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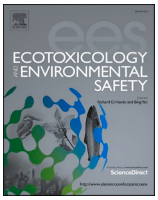

Main sources controlling atmospheric burdens of persistent organic pollutants on a national scale

Helene Lunder Halvorsen[a,b,*], Pernilla Bohlin-Nizzetto[a], Sabine Eckhardt[a], Alexey Gusev[c], Ingjerd Sunde Krogseth[a], Claudia Moeckel[a,1], Victor Shatalov[c], Lovise Pedersen Skogeng[a], Knut Breivik[a,b]

[a] *NILU - Norwegian Institute for Air Research, P.O. Box 100, 2027 Kjeller, Norway*
[b] *University of Oslo, 0351 Oslo, Norway*
[c] *Meteorological Synthesizing Centre-East, 115419 Moscow, Russian Federation*

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ABSTRACT

National long-term monitoring programs on persistent organic pollutants (POPs) in background air have traditionally relied on active air sampling techniques. Due to limited spatial coverage of active air samplers, questions remain (i) whether active air sampler monitoring sites are representative for atmospheric burdens within the larger geographical area targeted by the monitoring programs, and thus (ii) if the main sources affecting POPs in background air across a nation are understood. The main objective of this study was to explore the utility of spatial and temporal trends in concert with multiple modelling approaches to understand the main sources affecting polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in background air across a nation. For this purpose, a comprehensive campaign was carried out in summer 2016, measuring POPs in background air across Norway using passive air sampling. Results were compared to a similar campaign in 2006 to assess possible changes over one decade. We furthermore used the Global EMEP Multi-media Modeling System (GLEMOS) and the Flexible Particle dispersion model (FLEXPART) to predict and evaluate the relative importance of primary emissions, secondary emissions, long-range atmospheric transport (LRAT) and national emissions in controlling atmospheric burdens of PCB-153 on a national scale. The concentrations in air of both PCBs and most of the targeted OCPs were generally low, with the exception of hexachlorobenzene (HCB). A limited spatial variability for all POPs in this study, together with predictions by both models, suggest that LRAT dominates atmospheric burdens across Norway. Model predictions by the GLEMOS model, as well as measured isomeric ratios, further suggest that LRAT of some POPs are dictated by secondary emissions. Our results illustrate the utility of combining observations and mechanistic modelling approaches to help identify the main factors affecting atmospheric burdens of POPs across a nation, which, in turn, may be used to inform both national monitoring and control strategies.

1. Introduction

Persistent organic pollutants (POPs) are a group of organic chemicals, which mainly includes industrial chemicals and organochlorine pesticides. They are of international concern due to their slow degradation in the environment, potential to bioaccumulate through food chains, harmful effects, and ability to undergo long-range environmental transport (LRT). International agreements exist to eliminate or reduce the release of POPs into the environment (UNEP, 2018).

The atmosphere represents an important pathway of environmental transport of POPs from global source regions into background areas (Hung et al., 2010; Wania and Mackay, 1993). While temporal trends of POPs in air from remote regions are available through various international monitoring programs, e.g. in Europe (Tørseth et al., 2012) and North America (Venier and Hites, 2010), these monitoring programs are based on a limited network of conventional active air samplers (AAS). The need for trained personnel, electricity and high costs associated with AAS, may limit the use in terms of assessing the spatial variability of

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[*] Corresponding author at: NILU - Norwegian Institute for Air Research, P.O. Box 100, 2027 Kjeller, Norway.
E-mail address: hlu@nilu.no (H. Lunder Halvorsen).
[1] Present: Stockholm University, 11418 Stockholm, Sweden

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POPs in air. A complementary strategy to expand the spatial coverage, is to use passive air samplers (PAS) (Jaward et al., 2004; Shoeib and Harner, 2002). Two examples of major PAS networks are the Global Atmospheric Passive Sampling network (GAPS) (Pozo et al., 2006) and the Monitoring Network (MONET) in Europe, Africa and Asia (Holoubek et al., 2011), which both have contributed to assess spatial and temporal trends of POPs in air across the globe and on continental scales, respectively. Further examples of studies on a regional scale include case-studies in North America (Shen et al., 2005, 2006), Africa (Klánová et al., 2009), Europe (Halse et al., 2011; Jaward et al., 2004), Asia (Hogarh et al., 2012; Jaward et al., 2005), and the UK-Norway transect (Schuster et al., 2010). However, while there are examples of national monitoring efforts in individual countries like the Czech Republic (Kalina et al., 2018) and Spain (Muñoz-Arnanz et al., 2016) most case-studies target potential contaminated areas (Kurt-Karakus et al., 2018; Mari et al., 2008; Menichini et al., 2007; Wang et al., 2007; Zhang et al., 2008). The number of studies targeting the distribution of POPs across entire nations with focus on background sites remain limited. This limits our understanding of the relative significance of long-range atmospheric transport (LRAT) versus national emissions in the control of atmospheric burdens on national scales.

A complicating aspect when seeking to identify factors controlling concentrations of POPs in air, is the potential for some POPs to undergo reversible atmospheric deposition from surface media contaminated in the past (Jones, 1994; Ma et al., 2011; Wania and Mackay, 1996). Therefore, contemporary concentrations of POPs in air may in part be controlled by secondary emissions, continuing primary emissions - or both. If secondary emissions dictate atmospheric burdens across a nation, further national primary emission reductions may have a smaller effect on the reduction of national concentrations of POPs in air. As primary emissions of regulated POPs are likely to decline, the relative influence of secondary emissions will increase (Nizzetto et al., 2010). Yet, major uncertainties remain when and where this will happen for individual POPs. What is known, however, is that many POPs, and notably industrial chemicals, have a long lifetime in the anthroposphere, leading to continuing primary emissions. An example includes PCBs which have been extensively used in long-lived building materials and electrical products. Primary emissions thus remain decades after production has been banned, particularly because significant emissions largely occur during the waste stage (Breivik et al., 2016; Li and Wania, 2018). Hence, the immediate impact of the Stockholm Convention on temporal trends of POPs in air has been questioned (Wöhrnschimmel et al., 2016).

