Environmental Science
Processes & Impacts

PAPER

View Article Online
View Journal | View Issue

Cite this: *Environ. Sci.: Processes Impacts*, 2019, **21**, 1132

Comparability of long-term temporal trends of POPs from co-located active and passive air monitoring networks in Europe†

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The comparability of data from active (ACT) and passive sampling (PAS) of persistent organic pollutants (POPs) in air is hindered by uncertainties related to the derivation of sampling rates and concentrations, as well as differences in the duration, volume and frequency of sampling. Although data from ACT have been used extensively in short-term PAS calibration studies, no attempts have been made to evaluate the comparability of long-term trends calculated from PAS to established ACT trends. This is crucial, as continuous long-term ACT is unfeasible in most regions of the world. To address these challenges, we calculated and compared trends for organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) at the six sites in Europe with at least 5 years of co-located ACT and PAS data (2012–2016): Birkenes, Košetice, Pallas, Råö, Stórhöfði and Zeppelin. Strong agreement of ACT and PAS trends was observed for most OCPs and PCBs. Apart from two PCBs at Stórhöfði, all pairs of ACT and PAS trends followed the same direction. However, differences in the magnitude, significance and confidence intervals of their slopes were observed for some compounds and were primarily attributed to the short duration of the PAS time series. Despite some limitations, our results suggest that the comparability of ACT and PAS POP trends will continue to improve with additional years of data. This study confirms the suitability of PAS for the calculation of long-term POP trends in air, and highlights the importance of continuous sampling at established monitoring sites with consistent analytical methods.

Received 24th March 2019
Accepted 17th June 2019

DOI: 10.1039/c9em00136k

rsc.li/espi

Environmental significance

Long-term air monitoring of persistent organic pollutants (POPs) is essential for evaluating the effectiveness of global regulatory measures to restrict and ban the production of these compounds. Active sampling has historically been used to measure atmospheric concentrations of POPs but is unfeasible for long-term monitoring in most regions of the world. Passive sampling is a more sustainable alternative, however, the comparability of long-term temporal trends from passive sampling to established trends from active sampling is unclear. Our study confirms the suitability of passive air sampling for the determination of long-term temporal trends of POPs. It may also be used as a validation tool for passive sampling data in other regions where direct comparison to active sampling is not possible.

Introduction

Persistent organic pollutants (POPs) are a broad class of chemical compounds that reduce air quality and adversely affect human health. Although active air monitoring by the EMEP network (coordinated by the Norwegian Institute for Air Research, NILU) has established temporal trends for POPs in Northern Europe since the 1990s, long-term data were unavailable for most other regions prior to the entry-into-force of the Stockholm Convention on POPs in 2004. This led to the design of a Global Monitoring Plan (GMP) to generate consistent and reliable temporal trend data in order to evaluate the effectiveness of regulatory measures to eliminate or restrict the production of POPs. To address the needs of the GMP within Europe, the MONET network (operated by RECETOX, Masaryk University) deployed passive samplers across the continent – particularly in Central and Eastern Europe – as an alternative method for long-term air monitoring due to their ease of use and lower cost of operation.[1,2] As a result of these advantages, passive sampling has become an increasingly widespread method for monitoring of POPs in air. However, the extent of the agreement between active and passive air sampling data is still unclear.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9em00136k

The comparability of active and passive sampling is confounded by uncertainties in sampling rates and particle-phase dynamics (including sampling efficiency) which affect the derivation of air concentrations required for the interpretation of passive sampling data.[3–6] Differences in the sampling duration, volume and frequency between monitoring networks may also affect the comparability of active and passive sampling results (*e.g.* active sampling for 24 h once per week *vs.* continuous passive sampling for 84 d). Furthermore, due to the longer time series of large-scale active air monitoring networks, results from passive monitoring networks were not included in a recent assessment of global atmospheric POP concentrations and long-term temporal trends.[7] Despite these challenges, passive sampling is often the only method available for air monitoring in regions lacking the necessary infrastructure and resources for active sampling and is therefore better suited for capacity building and long-term operations where feasibility and sustainability are concerns.[1,2]

Results from active air sampling have been used extensively to calculate sampling rates and derive concentrations of POPs measured in short-term ($\leq$2 year) passive sampling calibration studies.[3,8–18] However, besides one previous study by our group,[19] there have been no attempts to calculate and compare long-term (>5 year) temporal trends of POPs from passive monitoring to established active monitoring trends. We have previously shown that temporal trends can be directly determined from concentrations of POPs within 28 d passive samplers without derivation of air concentrations, and that these trends show strong agreement with trends from active sampling at the same location in Košetice, Czech Republic.[19] To validate this approach for effectiveness evaluation under the Stockholm Convention, we applied the same methodology to all other sites in Europe with co-located active EMEP samplers and passive MONET samplers deployed for the more common 84 d duration with at least 5 years of data. Our aim was to evaluate the ability of a passive air monitoring network to accurately replicate long-term temporal trends of POPs derived from an established active air monitoring network, and to assess the suitability of long-term passive sampling in regions where long-term active sampling is not feasible.

