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TECHNICAL REPORT

Organic Compounds in the Environment

Local variability in snow concentrations of chlorinated persistent organic pollutants as a source of large uncertainty in interpreting spatial patterns at all scales

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Abstract

Single point sampling, a widespread practice in snow studies in remote areas, due to logistical constraints, can present an unquantified error to the final study results. The low concentrations of studied chemicals, such as chlorinated persistent organic pollutants, contribute to the uncertainty. We conducted a field experiment in the Arctic to estimate the error stemming from differences in the composition of snow at short distances (1–3 m), including 13 single organochlorine pesticides and 6 polychlorinated biphenyls, thus providing the most detailed published dataset on the subject. We contrasted this variability with the uncertainty at larger spatial scales, both within one valley (regional scale, this study) and as described in the worldwide literature. The range of values for the coefficient of variation for local samples was 20–58% for single organochlorine pesticides (OCPs) and 33–54% for polychlorinated biphenyls (PCBs), and for regional samples it was 21–69% for OCPs and 65–93% for PCBs. We suggest that, to observe the actual changes in the concentration of selected compounds in snow, they should vary at the level of 40–60%, depending on the compound in question. The uncertainty margin remains much smaller than the current discrepancy between observation data and atmospheric deposition models considering snow, deeming field data on snow concentrations a useful ground-truthing dataset. However, field observations on spatial differences at all scales need to be interpreted with caution, and the dataset provided here on the local sampling uncertainty helps define the margins of such interpretations.

Abbreviations: CoV, coefficient of quartile variation; DDD, dichlorodiphenyldichloroethane; DDE, dichlorodiphenyldichloroethylene; DDT, dichlorodiphenyltrichloroethane; HCB, hexachlorobenzene; HCH, hexachlorocyclohexane; IQR, interquartile range; LOD, limit of detection; LOQ, limit of quantification; OCP, organochlorine pesticide; PCB, polychlorinated biphenyl; POP, persistent organic pollutant.

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1 | INTRODUCTION

Collecting solid-state samples is a challenge for scientists worldwide, and although there exists guidance on collecting multiple replicates of each sample, the field logistics of remote areas, such as the Arctic, the Antarctic and mountainous areas, may prevent complying with these strict requirements (e.g., Cabrerizo et al., 2019; Garmash et al., 2013; Koziol et al., 2021; Koziol et al., 2017; Spolaor et al., 2021). Moreover, the fieldwork design may have been decided long ago, as in the case of recovering information from ice cores collected in the past (Hermanson et al., 2021). On the other hand, single-point sampling may contribute significant and frequently unknown error to the final interpretation of the sampling results. Therefore, we present here a dataset that estimates such an error and can be used to constrain the interpretation of single-point snow sampling (from fresh precipitation and snowpits). It may also be used as an approximate measure of the uncertainty in sampled ice cores, which are formed from the snow over time. However, this subject would be better studied as a self-standing investigation.

For an appropriate snow or ice sampling strategy, one needs to consider the following issues: (a) the number of locations; (b) the number of sites or samples per location; (c) logistical limitations; (d) weather conditions under which sampling may be carried out; (e) quality checks, such as field blanks; and (f) other issues potentially compromising sample integrity. A good sampling strategy has the flexibility to be adjusted based on conditions in the field (NOAA, 2014) and may be adjusted by reduction of sampling site numbers or repeats.

Snow and ice samples collected in the Arctic are typically subject to low human impact and are assumed to have low concentrations of various impurities, which invokes the use of higher sample volumes and more careful sampling protocols than elsewhere (Cabrerizo et al., 2019; von Schneidemesser et al., 2008). This is an assumption easily held for phased-out persistent organic pollutants (POPs), most of which note decreasing or low and stable atmospheric concentrations (AMAP, 2016). Of course, the assumption is not universal: local activities may elevate contaminant concentrations (e.g., Abramova et al., 2016), and comparisons between various remote areas may show that the Arctic is not exceptionally pristine (Pawlak et al., 2021). For example, trip blank and field blank samples for each sampling site are considered minimum quality assurance pertaining to the sampling stage (NOAA, 2014). At the analytical stage, the reagents used are ultrapure, and quality assurance/quality control is ensured. However, the mathematical consequence of experiencing low concentration levels that might fall below analytical quantification levels is that the variability across replicates is also difficult to quantify. Thus, in some studies the planned or collected number of replicates may not be suffi-