In spite of international agreements, there is still a need to assess further measures to protect human health and the environment from POPs. To inform policy makers in individual countries, there is a need for methodologies which may both help to better (i) identify the main sources controlling atmospheric burdens and (ii) evaluate the efficacy of any national monitoring strategies.

The key objective of this study is to apply and evaluate a methodology using measurements and models in concert to assess the relative importance of primary emissions, secondary emissions, LRAT and national emissions in controlling atmospheric burdens of individual POPs across a nation. For this purpose, a passive air sampling campaign was carried out, mapping concentrations of POPs in background air across Norway (Fig. 1). The focus on data-rich legacy POPs is a deliberate restriction as this allows us to (i) address chemicals which have seen significant historical use, both within and outside the country, (ii) compare our findings with studies carried out in the past, including long-term national monitoring efforts, and (iii) parameterize, evaluate and apply two existing models to help identify the main factors controlling atmospheric burdens.

While this study was carried out in Norway, the methodology may help inform monitoring programs in other countries, and ultimately guide opportunities for further control strategies, nationally and/or internationally.

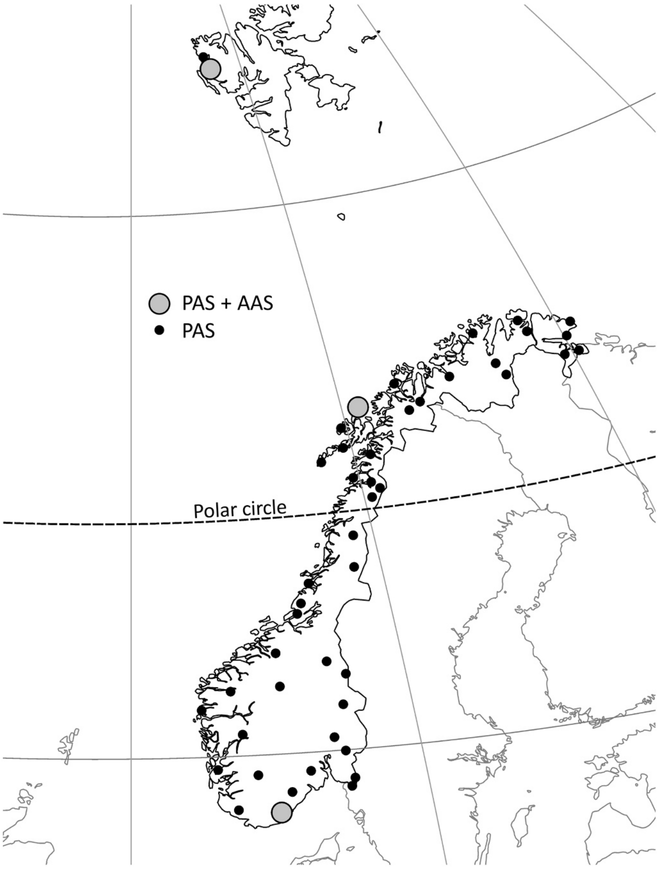

Fig. 1. The spatial coverage of sites monitoring POPs with AAS (grey) in the national monitoring program (Bohlin-Nizzetto et al., 2017) and the spatial coverage of sites measuring POPs with PAS (black) in this study.

2. Materials and methods

2.1. Sampling

In our study, air samples were collected across Norway (58°N to 79°N, 5°E to 31°E), using the same passive air samplers as within the MONET program (Kalina et al., 2017; Markovic et al., 2015), with polyurethane foam (PUF) as sampling medium, and with the same theoretical principles as described by Harner et al. (2004). The PUF disks were spiked with a performance reference compound (PRC) mixture (SI 1.1.3) for assessing sampling rate variability from site to site.

A total of 47 PUF-PAS were deployed for three months during summer 2016 (Fig. 1), at 45 remote sites (ranging from 58°N to 71°N) on mainland Norway, and two pristine sites on Svalbard (79°N). In addition, PUF-PAS were concurrently deployed at ten urban sites around the city of Oslo (60°N), to compare background concentrations with measurements from an area expected to be more influenced by local emissions. The obtained concentrations where compared to concentrations from AAS at three monitoring sites in the national monitoring program (Fig. 1) (Bohlin-Nizzetto et al., 2017). More details on the sampler preparation, deployment and exact locations of the sampling sites are given in the Supporting Information (SI).

2.2. Sample extraction and clean-up

At the end of the deployment period, the PUF-PAS were retrieved and returned to the laboratory at NILU - Norwegian Institute for Air Research. Details of sample extraction and clean-up are given in SI 1.2.

2.3. *Instrumental analysis*

The samples were analyzed for 31 polychlorinated biphenyls (PCBs), including six indicator PCBs (PCB-28, -52, -101, -138, -153 and -180), and 29 organochlorine pesticides (OCPs). The OCPs included penta- and hexachlorobenzene (PeCB/HCB), hexachlorocyclohexanes (HCHs), DDTs, chlordanes (CD), aldrin, endosulfans and their metabolites. Identification and quantification were carried out using a gas chromatograph (GC) coupled to a high-resolution mass spectrometer (HRMS). Details of the instrumental analysis and a list of all target compounds are given in (SI 1.3, Table SI-1.3b-c).

2.4. *Quality assurance/quality control*

Five method blanks and three field blanks were extracted and analyzed in the same way as the exposed samples (SI 1.4.1). All blanks had comparable levels and were used to calculate the method detection limit (MDL) (Table SI-2.1).

Of the 60 targeted analytes, only the analytes with high detection frequency ($>$ 60% above MDL) have been evaluated in this study, i.e. 18 PCBs and 14 OCPs. The average concentrations of these selected analytes in background air exceeded the MDLs by a factor of 2–185. Concentrations below MDL were set to ½ MDL for the calculation of sum, average and median, and for the statistical analysis.