Methods

Site and compound selection

To assess the comparability of active and passive air monitoring, we identified sites with co-located samplers from both the EMEP and MONET networks as well as reported concentration data for the same compounds during the same period. As of 2016, EMEP operates 12 active sampling sites that have long-term monitoring data for POPs in air and aerosol. Six of these sites have a co-located MONET passive sampler and were therefore selected for this study: Birkenes (Norway), Košetice (Czech Republic), Pallas (Finland), Råö (Sweden), Stórhöfði (Iceland) and Zeppelin (Norway/Svalbard). Each of these EMEP active samplers has been monitoring some legacy POPs since at least 2004; however, the temporal trends for more recently listed compounds are generally much shorter with some only beginning in 2014. Conversely, the passive MONET network has been monitoring for a much shorter period (84 d sampling since July 2011) but all sites are analyzed by the same laboratory for a full suite of POPs. As a result, compound selection was constrained by the available EMEP data, whereas the duration of the sampling period overlap for comparison was constrained by the available MONET data. To examine the longest possible temporal trends we selected four legacy organochlorine pesticides (OCPs): alpha- and gamma-hexachlorocyclohexane (α-HCH, γ-HCH), hexachlorobenzene (HCB) and *p*,*p*′-dichlorodiphenyldichloroethylene (*p*,*p*′-DDE); the six indicator polychlorinated biphenyls (PCB 28, 52, 101, 138, 153 and 180); and six commonly measured polybrominated diphenyl ethers (PBDE 47, 99, 100, 153, 154 and 209).

Sampling and analysis

Active EMEP monitoring data were obtained from the online EBAS database as well as annual reports.[20,21] Active air concentrations are reported in ng m^{-3} and are generally based on one continuous 24 h or 48 h sampling period per week using a high-volume sampler. However, some site-specific differences in sampling duration, frequency and volume exist among the different EMEP monitoring stations depending on the instrument and sampling methods used. Similarly, the analytical method and laboratory used to analyze the samples also vary depending on the country where the site is located. In Table S1† we provide more detailed sampling and analytical information on each EMEP site used in this study.

The MONET passive sampling network has gradually expanded in Europe since its inception in 2003 through several monitoring campaigns: identification of regional POP sources in the Czech Republic;[22,23] establishing background concentrations in Central and Eastern Europe (2006–2008);[24] and 28 d background monitoring across Europe (2009–2011). Since July 2011, MONET has been passively monitoring POPs at 28 sites throughout Europe (in addition to those within the Czech Republic) using identical polyurethane foam (PUF) disk samplers deployed for approximately 84 d and analyzed in-house at the RECETOX Trace Laboratory using GC-MS/MS. It should be noted that the initial two years (2011–2012) of MONET PUF samplers used in this study were analyzed by GC-MS instead. More detailed information on analytical methods and MONET sampler design is described elsewhere.[19,25]

Data treatment

Active air concentrations from EMEP were available either as primary (weekly) data or as monthly arithmetic means, in ng m^{-3}. This allowed us to construct homogenous, temporally equidistant time series in which the data are distributed regularly over time. Conversely, MONET data[26] are available as primary values (ng per PUF per sampling period). MONET passive sampling predominantly occurs over an 84 d period though some exceptions have occurred. Of the 213 MONET samples used in this study: 1% had sampling periods less than 42 d (minimum of 28 d), 7% between 42 and 76 d, 80% between 77 and 91 d (52% exactly 84 d), 9% between 92 and 126 d, and

2% more than 126 d (maximum of 171 d). The full distribution of the MONET sampling periods is depicted in Fig. S1.† To account for these differences, we computed normalized daily uptake rates for each MONET sample (ng per PUF per day), assuming linear uptake of all compounds during sampling.[27] To verify that the length of the sampling period had negligible effect on the values used in the temporal trend analyses, we calculated trends based on parallel 28 d and 84 d passive samples at Košetice and found insignificant differences in their rate constant for the majority of the assessed compounds (Fig. S2†). Some site- and time-specific gaps have also occurred in the MONET sampling regimes (Fig. S3†). These irregularities prevented us from annually averaging the passive MONET concentrations, even though averaging can significantly improve the robustness of trend estimates for equidistant time series.[19,28] We instead used the primary data in the temporal trend calculations to prevent any potential bias caused by the unequal distribution of measurements within years. For example, where available concentrations only reflect part of an entire year, annual averaging could result in highly biased results for compounds with strong seasonal fluctuations (HCHs, PCBs).

Certain individual air concentrations reported in the EBAS database were flagged as being 'invalid' due to issues with the air sampler or the analytical method. Thus, only 'valid' EMEP data were included. Of the active and passive data used in this study, some compounds selected for comparison were present at concentrations below the analytical limit of quantification (LOQ) resulting in the data being partially left-censored. The proportion of left-censored data was both site- and compound-specific and ranged from 0–10% for OCPs and lighter PCBs (28 and 52) at most sites and up to 100% for the heavier PBDEs (153, 154 and 209) at some sites (Table S2†). For the purposes of trend analysis, values below LOQ were replaced by one-half of the LOQ.[19] The potential effect of these LOQ values on the calculation of temporal trends is discussed in the Limitations section.