> **Core Ideas**
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> - We present a study of snow sampling uncertainty for persistent organic pollutant (POP) content studies.
> - Local variability (CoV) in organochlorine POP concentrations ranged from 20 to 58%.
> - Regional variability (CoV across one glacier) ranged from 29 to 98%.
> - Sampling uncertainty is significant in interpreting regional of wider variability.
> - Compounds suited for the study of spatial changes include DDT, DDE, DDD, and PCBs.

cient to provide interpretation brackets for significant differences between samples.

The sampling error (resulting from local variability in the snow cover concentrations of pollutants) may have far-reaching consequences for the interpretation of study results. One such example is the estimation of atmospheric deposition of impurities at a larger spatial scale in connection to a mathematical model. The estimates given by large-scale models need to be ground-truthed with the use of the spatially limited point measurement values. The error margin on the local variability in snow impurity concentrations influences the brackets in which a model would be considered to match the environmental observations (Fuentes & Raftery, 2005). Currently, the POP deposition models within the Arctic are considered to match field measurements within 300–400% or less (UNECE, 2010), with higher brackets attached to snow deposition models of organochlorine POPs (e.g., Hansen et al., 2006). Therefore, we intend to determine here how much of this uncertainty is easily explained by the heterogeneity of snow as a sampled medium, instead of the model efficiency issues, and therefore determine the limitations in such comparisons as a ground-truthing process. Another example of interest in the spatial variability of the concentrations of organochlorine pesticides and polychlorinated biphenyls (PCBs) connects to the possibility of their emission to the environment from secondary sources (e.g., the melting glaciers or the seawater uncovered by the melting sea ice), which may be induced from spatial concentration patterns (Ma et al., 2016; Pawlak et al., 2021; Pouch et al., 2021).

The main hypothesis we put forward here is that the variability resulting from the sampling method and heterogeneity of the snow itself (described by the local variability) may significantly affect the interpretation of spatial differences at larger scales, rendering some differences undetectable. To verify the hypothesis, we quantified the local and regional variability in the concentrations of a range of polychlorinated

biphenyls and organochlorine pesticides, determined in snow samples. We then compared them with spatial differences at larger scales, as quantified from our own data on regional variability (i.e., pertaining to one valley of mountain slope) and from the literature on the deposition of organochlorine POPs in snow and ice cores. Thus, we provide spatial variability measures for nine single organochlorine pesticide (OCP) compounds and six PCB compounds for the first time in the published literature, and we do so by using nonparametric measures to avoid the assumption of normality, which is typically not met by the environmental chemical concentration data.

2 | MATERIALS AND METHODS

2.1 | Sampling design

Snow samples were collected in the spring 2019 in the area surrounding the Polish Polar Station Hornsund in Svalbard. Samples were taken in two designs: (a) as the top 20-cm layer of the snow profile (at the Environmental Hut site, in triplicates of local samples collected there, $n = 18$) or (b) as the fresh snowfall layer (all other samples, $n = 32$). The fresh snow was distinguished in the field by an observation of its physical properties, especially hardness difference from the underlying layer, and collected within 48 h after the atmospheric precipitation event. Those samples were collected in transects spanning the length of a valley (Revdalen or Hans Glacier valley) in ~0.5–1 km spacing to represent spatial variability at a bigger scale than the local samples. Within each transect, there was a triplicate of local samples collected as well. We refer to local samples if they were taken at three points separated by a small distance of 1 and 3 m from the first point where the sample was taken. The larger spatial variability scale (of the valley bottom transects) is referred to herein as the regional scale.

All samples were collected into 6,000-cm^3, precleaned Teflon bags or 6,000-cm^3, precleaned aluminum cans using a 1,000-cm^3, precleaned stainless steel density cutter. Precleaning of sampling vessels and tools consisted of a triple 18 MΩ water wash and triple methanol wash (high-performance liquid chromatography quality) (USEPA, 2007). Each triplicate of local samples was taken with the same type of sampling containers and from the same type of snow layer, and all regional scale samples were collected into Teflon bags. Additionally, field blank samples were collected once per transect. Figure 1 shows all the sampling sites.