In addition to using ^{13}C-labelled internal standards (SI 1.4.2) to compensate for possible loss during sample preparation, three PUFs spiked with a ^{12}C-mixture of all target analytes were analyzed for method quality control (bias $-2\%-6\%$ for PCBs and $-13\%-16\%$ for OCPs, SI 1.4.3). In order to evaluate the reproducibility of the PAS method, two PUF-PAS were co-deployed at three sites (relative standard deviation 0–16% for PCBs and 0–17% for OCPs, SI 1.4.4).

2.5. *Deriving concentrations in air*

Concentrations of POPs in air were estimated from the amounts found in the samplers and the widely used template of Harner (2017). The uncertainties and semi-quantitative nature of PUF-PAS has been a topic of several publications (Bohlin et al., 2014; Holt et al., 2017; Kalina et al., 2017; Melymuk et al., 2014; Wania and Shunthirasingham, 2020). Studies show that PUF-PAS is a useful tool for compounds with similar volatility range, such as the PCBs and OCPs targeted in this study. In our study, the uncertainties were minimized by using PRCs and site-specific environmental conditions in estimating site-specific sampling rates, as recommended by the PAS community.

The PUF-characteristics, air temperature at each site (4–16 °C, average: 12 °C), measured loss of PRCs and their temperature-adjusted octanol-air partition coefficients (K_{OA}), were used to calculate site-specific sampling rates (2.8–4.5 m^3/day, average: 3.6 m^3/day) and to derive actual air concentrations (SI 1.5). This approach is described in detail by Moeckel et al. (2009). Compounds with low K_{OA} (e.g. HCB, PCB-18 and -28), will approach equilibrium between the PUF-PAS and the air during the deployment period in this study. This means that the uptake is not gradually increasing during the whole sampling period as predicted by the template (Harner, 2017) and that the PAS does not provide a true time-averaged concentration (Wania and Shunthirasingham, 2020). Underestimation of the concentrations in air for these compounds might therefore be possible.

2.6. *Data analysis*

The ratio between maximum and minimum concentrations in air (MMR) was used as a simple measure of the spatial variability, as utilized in e.g. Halse et al. (2011) and Jaward et al. (2004). Outliers outside the maximum according to a boxplot of the concentrations are excluded, as described in SI 1.6.1. When samples below MDL are present, MDL is used as the minimum value.

To further assess the variability across the study region, possible latitudinal gradients, differences in background concentration levels between southern- and northern Norway (divided by the Polar circle), and changes over the last decade were examined.

All statistical analyses (linear correlation, significance) were performed by using R Studio V1.1 as described in SI 1.6.

2.7. *Atmospheric transport modelling tools*

The Global EMEP Multi-media Modeling System (GLEMOS, 2020) developed by the Meteorological Synthesizing Centre - East under the European Monitoring and Evaluation Programme (EMEP), was used to evaluate whether the observed spatial patterns of PCB-153 can be reproduced by the model. Further, GLEMOS was used to predict the contributions attributed to the four source categories examined. The GLEMOS model predicts both the contributions of primary- and secondary emissions. While GLEMOS separates between contributions from primary emissions, whether attributed to national emissions or LRAT (within/outside the EMEP domain), the origin of secondary emissions is not defined. The contributions from primary emissions alone were further predicted by the Lagrangian particle dispersion model, FLEXPART V10.4 (Pisso et al., 2019). The model analysis does not include potential emissions of PCB-153 from wildfires (Eckhardt et al., 2007). The spatial resolution of GLEMOS was 0.4° x 0.4° within the EMEP domain, and 1° x 1° outside EMEP. As the model is gridded, the size of individual grid cells (0.4° x 0.4°) varies latitudinally from 1056 km^2 (58°N) to 352 km^2 (79°N). The spatial output resolution of FLEXPART was 1° x 1°. Both models generated predictions for each individual site, corresponding to the actual deployment periods. Further details of the modelling tools are given in SI 1.7.

3. Results and discussion

A summary of the calculated concentrations in air, method detection limits and MMRs of selected POPs in air at Norwegian background sites (including Svalbard) are presented in Table SI-2.1, and a more detailed discussion of the occurrence of the selected POPs is given in SI 2.1. Data for all target analytes at the individual sites are included in Table SI-2.2a-b.

For comparison, Table SI-2.3 shows literature data for background sites in other mapping studies of POPs with PUF-PAS on a regional/global level, and a more thorough comparison with the urban area is given in SI 2.2.

3.1. *PCBs*

18 PCB congeners were detected in more than 60% of the samples. The average concentrations of $\sum_{18}$PCBs from the background sites were 5 pg/m^3 (2–13 pg/m^3) and $\sum_6$PCBs 2 pg/m^3 (1–6 pg/m^3). The concentrations of $\sum_6$PCBs in air are in the lower range of the concentrations found in other studies using PUF-PAS from the last 20 years on a regional or global scale (2–121 pg/m^3, Table SI-2.3) (Gioia et al., 2007; Halse et al., 2011; Jaward et al., 2004; Pozo et al., 2009). The concentrations reported herein are also in the lower range of the more recent studies on a national level, e.g. $\sum_6$PCBs in air across Czech Republic that ranged 11–60 pg/m^3 (Kalina et al., 2018), Turkey that ranged 5.6–47 pg/m^3 (Kurt-Karakus et al., 2018) and Spain where $\sum_{18}$PCB ranged 0.1–386 pg/m^3 (of which 86% consists of Σ_6PCBs) (Torre et al., 2016).

However, the average concentration for $\sum_6$PCBs in air within the urban area included in this study was 23 pg/m^3 (ranging from 5 to 42 pg/m^3), which is approximately ten times higher than in Norwegian background air and more similar to the concentrations in Czech Republic and Turkey.