Temporal trend analysis

Due to the relatively short duration of the MONET passive time series (5–6 years), we were unable to use advanced methods for temporal trend analysis previously applied to active air monitoring datasets.[29–32] Instead, we were limited to the simpler methods previously used for passive air monitoring.[19,33] In this case, by assuming approximate first-order kinetics[34–36] and thus an exponential decrease in POP concentrations over time, the time series can simply be described by compound-specific half-lives (years) and rate constants (% change per year).

To prevent inappropriate application of a linear estimator in cases where air concentrations were affected by sudden non-linear changes in time[37] (*e.g.* the introduction of regulatory measures to ban or restrict the production of individual POPs), we analyzed all time series for break points as described by Hites.[37] This was done for both the active EMEP and passive MONET time series using both annual averages and primary air concentrations. In cases where break points were identified in the primary data less than 2 years from the initial or final point of the time series, the break point was considered an artifact of seasonal variation and was not taken into account. Furthermore, break points that were identified as a result of high proportions of LOQ values in the time series (>30%) were also not taken into account. On the other hand, all break points that were identified as being statistically significant either in the primary or annually aggregated data were considered valid and used to divide the time series into two parts with only the data following the break point used in the subsequent temporal trend analysis.

The Theil–Sen estimator, a robust non-parametric tool for temporal trend assessment,[38–40] was used to fit the data for each site and compound to an exponential trend. The trend was fit as a linear regression to log-transformed data, providing an estimation of the half-life and rate constant. The statistical significance of the calculated trends was then estimated by means of the non-parametric Mann–Kendall test.[41]

As previously discussed, direct comparison of active and passive sampling data requires conversion of passive-sampling concentrations from ng per PUF per d to ng m^{-3} using models.[27,42] However, we have previously shown that it is possible to calculate temporal trends directly from the primary ng per PUF per d concentrations[19,33] and therefore used the same methodology in this study. To compare the corresponding active and passive time series, we computed the value of each exponential trend at the middle point of their overlapping period. The ratio of these values was used as an estimate of the passive sampling rate in units of m^3 per PUF per day (Table S3†).[19] For the purposes of this study, these sampling rate estimates were used solely to align and scale the *y*-axes of the active and passive time series in order to present both on a single graph. A non-parametric method of trend comparison was then used to test the comparability of the corresponding active and passive time series: for each comparison, a dataset of slopes between all possible pairs of points was computed for both active and passive time series. Each resulting pair of datasets was compared using the non-parametric Mann–Whitney *U* test[43] which provided a *p*-value for the possible difference between each pair of time series.

Results and discussion

Comparability of active and passive temporal trends

As a result of the considerable length of the EMEP time series for OCPs and PCBs (minimum 12 years), the majority of the active sampling temporal trends calculated in this study show significant negative correlations with time and have narrow 95% confidence intervals (Tables 1 and S4–S7†). The majority of the MONET passive sampling trends also show OCPs and PCBs to be decreasing, but the time series are much shorter (5–6 years) and show weaker correlations and wider confidence intervals than the active trends. Active EMEP monitoring of PBDEs in air began later than that of the other POPs at most sites and their concentrations in air are also generally very low with some compounds heavily influenced by LOQs. As a result,

Table 1 Summary of exponential active and passive temporal trends for selected compounds (rate constants as annual change, % per year). Rate constants for all compounds are listed in Table S4 (half-lives in Table S5). Statistically significant ($p < 0.05$) trends are denoted with an asterisk (p-values are listed in Table S7). Time series consisting of more than 29.3% values below LOQ are underlined

		PCB 28	PCB 52	α-HCH	γ-HCH	HCB	p,p'-DDE	PBDE 47	PBDE 99
Birkenes	ACT	−8*	−6*	−8*	−10*	−1*	+1	−1	−14*
	PAS	−9*	−8*	−14*	−13*	−13*	+3	−13	−21
Košetice	ACT	−13*	−20*	−10*	−11*	−3*	−4*	n/a	n/a
	PAS	−13*	−14*	−20*	−19*	−13*	−9*	n/a	n/a
Pallas	ACT	−4*	−3*	−9*	−12*	+1	−2*	−20*	−16
	PAS	−16*	−14*	−22*	−25*	−10*	−12*	−11	−9
Råö	ACT	−6*	−4*	−10*	−11*	+1	−2*	−6	−13*
	PAS	−11*	−13*	−19*	−18*	−8*	−8	−2	−7
Stórhöfði	ACT	−2*	+3*	−11*	−9*	−1	0	−20*	+25
	PAS	−20*	−18*	−22*	−26*	−11*	−16*	+44	+88
Zeppelin	ACT	−6*	−5*	−12*	−14*	+1*	−9*	−5	−7*
	PAS	−14	−12	−3	−15	−9	+5	−2	−3

the temporal trends for these compounds are shorter and often more difficult to assess.

