SPATIAL AND TEMPORAL PATTERN OF ORGANOCHLORINE AND CURRENT-USE PESTICIDES IN THE GLOBAL ATMOSPHERE

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Introduction

In the past organochlorine pesticides (OCPs) were used intensively around the world in agriculture and also to control vector borne diseases. Because these pesticides were found to persist in the environment and to bioaccumulate in the food chain, many industrialized countries banned or restricted the use of legacy OCPs in the 1970s. Eventually, the Stockholm Convention on Persistent Organic Pollutants (POPs) led to world-wide bans and restrictions on OCPs (aldrin, endrin, dieldrin, heptachlor, chlordane, mirex, toxaphene, DDT and hexachlorobenzene (HCB), and more recently on hexachlorocyclohexanes (HCHs)). Less persistent pesticides continue to be used in large quantities and are often referred to as current use pesticides (CUPs).

The Global Atmospheric Passive Sampling (GAPS) study, started in December 2004, is a multi-year pilot project with the objective to prove the feasibility of monitoring POPs in the global atmosphere with the help of passive air samplers (PAS) (Pozo et al., 2006). Compared to conventional active sampling, PAS are inexpensive, simple to use, shippable, and require no power supply, making them powerful tools for large-scale spatial and temporal studies. Within GAPS, XAD resin-based PAS (Wania et al., 2003) are deployed for one year and yield annually average concentrations. Whereas early results based on polyurethane foam disk PAS within GAPS have been described earlier (Pozo et al. 2006, 2009), we report here the results from the XAD-based PAS deployed during the first three years of GAPS.

Materials and Methods

PAS were deployed for a full year at 35, 34 and 46 sites during the first, second and third year, respectively. The sites are located in agricultural, background, polar, rural and urban areas. After return to the lab, the XAD-2 resin was Soxhlet-extracted with 350 ml of DCM for 20 hours. Reduced extracts were passed through sodium sulfate columns to remove water and analyzed for legacy OCPs and CUPs using gas chromatography mass spectrometry with negative chemical ionization. Concentrations of the analytes in blanks were very low, indicating that samples were not contaminated during transport, storage or analysis.

Results and Discussion

Concentrations of pesticides in the XAD-PAS from the first three years of GAPS are summarized in a box-and-whisker plot (Figure 1). HCB has by far the highest median value of all the analytes and is thus the dominant pesticide in the global atmosphere. Although there are minor differences in the sequence during the three sampling years, the next most abundant pesticides in the global atmosphere are α-HCH, γ-HCH as well as the CUPs α-endosulfan, chlorothalonil, and trifluralin. Dieldrin, metribuzin, heptachlor, heptachlor epoxide and DDT and its metabolites are not included in Fig. 1 because they were only detected in a few samples and their concentrations were low.

The PAS network reveals the large scale distributions patterns of pesticides in the global atmosphere (Figure 2). In general CUPs tend to have higher levels in North America as well as in Europe, whereas the legacy OCPs are particularly high in Asia. Asia appears to be a significant source of legacy pesticides to the global atmosphere. The levels in air reflect that developing countries are continuing the use of legacy pesticides, while the use of CUPs is more prevalent in the more developed countries of Europe and North America.

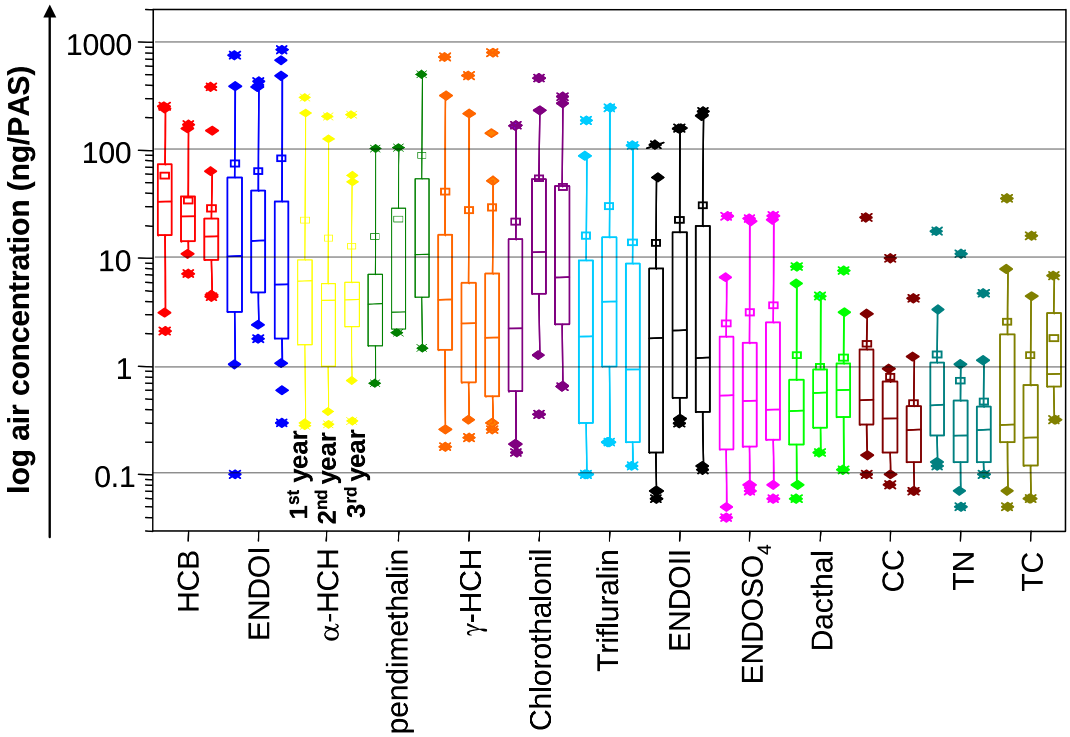

Fig. 1 Box-and whisker plot of the concentrations of pesticides most frequently detected in the global atmosphere.