The concentrations of $\sum_6$PCBs in 2016 were significantly reduced (by ca. 50%) compared to the concentrations in 2006 from the same sites (Table 1). This decline is in agreement with a declining trend from 2006

Table 1

Percentage change in concentrations in air of selected PCBs, OCPs and relevant isomer-ratios since 2006. The difference in concentrations at each site was used in the calculation of p-values. P-values less than 0.05 (bold) indicate a significant increase or decrease for all sites combined.

Site	Zeppelin[a]	Birkenes[a]	Hurdal[a]	Kaarvatn[a]	Tustervatn[a]	Karasjok[a]	Oslo[b]	P-value[c]
$\sum_6$PCBs	–48%	–32%	–69%	25%	–31%	–60%	–52%	**0.016**
PCB-28	–57%	–44%	–63%	–21%	–44%	–64%	–41%	**0.008**
PCB-153	–10%	–28%	–78%	116%	33%	–53%	–42%	0.078
HCB	30%	85%	50%	146%	132%	58%	59%	**0.008**
$\sum_3$DDXs	–77%	48%	–18%	7%	–43%	–51%	–11%	0.19
α-HCH	–21%	–8%	–36%	43%	10%	–17%	–46%	0.078
γ-HCH	–3%	5%	–27%	98%	–4%	–23%	–33%	0.23
$\sum_2$HCHs	–19%	–3%	–32%	63%	7%	–18%	–39%	0.23
$\sum_4$Chlordanes	–46%	26%		100%	38%	–53%		0.41

[a] Halse et al. (2011).

[b] Halse et al. (2012), 2016-data based on the average for the urban sites.

[c] Two-sample Wilcoxon, paired, 1-sided.

to 2016 of PCBs in Norway and the Norwegian Arctic as reported within the national air monitoring program using AAS (Bohlin-Nizzetto et al., 2017; Hung et al., 2016).

The most abundant PCBs were PCB-18 (17%), PCB-52 (14%), PCB-28 (10%), PCB-31 (10%) and PCB-101 (10%), with the contribution to the average concentration of $\sum_{18}$PCBs given in parentheses. $\sum_6$PCBs contributed 44% to $\sum_{18}$PCBs, and the contribution of each of the six indicator PCB congeners to $\sum_6$PCBs is given in Figure SI 2.1. The abundances generally reflect the dominance of these specific PCB congeners in technical PCB mixtures (Breivik et al., 2007), but with a higher relative abundance of the more volatile tri- and tetra-CBs.

Spatial differences in the influence of LRAT and national emissions were anticipated as Norway is geographically located along an expected pollution gradient from south to north (58°N to 79°N). The spatial distribution of concentrations of $\sum_6$PCBs in air is shown in Fig. 2a. Large differences in concentrations within a region suggest that local atmospheric primary- and/or secondary emissions are influencing the atmospheric concentrations (Jaward et al., 2004). The MMRs of the six indicator PCBs detected at all sites varied between 3 and 4 (Table SI-2.1). The highest concentrations were generally observed in southern Norway while the lowest were observed in Northern Norway (Fig. 2a). The exception is the eastern-most part of northern Norway where elevated concentrations of $\sum_6$PCBs were observed (2.2–4.1 pg/m^3), comparable to the southern-most sites. This part is close to the Kola peninsula, a highly industrialized area considered to be a source region for many different environmental pollutants (Berglen et al., 2015; Polder et al., 2008; Sandanger et al., 2013; Tørseth and Semb, 1998).

The obtained MMRs in Norway (Table SI-2.1) are small compared to the MMRs in Europe (35, 25, 84, 102, 87 and 122 for PCB-28, -52, -101, -138, -153 and -180 respectively) in the study by Halse et al. (2011). MMR of $\sum_6$PCBs from the background sites within the southern Norway region (5) does not differ significantly from MMR within the northern region (4), despite that southern Norway is more densely populated. These findings suggest a limited importance of local sources at background sites in our study. The declining trend of $\sum_6$PCBs with latitude (p-value 0.03, r −0.33) and significantly higher levels in southern Norway (one-sided p-value < 0.05), point towards an enhanced influence from source areas in this region. Source regions in Europe are identified to exist (Breivik et al., 2007). This, combined with differences in MMRs between Norway and Europe indicates that the occurrence of PCBs in Norway may be influenced by source regions in Europe.

Minor differences in the spatial patterns for the individual congeners were expected, due to differences in LRAT potential (Beyer et al., 2003). In our study, concentrations of PCB-153 significantly decreased with latitude (p-value 0.0016, r −0.46) and were significantly higher (by a factor of two) in southern Norway than in northern Norway (p-value 0.022). The concentrations of a more volatile congener, PCB-28, showed no significant correlation with latitude (p-value 0.16, r −0.21). However, the local contribution in the eastern-most part of northern Norway was prominent for the concentrations of PCB-28 (Figure SI-2.2a). Consequently, the correlation with latitude was significant also for PCB-28 (p-value 0.020, r −0.37) when disregarding samples from this area. The LRAT potential is limited by a combination of net atmospheric deposition and reactivity of the PCB congener in air (Beyer et al., 2003). Both processes are strongly affected by temperature. While colder air temperatures favor atmospheric deposition, higher temperatures favor atmospheric reaction. Our study was carried out during summer, with average temperatures during the sampling period ranging from 4° to 16 °C (Table SI-1.6), declining with latitude (r −0.70). Taken together, this suggests that the observed reduction in concentrations of PCB-153 with latitude may be better explained by atmospheric deposition, rather than atmospheric reaction. Removal by atmospheric reactions, on the other hand, is likely to have a greater relative importance for PCB-28 (Wania and Daly, 2002).

The dominance of LRAT in Norway was also evident in the studies of Halse et al. (2012) and Schuster et al. (2010). The statistical analysis suggested that there were no significant changes in spatial patterns of PCB-28 or PCB-153 over the last decade (Figure SI-2.4). A halving of the MMR of PCB-153 from 2006 to 2016 (Table SI-2.4), indicates that the influence from primary sources may have decreased, but there was no significant decline in the concentrations of PCB-153 (Table 1) supporting this indication. Altogether, this suggests that the sources of PCB-28 and PCB-153 in 2006 and 2016 are comparable.