Three break points were identified in either the primary or annually aggregated EMEP data (in 2000 for PCB 52 at Košetice, in 2009 for PCB 101 at Stórhöfði and in 2013 for PBDE 47 at Zeppelin) and another three were identified in the MONET data (in 2015 for PBDE 100 and PBDE 154 at Råö, as well as HCB at Zeppelin). Data prior to these points were excluded from the trend analyses. The comparability of active and passive temporal trends is discussed in the following compound group subsections.

Polychlorinated biphenyls. Polychlorinated biphenyls (PCBs) were used for decades as lubricants, dielectric fluids and solvents, with production peaking in the 1970s and then generally ceasing in the 1990s. Although PCBs are still in limited use, their atmospheric levels have decreased over the globe.[7,33–36,44–47] Active EMEP temporal trends for all six indicator PCBs show statistically significant ($p < 0.05$) decreases at Birkenes, Košetice, Pallas, Råö and Zeppelin ranging from 2–20% per year. This is supported by similar and consistent decreases in the passive MONET trends for all PCBs and all sites ranging from 1–30% per year. The only exception is an increase of 9% per year in PCB 138 at Zeppelin, likely due to a high proportion of values below LOQ (27%). Passive trends are less statistically significant than the active trends due to the shorter time series, with most PCBs significantly decreasing at Birkenes, Košetice and Pallas, as well as some at the other three sites (Tables 1 and S6a†).

The agreement between the active and passive PCB trends is strong for all sites except Stórhöfði which exhibits a steeper decrease in the active trends for most PCBs by a factor of 2 or 3. Overall, the trends are consistent with previously published studies of PCBs[7,44–47] (Table S8†) with decreases ranging from 3–20% per year for the active trends and 1–30% per year for the passive trends. However, significant discrepancies are visible in the active PCB trends at Stórhöfði: PCB 28 significantly decreases, PCB 52 significantly increases, while the remaining (heavier) PCBs remain around the same constant concentration (between 0.1 and 0.2 pg m^{-3}). Although this increase observed in PCB 52 is already apparent in previous studies of Stórhöfði,[7,45–47] our analysis shows that the trend appears to begin decreasing after 2010 (though no statistically significant break point was identified). This is further supported by the passive trends, which reveal highly consistent decreases of 12–20% per year for the lighter PCBs and 9–11% per year for the heavier PCBs at Stórhöfði, similar to the trends at the other sites (Fig. 1).

Organochlorine pesticides. Organochlorine pesticides (OCPs) are a relatively heterogeneous group of compounds that were used globally in agriculture. Despite the differences in their chemical structures and use patterns, OCPs in our study (with the exception of HCB) show generally consistent annual decreases according to both the active and passive sampling data. The agreement between active and passive temporal trends is strongest for the HCHs, with decreases of 8–14% per year for the active time series compared to 3–26% per year for the passive time series. Overall, passive trends for α-HCH and γ-HCH are slightly steeper than the active trends. All decreasing HCH trends are statistically significant ($p < 0.05$) except for the passive trends at Zeppelin, likely due to large gaps in the time series (only 11 samples). These annual decreases are generally consistent with previously published trends of HCHs at the same sites (6–16% per year for α-HCH and 7–23% per year for γ-HCH; Table S8†).[7,19,45–47]

Annual changes in p,p'-DDE vary from −4% per year to +1% per year for the active time series, compared to a range of −16% per year to +5% per year for the passive time series. At sites where atmospheric concentrations of p,p'-DDE are extremely low (approximately one order of magnitude lower than HCHs at Pallas and Stórhöfði) the poorer agreement between active and passive trends may be a result of higher uncertainty in the measurements of the concentrations. The annual decreases are statistically significant at Košetice, Pallas, Råö and Zeppelin for the active time series, but just for Košetice and Pallas for the passive time series, and are consistent with previously reported decreases ranging from 1–9% per year (Table S8†) (Fig. 2).[7,19,45–47]