2.2 | Analytical method

After collecting snow samples and thawing them, 5 cm^3 methanol per 1-kg sample was added to the samples, as well as hydrochloric acid in the amount enabling pH 2 in the sample. Then, before extraction, labeled internal standards (p,p'-DDT-d8, PCB 28 ^{13}C, and PCB 180 ^{13}C) in the amount of 10 mm^{-3} at a concentration of 100 ng cm^{-3} in dichloromethane were added. Extractions were carried out on octadecyl (C18) solid phase extraction tubes (6 cm^3, 0.5 g) (Supelclean ENVI, Supelco). Before extraction, the stationary phase was activated by washing the stationary phase successively with 5 cm^3 dichloromethane, 5 cm^3 ethyl acetate, 10 cm^3 methanol, and 10 cm^3 deionized water. The test sample was then passed through the stationary phase at a flow rate of 5 cm^3 min^{-1}. After the solid phase extraction stage, the stationary phase was rinsed with 3 cm^3 of a 1:1 (v/v) water/methanol mixture, and the bed was allowed to dry for 10 min. This step was followed by an elution step of the analytes from the column with 2.5 cm^3 × 4 ethyl acetate and 2.5 cm^3 × 4 dichloromethane. The eluate obtained was evaporated under nitrogen flow until almost dry and then reconstituted to 0.1 cm^3 using isooctane.

To determine OCPs and PCBs, a gas chromatograph (7890B, Agilent Technologies) coupled with a triple-quadrupole mass spectrometer (7000D, Agilent Technologies) was used. The determined OCPs were dichlorodiphenyldichloroethylene (DDE), dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethane (DDD), hexachlorocyclohexane (α-, β-, and γ-HCH), hexachlorobenzene (HCB), heptachlor, heptachlor epoxide, aldrin, and mirex. The determined PCBs were congeners 28, 52, 118, 138, 153, and 180. The analytical column HP5-MS (5% phenyl-methylpolysiloxane, 30 m × 250 μm × 0.25 μm) provided the separation of analytes, with helium as mobile phase, at a flow rate of 1.0 cm^3 min^{-1}. The temperature program is presented in Supplemental Table S1. A solvent delay of 6 min was used to prevent filament damage. Splitless mode was used. Injection volume was 5 mm^3, N$_2$ was used as collision gas (1.5 cm^3 min^{-1}), and He was used as quench gas (2.5 cm^3 min^{-1}). The mass spectrometer was operated in the dynamic multiple reaction monitoring mode. Supplemental Table S2 presents the mass/charge ratios, and time retentions of the compounds were monitored.