A comparison of the concentrations obtained by the PUF-PAS and conventional AAS (Bohlin-Nizzetto et al., 2017) are provided in Table SI-2.5 and Figure SI-2.5. The PUF-PAS resulted in higher concentrations of most PCB congeners at Birkenes and Andøya while the tri- and tetra-CBs were lower with PUF-PAS than AAS at Zeppelin. At Birkenes, the percentage deviation relative to AAS results varied from −58% up to −150% for 17 of the PCBs. A larger negative deviation was observed at Andøya (−139% up to −473%), where the concentrations from PUF-PAS most likely are overestimated as a consequence of underestimated sampling rate due to wind effects (SI 1.5.5). At Zeppelin, negative deviation values (−24% up to −122%) were observed for the penta-, hexa- and hepta-CBs, while positive deviation values were observed for tri- and tetra-CBs (+24% up to +86%). Both data sets also report high detection frequency of tri-CBs. PCB-180, the least volatile indicator PCB, contributed to the same extent to $\sum_6$PCBs in the passive air samplers as in the high-volume AAS confirming the utility of PAS for PCBs in air. The national monitoring using AAS shows that the concentration of $\sum_6$PCBs is almost a factor of three higher at Birkenes (southern Norway) than at Andøya (northern Norway) (Bohlin-Nizzetto et al., 2017). Both the observation of higher $\sum_6$PCBs concentrations in southern Norway and low spatial variability are consistent with our data using PAS. This suggests that the data from the existing monitoring stations in Norway largely explain the spatial variability of PCBs in air across Norway. However, elevated concentrations in hotspots/source

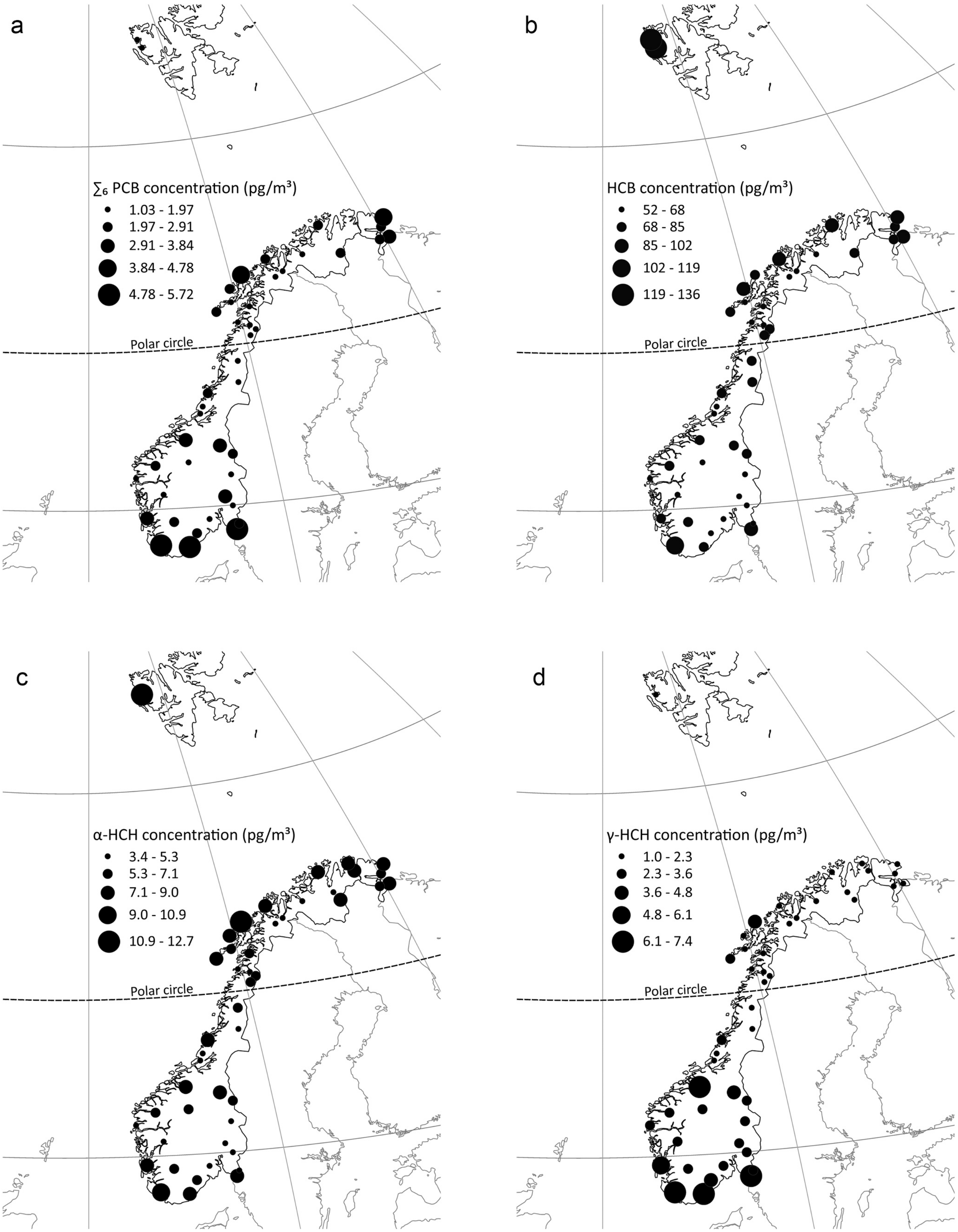

Fig. 2. (a)-(d): Concentrations of $\sum_6$PCBs(a), HCB (b), α-HCH (c) and γ-HCH (d) at 45 remote sites (ranging from 58°N to 71°N) and two pristine sites on Svalbard (79°N). Exact locations of the background sites are given in Table SI-1.1. Data for all target analytes at the individual sites, including the ten urban sites around Oslo (60°N) are included in Table SI-2.2a-b.

areas like urban areas and industrial sites are not captured by the background monitoring sites.

