature
of the concentration values it yields, which is due to the uncer-
tainty in the sampling rate, is a minor impediment in the use for
time trend detection as long as site continuity is assured. Any
influence of temperature, wind speed, atmospheric pressure, etc.
on is subject to only minor inter-annual fluctuations and so the
concentration variability is not only
determined by the scale of the network area but also by the
diversity of the sampling site types. The number of
sites currently used in GAPS would not be sufficient for a global
monitoring effort, mostly because it aims not only for the
largest possible spatial coverage, but also for a wide variety of
sampling site types (urban, agricultural, remote, etc.). A large
variety of sites is desirable if the entire concentration variability
of a compound is to be explored. If, however, the focus is on

Comparing PAS networks at different scales

XAD-based PAS deployed for one year periods have now been
used in networks on the global and continental scale, as well
as in two regional studies in Costa Rica and in the mountains
of Western Canada. This affords the opportunity to compare
the results from differently scaled networks that are “nested”, i.e.
the areas covered by the larger networks comprise the areas
of the smaller ones. For example, the North American network
by Shen et al. included four sites in the Western Canadian
mountains and one site in Costa Rica. When comparing the
measured distributions for four pesticides (Fig. 5), the
concentration variability tends to decrease with decreasing scale of
the network: the boxes and whiskers for the global concentration
distributions are wider than those for the North American and
the regional networks. This is expected as sites that are in closer
proximity should have more uniform air concentrations than those that are farther apart. Also, sites within the same juris-
diction share the same pesticide regulatory status. However, it is
also apparent that the concentration variability is not only
determined by the scale of the network area but also by the
uniformity of the regional geography and/or of the sampling
sites. In particular, the Costa Rican concentration distributions
are markedly wider than those for the Western Canadian
mountains (Fig. 5), which is consistent with a much larger
geographical variability and a more diverse set of sampling sites
in Central America. The Costa Rican network included sites in
agricultural areas, urban areas and National Parks, sites along
the Atlantic and Pacific coast, as well as in the coastal plains,
valleys and mountains, whereas all of the Western Canadian
sampling sites were in remote mountainous National Parks. A
der wider variety of sampling site types may also explain why the
Costa Rican network shows concentration variability comparable
to that of the much larger North American network. The latter
included mostly sites in background regions and only a single
urban location. Also, most sites were in only two countries
(Canada and USA) with similar economic development.

Clearly, the number of sites required for a network depends on
the scale and geographical diversity of the area to be covered, as
well as the diversity of the sampling site types. The number of
sites currently used in GAPS would not be sufficient for a global
scale monitoring effort, mostly because it aims not only for the
largest possible spatial coverage, but also for a wide variety of
sampling site types (urban, agricultural, remote, etc.). A large
variety of sites is desirable if the entire concentration variability
of a compound is to be explored. If, however, the focus is on

Fig. 5 Air concentrations of α-endosulfan, HCB, trans-chlordane and γ-HCH in the global atmosphere, and the atmosphere over North America, Costa Rica and the Western Canadian mountains.
effectiveness evaluation and therefore on the derivation of long term concentration trends and if the number of sampling sites has to be limited, it may be more cost effective to focus on sites in reasonably remote regions, because sites in urban and agricultural source areas will yield information on concentration and usage trends on a local rather than a regional scale.\(^5\)

GAPS was conceived not as a global monitoring network but as a feasibility test to confirm the ability of PAS to serve in the effectiveness evaluation of international agreements on POPs. The first four years of GAPS data have proven that networks based on PAS are indeed capable of detecting inter-annual time trends with a surprisingly small number of samples and in particular seem to be able to allow for differentiation in time trends in different regions. However, for this to be achieved, a number of requirements have to be met: sites have to operate continuously. A long term commitment of the network participants is therefore paramount. For a valid regional differentiation, it is important that the number and type of sites are similar in each region, i.e. include a comparable mix of urban, agricultural, remote and polar regions.

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Notes and references