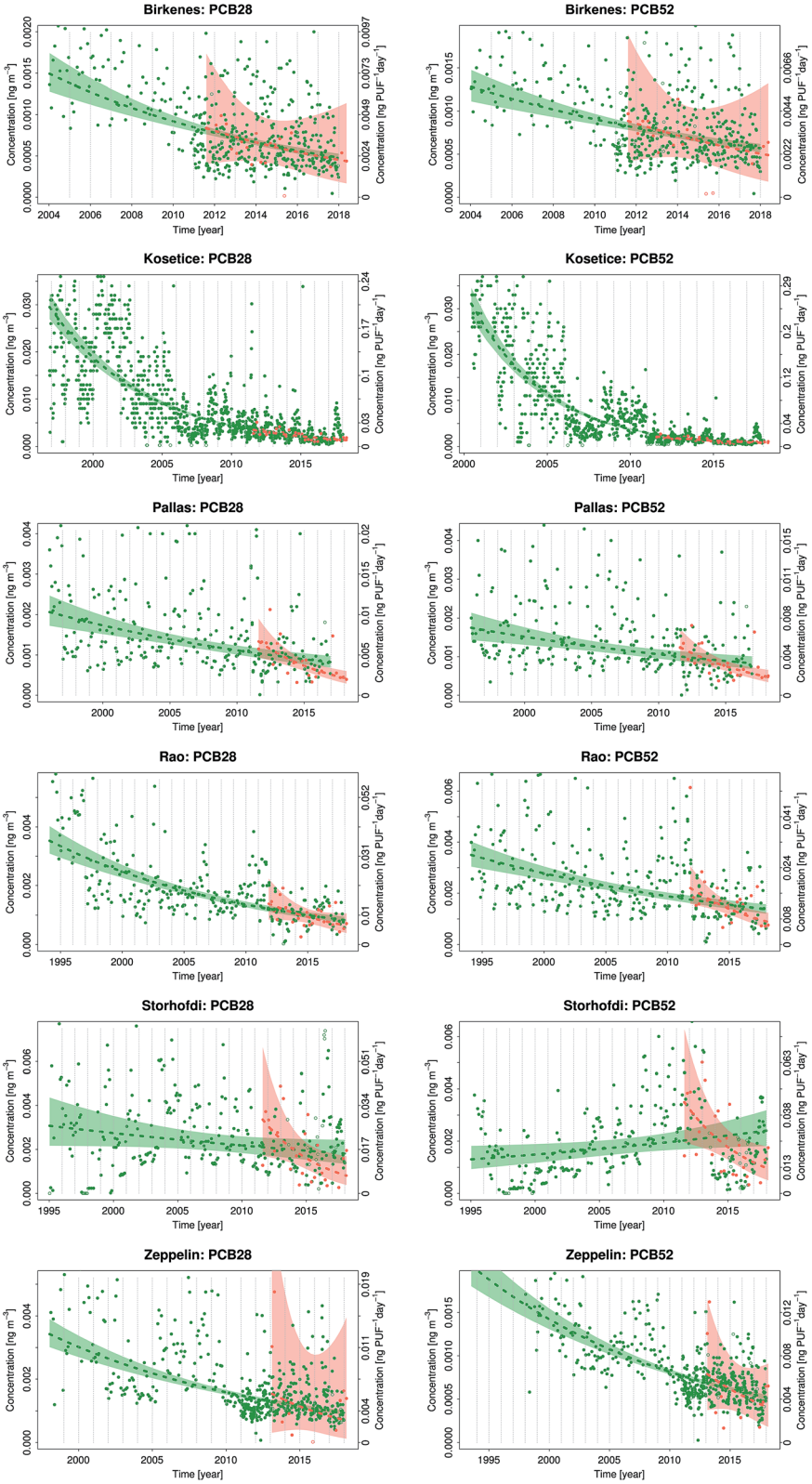

Fig. 1 Exponential active and passive temporal trends at each site for the two PCBs with the most consistent analytical detection (28 and 52). Plots for all remaining PCBs are provided in Fig. S5a.† Individual active (green) and passive (red) sampling measurements are drawn as points, with the calculated exponential trends and their 95% confidence interval shown as lines and shaded areas, respectively. The y-axis scales range from 0 to the 95th percentile of the concentrations in the dataset to remove the potential visual influence of large outliers.