3.2. OCPs

Among the targeted 29 OCPs, only 14 OCPs were detected in more than 60% of the samples. These included PeCB/HCB, α-/γ-HCH ($\sum_2$HCHs), p,p′-DDE/o,p′-DDT/ p,p′-DDT ($\sum_3$DDXs), chlordanes (i.e. trans-/cis-Chlordane/-Nonachlor), Heptachlor-exo-epoxide, Dieldrin and Endosulfan I. Except for HCB, the OCP concentrations (< MDL-13 pg/m^3) are generally in the lower range of concentrations found in other studies using PUF-PAS (Table SI-2.3). The highest average concentrations of OCPs in this study were observed for HCB (75 pg/m^3) and PeCB (22 pg/m^3), followed by α- and γ-HCH, Endosulfan I and Dieldrin (2–7 pg/m^3). The concentrations of HCB, HCHs and DDXs were, like the PCBs, in agreement with active air measurements in the national air monitoring program (Bohlin-Nizzetto et al., 2017) (Table SI-2.5). The PAS resulted in higher concentrations for all OCPs at all three sites. At Birkenes and Zeppelin, the percentage deviation of PAS relative to AAS varied from −55% up to −178% for all OCPs. Similar to the PCBs, the largest negative relative deviations were observed at Andøya, which varied from −241% up to −500% for all OCPs. This is most likely caused by poor performance of the PAS under the high wind speeds at Andøya.

The concentrations of HCB in our study were in the upper range of the concentrations reported in other studies (Table SI-2.3), with the highest concentrations of HCB observed in the Norwegian Arctic (130–136 pg/m^3). While the HCHs, DDXs and chlordanes did not show any significant change in concentrations between 2006 (Halse et al., 2011) and 2016 (Table 1), the concentrations of HCB were similar or higher (up to a factor of 2.5) than the concentrations measured at the same sites a decade ago. This suggests increasing HCB concentrations in this region. High concentrations of HCB as well as increasing concentrations of HCB in the Arctic during the same decade have also been reported under the Arctic Monitoring and Assessment Programme (AMAP) (Bohlin-Nizzetto et al., 2017; Hung et al., 2016). Re-emissions due to increased temperatures and e.g. reduced sea ice coverage has been put forward as one explanation (Hung et al., 2010; Ma et al., 2011). One reason for apparent lower concentrations in warmer regions (Table SI-2.3), may be that HCB, due to its low K_{OA} that decreases with temperature, has entered the curvilinear uptake phase during the deployment period. Assuming linear uptake for all the deployment time may have lead to an overestimation of the effective air sample volume and hence an underestimation of the concentrations in air is likely.

The spatial patterns of selected OCPs are presented in Fig. 2b-d. The MMRs varied between 2 and 7 for the compounds detected at all sites (Table SI-2.1). The low spatial variability indicates that LRAT is the main source for these OCPs in Norway.

Despite the low spatial variability for most OCPs, there are some differences for individual OCPs. Similar to the PCBs, these differences are likely influenced by differences in LRAT potential (Beyer et al., 2003). The OCPs with highest volatility, e.g. the chlorobenzenes and HCHs, have low MMRs (2–4). There is no significant difference between the concentrations of HCB in southern Norway (52–103 pg/m^3) and northern Norway (52–136 pg/m^3) (p-value 0.35), nor between the background sites (52–136 pg/m^3) and the urban sites (45–85 pg/m^3) (p-value 0.48). The consistent concentrations of HCBs across Norway testifies that atmospheric burdens are controlled by LRAT. This has also been shown on regional levels (Jaward et al., 2004; Koblizkova et al., 2012). As HCB is both relatively volatile and very persistent in the atmosphere, it is not possible to make any inferences about the likely source regions on the basis of data presented herein. The concentrations of α-HCH (4–13 pg/m^3) were also uniformly distributed across the study region (south/north p-value 0.35, urban sites 3–8 pg/m^3). However, the concentrations of the γ-isomer were significantly higher in southern Norway than in northern Norway (p-value < 0.001). Consequently, the α/γ-HCH ratio in northern Norway (4) was significantly higher compared to southern Norway (2). Even lower ratios than 2 are observed at more southern sites in continental Europe (Halse et al., 2011; Aas and Bohlin-Nizzetto, 2018), as a consequence of higher concentrations of γ-HCH. The south-north differences of the α- and γ-isomers may reflect that the γ-isomer is more prone to wet deposition than the α-isomer during atmospheric transport (Shen and Wania, 2005), but also the proximity of southern Norway to historical source regions of γ-HCH (Breivik et al., 1999).

The concentrations of $\sum_4$Chlordanes or Heptachlor-exo-epoxide did also not differ significantly between southern and northern Norway (p-value 0.48 and 0.12, respectively). On the other hand, the concentrations of the less volatile OCPs, e.g. $\sum_3$DDXs and Endosulfan I, were significantly higher in southern Norway than northern Norway (p-value < 0.001 and 0.027, respectively), and showed the highest MMRs of the OCPs (6 and 7, respectively). The spatial patterns were similar for all the three individual DDX-isomers. Elevated concentrations of Dieldrin were also found in the south (p-value 0.019).

Concentrations of Endosulfans in background air were dominated by Endosulfan I, and Endosulfan II was only detected in 5% of the samples. This pattern could be expected as the composition of the technical mixture is 70:30 Endosulfan I: Endosulfan II. Secondly, Endosulfan II is more water-soluble than Endosulfan I (Shen and Wania, 2005) and thereby more easily washed out from the atmosphere, i.e. Endosulfan II is less prone to LRAT. Finally, it has also been reported that Endosulfan II is converted to Endosulfan I in environmental matrices (Schmidt et al., 1997; Weber et al., 2010).