From the first three years of GAPS data we are able to observe general time trends for some pesticides in the global atmosphere. The levels of HCB, α-HCH, γ-HCH, and some components of chlordane (CC, TN) in the second and third year global air samples are generally lower than in the first year samples. The ban and/or restrictions on legacy pesticides imposed by national jurisdictions and in some cases globally through the Stockholm Convention are apparently reflected in declining air concentrations in all world regions, which suggests that these measures are indeed effective in reducing the emissions of those substances to the global atmosphere. The changes of the CUP concentrations with time tend to be different in different world regions. For example, there are indications that endosulfan and other CUPs are declining in Europe, yet remain constant or even increase in other world regions. Interestingly, the levels of HCB have declined, while pesticides believed to contain HCB as a by-product, such as dacthal and chlorothalonil, experienced stable or even increasing levels. This may suggest that that the contamination of CUPs with HCB either has been reduced or is not an important sources for HCB to the atmosphere.

Acknowledgements

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References

1. Pozo, K.; Harner, T.; Wania, F.; Muir, D.C.G., Jones, K.C.; Barrie, L.A.. *Environ. Sci. Technol.* **2006**, *40*, 4867-4873.
2. Pozo, K.; Harner, T.; Lee, S.C.; Wania, F.; Muir, D.C.G., Jones, K.C. *Environ. Sci. Technol.* **2009**, *43*, 796–803.
3. Wania, F., L. Shen, Y. D. Lei, C. Teixeira, D. C. G. Muir. *Environ. Sci. Technol.* **2003**, *37*, 1352-1359.

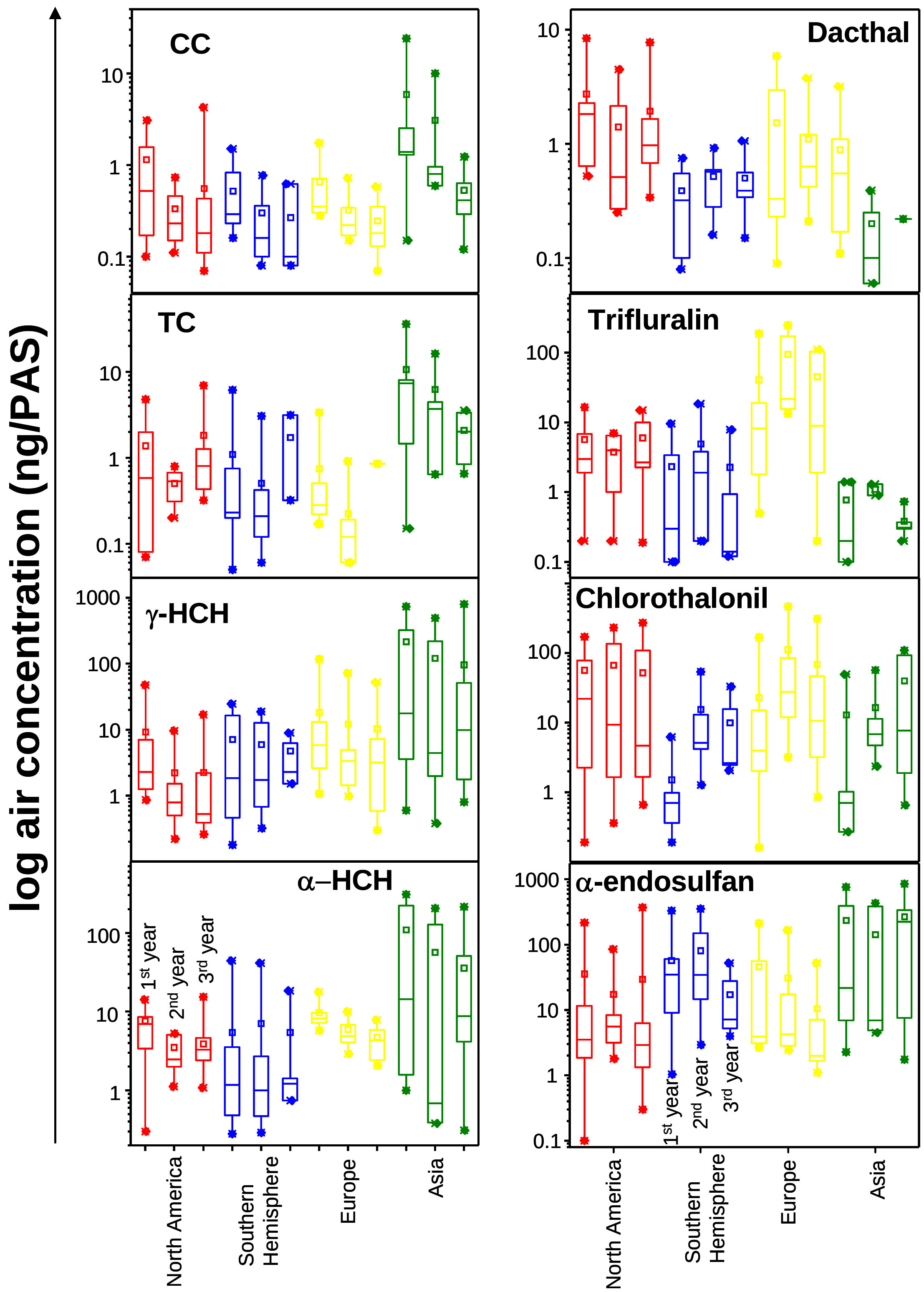

Fig. 2 Box plot of the concentrations of legacy organochlorine pesticides (left) and current use pesticides (right) in the first, second and third year passive air samples from different continents.