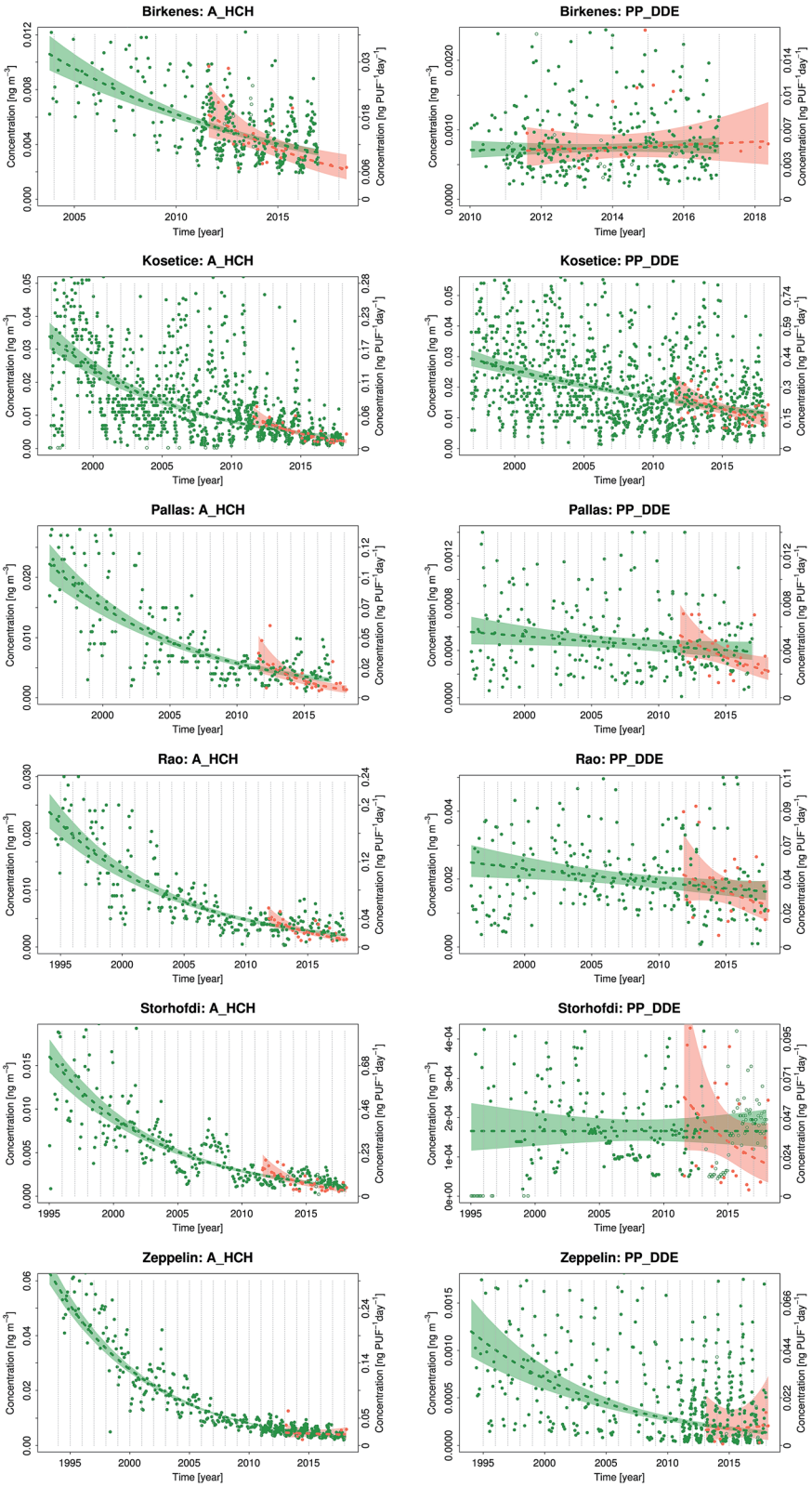

Fig. 2 Exponential active and passive temporal trends at each site for an OCP with strong agreement (α-HCH) and poorer agreement (*p*,*p*′-DDE) between active and passive sampling. Plots for all remaining OCPs are provided in Fig. S5b.† Individual active (green) and passive (red) sampling measurements are drawn as points, with the calculated exponential trends and their 95% confidence interval shown as lines and shaded areas, respectively. The *y*-axis scales range from 0 to the 95th percentile of the concentrations in the dataset to remove the potential visual influence of large outliers.

Compared to the trends among the other OCPs, trends for HCB are less consistent. The active trends show a significant decrease of HCB at Birkenes and Košetice, a significant increase at Zeppelin, and no significant changes at Pallas, Råö and Stórhöfði. Conversely, the passive trends show a significant decrease at all sites except Zeppelin which was affected by a break point late in the time series. This situation may be partially explained by the more complex behavior of HCB concentrations in the atmosphere. For example, the active time series show a clear decrease in the period before 2003 for most sites, followed by a period of stagnation up to 2010, an increase between 2010 and 2014, and then a final decrease that is also captured by the passive sampling due to its later deployment. Nevertheless, no statistically significant break points were identified in the active HCB time series.[37] These complications in HCB trend analysis have been previously reported and may be due to ongoing emissions of HCB as a combustion by-product.[45] Moreover, active HCB sampling can be biased by breakthrough,[4,46] thus the use of exponential trends applicable to the other chlorinated compounds is probably inappropriate for long-term HCB monitoring.

Polybrominated diphenyl ethers. Polybrominated diphenyl ethers (PBDEs) are a class of brominated organic compounds that have been used ubiquitously as flame-retardants in consumer products. Compared to the legacy OCPs and PCBs listed in 2001, PBDEs are 'new' POPs listed under the Stockholm Convention in 2009, after their phase-out in North America and Europe between 2004 and 2006.[48] As previously discussed, continuous active monitoring of PBDEs under EMEP began later than that of the legacy POPs, and many sites still do not monitor them. The available active monitoring data reveal significant decreases of PBDE 99 at Birkenes, Råö and Zeppelin, while PBDE 100 significantly increases at Råö and PBDE 154 significantly decreases at Zeppelin. These trends are well-aligned with previous results for PBDE 47, 99 and 100 with annual decreases of 9–27% per year at Zeppelin and Pallas (47 and 99 only at Pallas), as well as a decrease of 19% per year for PBDE 47 at Stórhöfði.[7,46,49] However, with the exception of PBDE 47 (and 99 at some sites), the atmospheric concentrations of all PBDEs were very low and often reported at levels below the analytical limits of detection/quantification. The active trends for this group of compounds are thus highly uncertain. This is mainly the case for PBDE 153 (74% of values below LOQ), PBDE 100 (62% of values below LOQ), PBDE 154 (59% of values below LOQ) and PBDE 209 (56% of values below LOQ).