The relative abundance of parent and metabolite compounds can be used to evaluate possible recent use of OCPs like DDTs (Pozo et al., 2009; Su et al., 2008). The p,p′-DDE/p,p′-DDT ratio was high (2–5) for all sampling sites, indicating influence from aged DDT. The high ratio may however also be caused by a higher volatility of p,p′-DDE than p,p′-DDT (Ricking and Schwarzbauer, 2012), resulting in higher mobilization of p,p′-DDE from source areas (e.g. contaminated soil) to air. The high ratio, together with dominance of other transformation products/metabolites indicative of past usage, i.e. oxy-chlordane, heptachlor-exo-epoxide and dieldrin, may suggest that secondary sources are important for the occurrence of other OCPs in the Norwegian atmosphere. Given that trans-Chlordane degrades more easily in the environment than cis-Chlordane, the low trans-CD/cis-CD ratio (< 1) substantiates that the levels of Chlordanes are mainly due to previous use (Bidleman et al., 2002; Harner et al., 2004).

Norway comprises both areas dominated by coastal and by inland climate. It has previously been established that oceans are major reservoirs of α-HCH (Jantunen and Bidleman, 1996; Macdonald et al., 2000). In a study by Shen et al. (2004) on HCHs in air across Northern America, elevated concentrations of α-HCH were observed in air at coastal sites, reflecting re-emissions from the sea. A similar finding has been reported in Norway (Halse et al., 2012). Figure SI-2.7 shows that the concentrations of α-HCH in air at coastal areas in our study are significantly higher (p-value 0.04) than in inland areas. This indicates a possible difference in secondary emissions from marine and terrestrial pollutant reservoirs, respectively.

3.3. Model predictions of PCB-153

3.3.1. Evaluation against observations

The map in Fig. 3 illustrates the observed spatial pattern of PCB-153 in concert with the reproduction by GLEMOS. In general, GLEMOS largely captures the observed PCB-153 concentrations; 75% of the predicted concentrations were within a factor of three of the observations (Figure SI-2.15 a). For FLEXPART, 80% were within a factor of three of the observations (Figure SI-2.15 b). Both models underestimate concentrations in air. This may in part be due to differences and large uncertainties in primary emissions used as input to the models. In FLEXPART, the European emissions were 3 kt, based on data from a global emission inventory (Breivik et al., 2007), while for GLEMOS

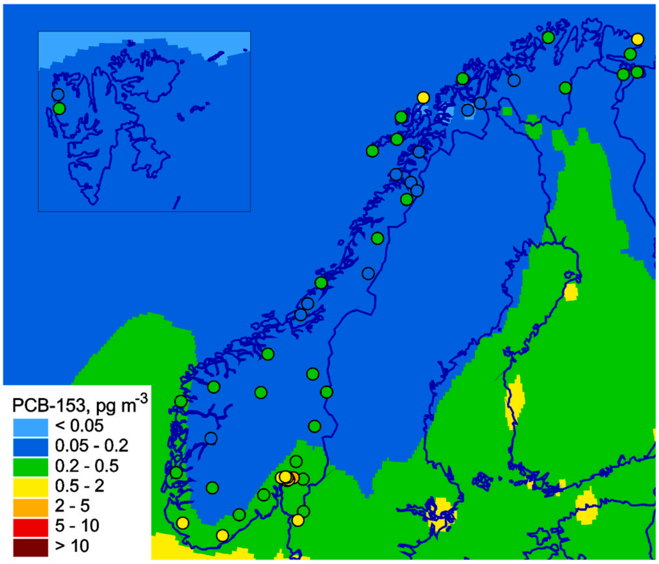

Fig. 3. The observed spatial pattern of PCB-153 across all Norwegian sites (dots) in concert with concentrations predicted by GLEMOS (colored background). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

primary emissions of 1 kt were used as input. In contrast to FLEXPART, GLEMOS relies on national emission data whenever available, complemented with data from the global emission inventory for gap filling whenever official data is lacking. Hence, differences in predicted concentrations were anticipated. This may also help to explain why FLEXPART predicted higher concentrations than GLEMOS in 61% of the cases (Figure SI 2.15c).

However, the FLEXPART predicted concentrations of PCB-153 in air at Svalbard (0.02 pg/m^3) were more than a factor of three lower than both the measured concentrations (Figure SI-2,15b) and the concentrations predicted by the GLEMOS model (Figure SI-2.15c), in spite of using higher emissions as model input. FLEXPART furthermore predicts a higher spatial variability (MMR = 27) than both observed (MMR = 4) and predicted by GLEMOS (MMR = 6). Possible explanations could be that FLEXPART overestimates atmospheric loss processes during LRAT, e.g. atmospheric reaction, and that it ignores secondary emissions.

3.3.2. Predicted sources and source regions

As climatic conditions in Norway are highly variable, e.g. between high and low latitudes, the relative significance of primary- and secondary emissions may vary spatially. GLEMOS predicted secondary emissions to be approximately four times more important (82%, median value) than primary emissions of PCB-153 at all Norwegian background sites combined (Fig. 4). Table SI-2.6 shows the predicted source contributions to the concentrations of PCB-153 (in %) from secondary- and primary emissions for each site. Differences in source contributions to the concentrations of PCB-153 in southern- and northern Norway, are illustrated by the southern site 49 (0.78 pg/m^3) and the northern site 23 (0.13 pg/m^3), in Figure SI-2.16a and 2.17a. Contribution from secondary emissions were dominating at both sites (83% and 77%, respectively).