In this study, 50 samples of fresh snow were analyzed for the content of six PCBs (PCB 28, 52, 118, 138, 153, and 180) and 13 OCPs (α-HCH, γ-HCH, β-HCH, aldrin, HCB, heptachlor, heptachlor epoxide, mirex, DDD, o,p'-DDE, p,p'-DDE, o,p'-DDT, and p,p'-DDT). Before sample analysis, standard solutions were analyzed to check column performance, peak height, and resolution. Using a blank sample, we calculated the limit of detection (LOD) and the limit of quantification (LOQ) using the formula LOD = $S + 3.3σ$, where S is the mean value for 10 replicates, σ is the value of the standard deviation for these replicates, and LOQ = $3 × $ LOD. We also analyzed field blank samples to assess the degree of contamination of the samples by transport and laboratory
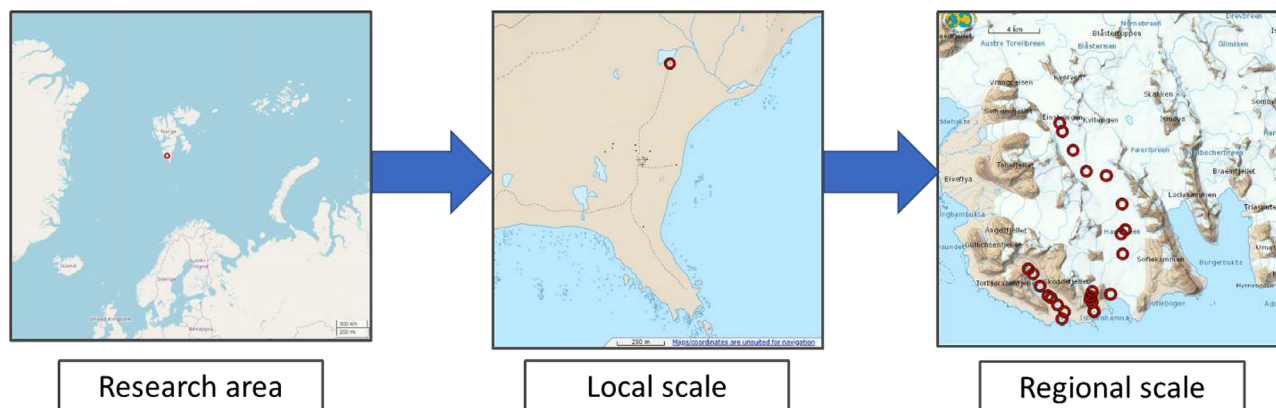
FIGURE 1 Map of sampling locations in the vicinity of the Polish Polar Station Hornsund. Source of the maps: Norwegian Polar Institute (https://toposvalbard.npolar.no) and OpenStreetMap (https://www.openstreetmap.org/#map=3/76.38/22.57)

influences. On the basis of a standard sample prepared by adding a certain amount of standard solutions and certified reference material to water, we determined the recovery value and the CV for the analytes (27–137% and 0.35–19.3, respectively). For the internal standards, recovery and CV were 70–98% and 10–25, respectively. Validation parameters (e.g., recovery, CV, LOD, and LOQ) are presented in Supplemental Table S3. After every 10 analyses, we performed an analysis on a standard made of certified reference material and standard solutions to control for chromatographic parameters.

2.3 | Statistical analysis

The statistical analyses of spatial variability were performed in R version 3.6.2. The hypothesis of the normal distribution of the chemical concentrations measured was tested by using the qqplot function and rejected based on the strong departures from the normality line on the graphs (confirmed also by χ^2 test calculations where possible); therefore, nonparametric measures were used to quantify variability of the obtained results. Such measures are the nonparametric CV, based on median, or the coefficient of quartile variation (CoV), based on the interquartile range (IQR; i.e., the difference between the third and the first quartile) (Altunkaynak & Gamgam, 2019; Arachchige et al., 2020). As a measure better connected to the properties of the data distribution, the CoV was used here to report the final results. For statistical manipulations related to variability measures, all values below the LOQ were replaced with half of the LOQ value.

3 | RESULTS AND DISCUSSION

The concentrations of all compounds are available in the online repository MOST Wiedzy Open Research Data Catalogue (https://doi.org/10.34808/2cd8-pk41)). For the entire

studied area, the concentration range and the average content were as follows: $\Sigma PCBs_6$ = range: <LOD–4.48 ng dm^{-3}, median: 0.21 ng dm^{-3}, IQR: 0.61 ng dm^{-3}, average: 0.58 ± 0.94 ng dm^{-3}, where PCB 28 had the largest contribution to the average content (30%); ΣHCH_3 = range: <LOD–1.84 ng dm^{-3}, median: 0.16 ng dm^{-3}, IQR: 0.25 ng dm^{-3}, average: 0.255 ± 0.34 ng dm^{-3}, where γ-HCH had the largest contribution to the average content (56%); ΣDDX = range: <LOD–5.72 ng dm^{-3}, median: 0.153 ng dm^{-3}, IQR: 0.54 average: 0.64 ± 1.2 ng dm^{-3}, where ΣDDX refers to the sum of DDT, DDE and DDD contents, of which o,p′-DDE had the largest contribution to the average content (36%). The remaining pesticides were detected so rarely that we decided to quote their ranges and average levels only. To calculate the average content conservatively, the value of 1/3 LOD was substituted for the LOD values.