Conversely, the passive data provide consistent, but generally insignificant, decreases for most PBDEs at Birkenes, Pallas, Råö and Zeppelin ranging from 1–21% per year. The only exceptions are insignificant increases of PBDE 100 at Pallas and Råö (+2% and +102% per year) and PBDE 154 at Zeppelin (+6% per year). The extremely high increase of PBDE 100 at Råö is likely due to the relatively short length of the MONET time series after the break point identified in 2015 (9 values from 2015 to 2018). Compared to the other congeners, levels of PBDE 209 appear to increase at all sites, which is consistent with the known differences in its use and emissions compared to the other PBDEs (Fig. 3).[50]

Limitations

Four broad sources of uncertainty may influence the assessment of temporal trends from air monitoring, including those affecting: (1) sampling, such as weather conditions and seasonality, as well as the regularity and duration of sampling events; (2) the sampler itself, such as artifacts and breakthrough, or insufficient sorption capacity; (3) compound analysis, such as instrumentation and detection limits; and (4) the trend analysis, such as data censoring and outliers.[4,5,19] The overall uncertainty of monitoring is most easily reduced by smoothing the possible effects of these uncertainties by assessing a sufficiently long time series. Ideally, this requires tens of samples for each time series.[29] The relatively short duration of the overlapping active and passive time series was therefore a significant limitation in this study. The shortest passive-sampling time series consisted of only 10 samples over 3 years (PBDEs 100 and 154 at Råö), while the shortest active-sampling time series consisted of 30 samples over 3 years (PBDE 209 at Pallas). Except for the two PBDEs at Råö, all time series consisting of less than 20 samples (<5 years based on 84 d passive samples) were insufficient to provide a significant temporal trend estimate. For all compounds, the addition of more samples and years of data will continue to reduce the width of confidence intervals and improve the significance of trend estimates using the methods described herein.

It is also important to reiterate that some of the time series contain left-censored data (values below the analytical LOQ). For both the active and passive time series, these missing values were substituted by one-half of the LOQ. The Theil–Sen estimator used in this study is a relatively robust method, resistant to bias up to a total of 29.3% left-censored values.[51] Only a small proportion (≤13%) of left-censored value substitutions were necessary for α-HCH, γ-HCH, HCB, PCB 28, PCB 52 and PBDE 47 for both active and passive data at all sites (except *p*,*p*′-DDE and PBDE 47 at Stórhöfði). As a result, the temporal trends for these compounds can be considered unbiased. However, censored values were more frequent (>30%) and/or of variable magnitude for some other compounds, which may have significantly affected the estimated trends. This was predominantly the case for the heavier PCBs (138, 153 and 180) at Birkenes, Pallas and Stórhöfði, as well as most of the PBDEs (except PBDE 47 and 99) at all sites. In these cases, temporal trends may have been incorrectly determined by the different magnitudes of the substituted values, with no evidence of the real atmospheric concentrations. These trends exhibit noticeably less agreement between active and passive sampling compared to those with no left-censored value substitutions.

The passive-sampling time series often provided steeper decreasing trend estimates compared to the active-sampling time series, which is apparent for most of the PCBs at all sites, all OCPs except at Zeppelin, but not for the PBDEs. This may have been due to a change in instrumentation within the MONET network from GC-MS (2011/2012) to GC-MS/MS (2013/2014 onwards). In some cases, this led to a small step-change in the censored values for some compounds due to improved limits of detection and quantification on the GC-MS/MS. The