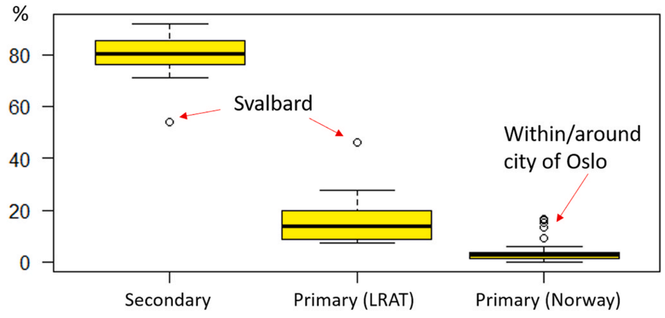

Fig. 4. Predicted contributions from primary and secondary emissions controlling atmospheric burden of PCB-153 across all Norwegian sites. Data represent the distribution of predictions by GLEMOS.

The median contribution from primary emissions was predicted to be 17% across all background sites, mostly attributed to LRAT (15%). Hence, the predicted median contribution from national emissions was only 2% for the background sites. As the spatial variability predicted by GLEMOS (MMR = 6) was comparable to observations (MMR = 4), this provides a strong argument for secondary emissions (whether domestic or not) and LRAT being highly influential.

GLEMOS predicted that LRAT due to primary emissions from western Europe (e.g. UK, Germany and France) were more influential in southern Norway (site 49) than in northern Norway (site 23). The predicted source regions are in accordance with model predictions from FLEXPART (Figure SI-2.16b). GLEMOS further predicted that the primary source contribution from Sweden (1%), Finland (2%) and non-EMEP countries (10%) were higher for the site in northern Norway, compared to the site in southern Norway (0%, 0% and 3% respectively). The predicted relative contributions from primary emissions at the eastern-most part of northern Norway using GLEMOS (e.g. site 12 Figure SI-2.18a-b), were dominated by non-EMEP countries (6%), followed by Russia (3%), and may explain the somewhat elevated concentrations observed in this region (Fig. 3).

GLEMOS predicted secondary emissions to be least important for PCB-153 at Svalbard in relative terms (54% for site 96, Figure SI-2.19a). While the absolute contribution from primary emissions is comparable to other Norwegian sites, this suggest secondary emissions are far less influential in absolute terms, compared to the other sites discussed. Interestingly, the relative contribution from primary emission sources outside EMEP (42%) is also predicted to be higher than at any of the other Norwegian sites (2%–16%).

3.3.3. Spatial variability in an urban area

The measured concentrations of PCB-153 in the urban area (one of the ten urban samples was excluded due to contamination during deployment) (Figure SI-2.12) ranged from 0.57 to 6.2 pg/m^3, and hence the spatial variability within the urban area was higher (MMR=11) than for the background sites (MMR = 4). The median concentration of PCB-153 in the urban area was eight times higher than all the background sites combined. However, the GLEMOS predicted concentrations within the city of Oslo were generally underestimated and did not show any variability (0.33–0.37 pg/m^3, dark blue, Figure SI-2.15a). This could be expected as GLEMOS is not designed to accurately resolve urban-rural gradients at a fine spatial resolution. Secondly, the sampling strategy in Oslo was targeting urban areas, rather than individual model grid cells. Hence, the measurements are probably biased towards areas with elevated emissions, while the predicted concentrations are based on emissions averaged over larger areas in the model.

Despite this, the model predicted the highest contribution from primary emissions in the urban area (23% on average) and at two sites in the vicinity of Oslo (sites 54 and 55). The contribution from national primary emissions was predicted to be 16%, compared to 2% for the background sites, suggesting local sources in the urban area.

4. Conclusions

The results of this multi-sited passive air sampling campaign are consistent with data reported from active air measurements from the national monitoring program. This suggests that the existing background monitoring stations largely capture the spatial variability of most of the selected POPs across Norway. A larger spatial variability was observed in some specific regions (the city of Oslo and north-eastern

Norway). Elevated concentrations in the urban area may also call for complementary monitoring efforts in source regions.

Minor temporal changes were observed for most POPs when compared to concentrations measured a decade ago. This is also in line with the national monitoring program. A less noticeable decline in air concentrations of POPs has been reported in recent years, despite a reduction in primary emissions. This may be due to an increasing influence of secondary emissions from reservoirs contaminated in the past. This aligns well with measured isomeric ratios which indicated weathered signals.

The results indicate dominance of LRAT in this region as i) the spatial variability is limited for most of the targeted POPs, ii) the concentrations of the POPs in background air are low, and iii) there is a typical south-north gradient of less volatile compounds prone to wet deposition (e.g. γ-HCH, DDXs and Endosulfan I).

Model predictions for PCB-153 by two different atmospheric transport models (GLEMOS and FLEXPART) indicated that LRAT mainly originates from western Europe. The GLEMOS model predicted further that secondary emissions of PCB-153 dominated (54%–92%) across the whole study area.

Though GLEMOS predicted the relative importance of primary emissions, secondary emissions, LRAT and national emissions, these results are restricted to PCB-153. The predicted spatial patterns need to be confronted with measurements to evaluate whether models obtain satisfactory results. Nonetheless, this example illustrates that a combination of spatial mapping using PAS and mechanistic modelling may provide valuable insights into the main sources controlling atmospheric burdens of PCB-153 on a national scale which cannot be readily inferred from measurements alone. The methodological approach explored in this study may be further developed and used to inform national monitoring efforts in countries other than Norway and for chemicals other than PCB-153.

CRediT authorship contribution statement

Lunder Halvorsen, H: Methodology, Validation, Formal analysis, Investigation, Writing - original draft, Project administration, Visualization. **Bohlin-Nizzetto, P:** Methodology, Validation, Writing - review & editing, Supervision. **Eckhardt, S:** Formal analysis, Writing - review & editing, Visualization. **Gusev, A:** Formal analysis, Visualization. **Krogseth, IS:** Investigation, Writing - review & editing. **Moeckel C:** Validation, Formal analysis, Investigation, Writing - review & editing, Visualization. **Skogeng, LP:** Investigation. **Shatalov, V:** Formal analysis, Visualization. **Breivik, K:** Conceptualization, Validation, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2021.112172.

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