3.1 | Local variability

To determine the local variability, an experiment was performed that consisted of collecting three snow samples at intervals of 1–3 m. The samples were collected on six occasions at three different sites (Environmental Hut, Revdalen at R5 point, and Hans glacier at H9 point). The contents of OCPs and PCBs are presented in Figures 2 and 3. Polychlorinated biphenyls from the Environmental Hut sampling on 26 Apr. 2019 are not reported because the content of the analytes determined was below the detection limit.

The error bars in Figures 2 and 3 delimit the standard deviation of analytical repeatability, where normal distribution should be held because it pertains to repeats of the same sample. Therefore, according to the three sigma rule, 68% of all data should lie within those brackets if the analytical repeatability was the main error source (Miller & Miller, 2005). However, the variability expressed by the sampling replicates exceeds markedly the analytical replicate differences.
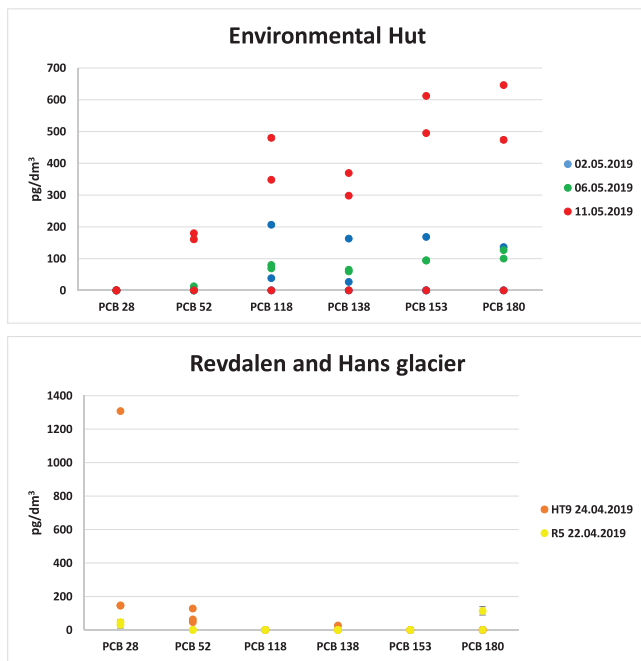
FIGURE 2 Concentration of polychlorinated biphenyls (PCBs) with analytical error bars (as CV) in local triplicate samples
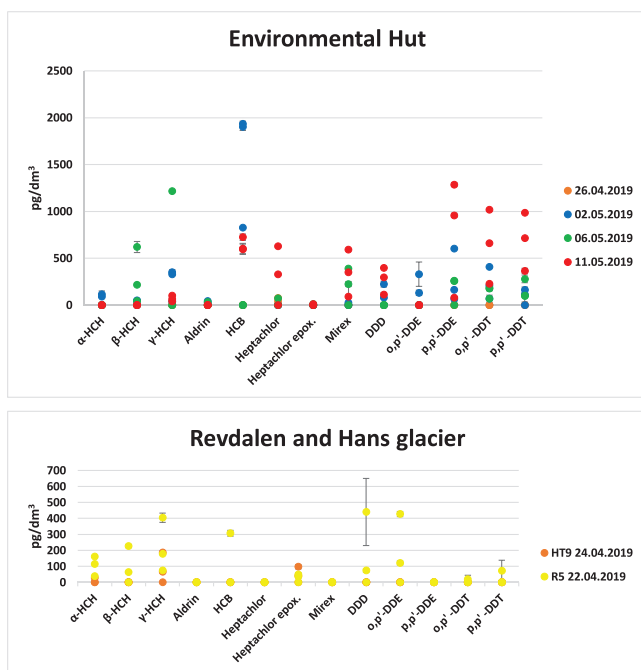

FIGURE 3 Concentrations of organochlorine pesticides with analytical error bars (as CV) in local triplicate samples. Most error bars span too small a range to be visible in the graph scale. DDD, dichlorodiphenyldichloroethane; DDE, dichlorodiphenyldichloroethylene; DDT, dichlorodiphenyltrichloroethane; HCB, hexachlorobenzene; HCH, hexachlorocyclohexane