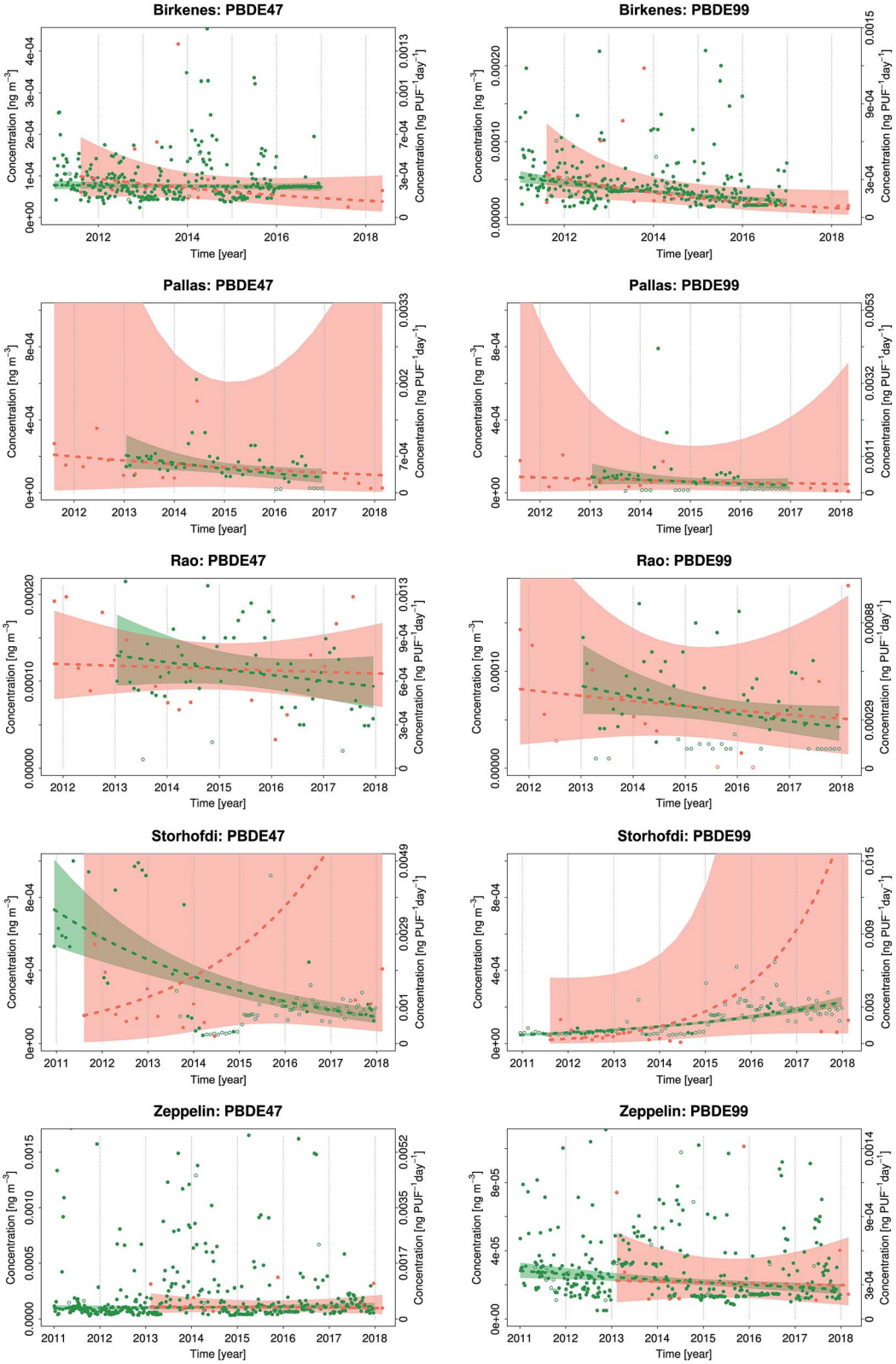

Fig. 3 Exponential active and passive time trends at each site for the two PBDEs with the most consistent analytical detection (47 and 99). Plots for all remaining PBDEs are provided in Fig. S5c.† Individual active (green) and passive (red) sampling measurements are drawn as points, with the calculated exponential trends and their 95% confidence interval shown as lines and shaded areas, respectively. Plots for Košetice are not included as no data were available. The *y*-axis scales range from 0 to the 95th percentile of the concentrations in the dataset to remove the potential visual influence of large outliers.

influence of this step-change on the estimated temporal trends could be amplified since it occurs in the initial phase of monitoring for most compounds and sites.[52]

All of these limitations can be overcome by increasing the duration of parallel active and passive monitoring and by using consistent analytical instrumentation with higher accuracy and lower limits of quantification. Considering that all of these parameters have improved during the most recent years of monitoring investigated in this study, a continued increase in the agreement between the active and passive temporal trends can be expected.

Conclusions

Fifteen years after the entry-into-force of the Stockholm Convention, the sustainability of global POP monitoring is becoming an increasingly important consideration. The original goal of the Global Monitoring Plan was to establish a few active samplers per region supported by a network of passive samplers to optimize the generation of reliable temporal data while minimizing the costs of continuous long-term monitoring.[28] The strong agreement observed between active temporal trends and the initial passive trends identified in this study supports this monitoring concept and confirms passive sampling as a suitable alternative for long-term monitoring of POPs in air. Our results may also be used as proof-of-concept validation for temporal trends generated from other passive samplers in regions where direct comparison to active sampling is not possible. However, our results indicate that passive air monitoring should span at least five years before statistically significant trend estimates can be calculated if samplers are deployed for 84 d periods. Several limitations were also identified, all of which highlight the need for longer passive-sampling time series and the importance of continuous long-term monitoring at established sampling sites with consistent laboratory analysis. Based on the length of time series from active EMEP monitoring, we recommend at least ten years of continuous sampling to determine accurate and consistent passive-sampling temporal trends for PCBs, OCPs and potentially PBDEs.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the ERA PLANET project (No. 689443) of the EU Horizon 2020 programme, the Czech Ministry of Education, Youth and Sports (RECETOX RI: LM2015051, ACTRIS_CZ RI: LM2015037) and the European Structural and Investment Funds (RECETOX RI: CZ.02.1.01/0.0/0.0/16_013/0001761, ACTRIS_CZ RI: CZ.02.1.01/0.0/0.0/16_013/0001315, and CETOCOEN PLUS: CZ.02.1.01/0.0/0.0/15_003/0000469). We thank our sampling technicians, laboratory staff and on-site monitoring partners without whom the MONET network would not be possible. We also acknowledge the Norwegian Institute of Air Research for their continued maintenance of the open access EBAS database used in this study, as well as Pernilla Bohlin-Nizzetto, Roland Kallenborn and Eva Brorström-Lundén for providing additional information about EMEP sampling sites. Access to computing and storage facilities owned by parties and projects contributing to the National Grid Infrastructure MetaCentrum provided under the programme "Projects of Large Research, Development, and Innovations Infrastructures" (CESNET LM2015042) is greatly appreciated.

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