To better express the variability numerically and to account for the nonparametric character of the dataset, we calculated the CoV. The mean CoV value (not including values below LOD) was in the range of 20–58% for OCPs and 33–54% for PCBs, which proves significant variability of OCPs and PCBs content in snow. Taking into account the sums of PCB and OCP contents, the mean values of the CoV were 38 and 23%, respectively. The smaller error margin for sums of several compound concentrations than for single concentrations is consistent with the likelihood for random errors to cancel out during the totaling (Miller & Miller, 2005). To our knowledge, the two publications that give the value of the standard deviation related to the sampling for the content of OCPs and PCBs in snow are Hageman et al. (2010) and Herbert et al. (2006). Herbert et al. (2006) give the value of the relative standard deviation (RSD = CV) for samples taken from the same snow layer across an area of 4 m^2, and this value is 30 and 25% for ΣPCB and ΣOCP, respectively. They also suggest that to observe real changes in the concentration of selected compounds in snow, they should be between 20 and 40%. Such a result is very similar to our calculations. However, because the CoV for individual compounds may be greater, when interpreting single compound results, larger differences of the order of 40–60% should occur so as to be interpreted as genuine spatial or temporal differences. However, the calculated mean CoV for pesticides by (Hageman et al., 2010) for the 61 samples of annual snow profiles are lower and amount to 15% (IQR, 6–20%). This may indicate that variability in POP content in snow may decrease as the snow ages or accumulates several layers, with errors cancelling out. Detailed values calculated here for particular compounds (Supplemental Tables S4–S11) may be used a guide in future interpretations of such differences in snow samples.

3.2 | Comparison of local variability and analytical method repeatability

In the graph in Figure 4, we have compiled the value of local variability and repeatability of the analytical method used. The local CoV is greater than the repeatability of the analytical method, from 1.5 times to 155 times. The CV of the analytical method may have a significant effect only in the case of PCB-138; for the remaining compounds, the analytical method used should not significantly affect the local variation.

3.3 | Regional variability

To determine the regional variability and test whether it is measurable above the random noise generated by the variability of locally collected samples, snow samples were taken in three transects: the Revdalen valley, the Fuglebekken slope, and the Hans Glacier. In the case of the Hans Glacier, snow
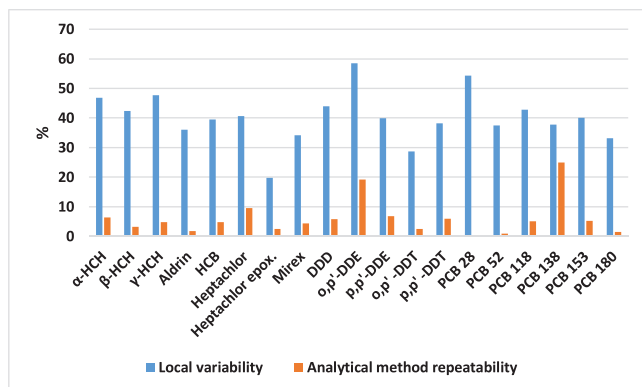
FIGURE 4 Comparison of local variability and analytical method repeatability (as CV) ($n = 10$). DDD, dichlorodiphenyldichloroethane; DDE, dichlorodiphenyldichloroethylene; DDT, dichlorodiphenyltrichloroethane; HCB, hexachlorobenzene; HCH, hexachlorocyclohexane; PCB, polychlorinated biphenyl

samples were taken twice (23–24 Apr. 2019 and 10 May 2019). The content of organochlorine pesticides and polychlorinated biphenyls is presented by means of boxplots in Figure 5.

For pesticides such as mirex, heptachlor, heptachlor epoxide, and aldrin, there was no noticeable variability because in most cases the concentration values were below the LOQ. Only in individual cases was the concentration higher (in the case of mirex and heptachlor epoxide), and then it was possible to calculate the CoV (at 29 and 56%, respectively). The content of pesticides such as α-HCH, β-HCH, and γ-HCH was also characterized by low variability, with CoVs of 40, 40, and 50%, respectively. The variability was expressed only for samples taken at the Hans Glacier on 10 May and in the Revdalen in the case of α-HCH and β-HCH, respectively (and for all places, in the case of γ-HCH). Other pesticides with low variability were p,p′-DDE, DDD, heptachlor epoxide, and HCB, with CoVs of 50, 54, 57, and 58%, respectively. In the case of other pesticides (e.g., p,p′-DDT, o,p′-DDT, and o,p′-DDE, with CoVs of 64, 69, and 98% respectively) and all determined PCBs (PCB 28, 52, 118, 138, 153, and 180, with variabilities of 81, 73, 68, 68, 84 and 66%, respectively), the noticeable variability was strongly influenced by high-concentration outliers. This diagnosis is confirmed by the median remaining near low concentrations levels. On the other hand, from the comparison with local variability levels, it was determined that the regional variability for individual compounds would be noticeable for all compounds only when the calculated regional CoV is >60% (depending on the compound in question). Finally, it was calculated that the CoV for the sum of pesticides is much lower than the average value for individual compounds (29%), whereas in the case of the sum of PCBs, the CoV is not so different from the average CoV for individual PCBs (66%).

The transects of Fuglebekken and Hans Glacier are characterized by the greatest variability. In the case of the Fuglebekken transect, an increase in PCB content was observed with increasing the altitude at which the sample was taken. This fact may partly explain the large variability of PCBs in this transect because at the same time the Fuglebekken transect shows the largest altitude span of all the analyzed profiles. However, our observations are in opposition to the results by Blais et al. (1998), who noted an increase with elevation for more volatile POP concentrations and no such change for the less volatile POPs, such as PCBs and DDX. However, Wang et al. (2007) observed also an increase with altitude in the content of pp-DDT and pp-DDD. All such elevation-related phenomena may be a demonstration of the cold condensation effect (Wania & Mackay, 1993). Additional variables possibly influencing the regional variability are the physical properties of the snow cover, with a large variety in snow thickness and density testifying to the influence of wind action on the samples (Figure 6). This has been the case especially for the precipitation event sampled in Revdalen and on the Hans Glacier on 22–24 Apr. 2019. The snow cover on 10 May 2019 was sampled uniformly from the top 10 cm of a thicker fresh snow layer, yet it also was subject to wind action, which has been expressed by its relatively high and variable density. There were no significant correlations between these snow properties and the determined POP content. On the other hand, the result of wind action may have been an opportunity for the regional concentration levels of POPs to become more uniform due to physical mixing of snow across the area. In such a case, the Fuglebekken transect should be the most varied in terms of POPs content in snow. However, this assumption is not confirmed in the concentration dataset, where Fuglebekken transect has the highest differences in the concentrations of PCBs alone, instead of all the measured compounds.

3.4 | Comparison of local variability and regional variability

For both the local and the regional variability, the CoV was calculated, that is, a variability measure based on the IQR. Both values were juxtaposed to form the diagram in Figure 7.

For compounds like heptachlor and aldrin, it was not possible to calculate a regional CoV because most concentrations were below the LOQ. Therefore, it is not possible to compare the CoV for these compounds. In the case of α-HCH, β-HCH, and y-HCH, the differences between the local and regional variability levels were too small to find a significant spatial variability with the applied sampling design. For all these four compounds, we conclude no regional variability was detected in the collected dataset. Even for the remaining relationships, the impact of local variability was large enough to be considered an important source of uncertainty in
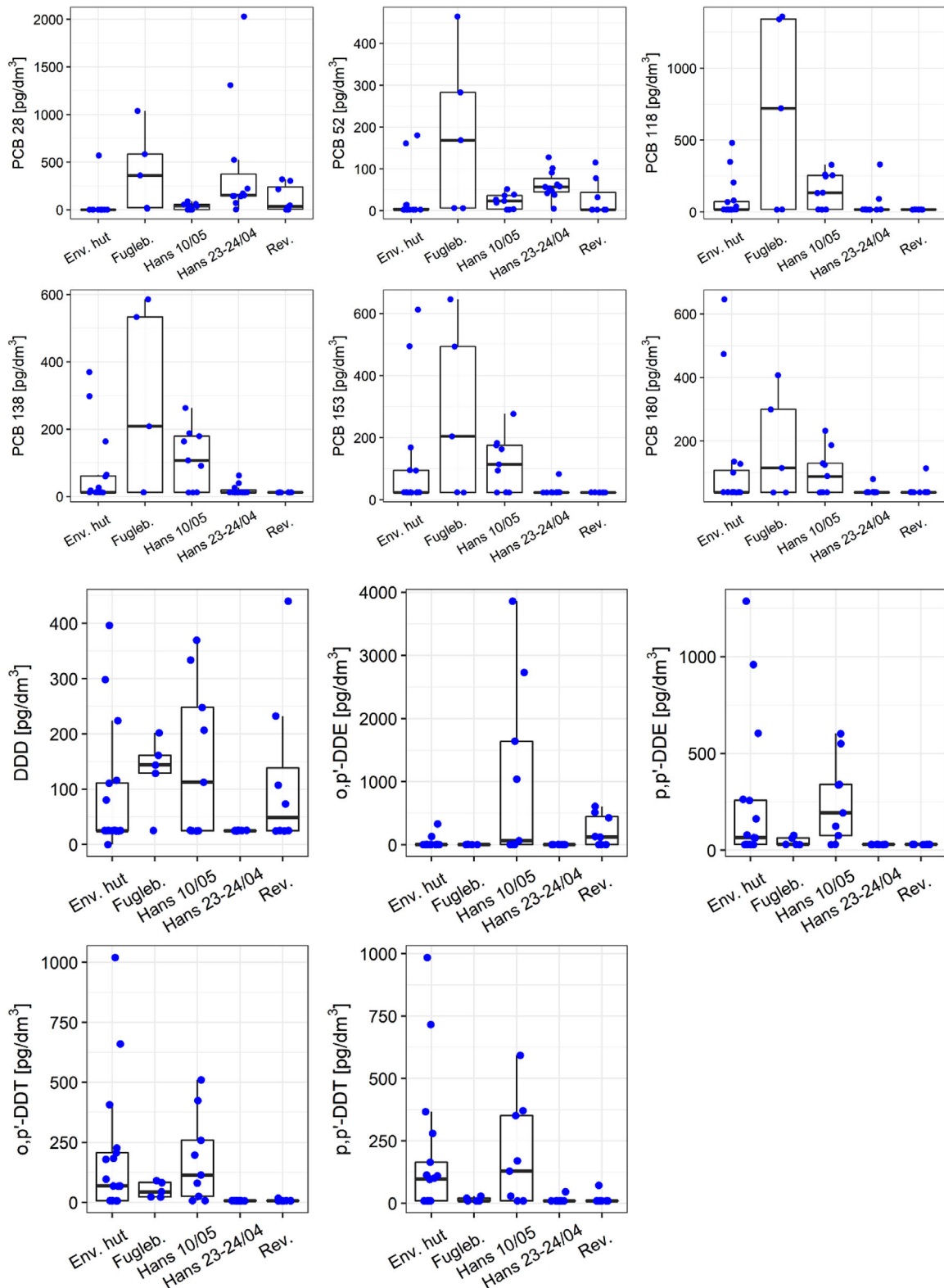
FIGURE 5 Organochlorine pesticide and polychlorinated biphenyl (PCB) contents in the collected snow samples, grouped by data series. Boxplots (with full data distribution as points) present the variability of organochlorine compound concentrations obtained in the samples collected within four sampling locations: Env. hut, the Environmental hut, next to the Polish Polar Station (showing variability within a time series); Fugleb., Fugleberget slope; Hans, the Hans glacier; Rev., Revdalen, a nonglaciated valley; all three represent within-landform (regional) variability. The Hans data are divided into two sets from two sampling dates. The box marks the Q1–Q3 span (i.e., the interquartile range [IQR]), with median marked as a thick line. Whiskers reach no further than 1.5 × IQR from the box hinge, where IQR = Q3−Q1. DDD, dichlorodiphenyldichloroethane; DDE, dichlorodiphenyldichloroethylene; DDT, dichlorodiphenyltrichloroethane
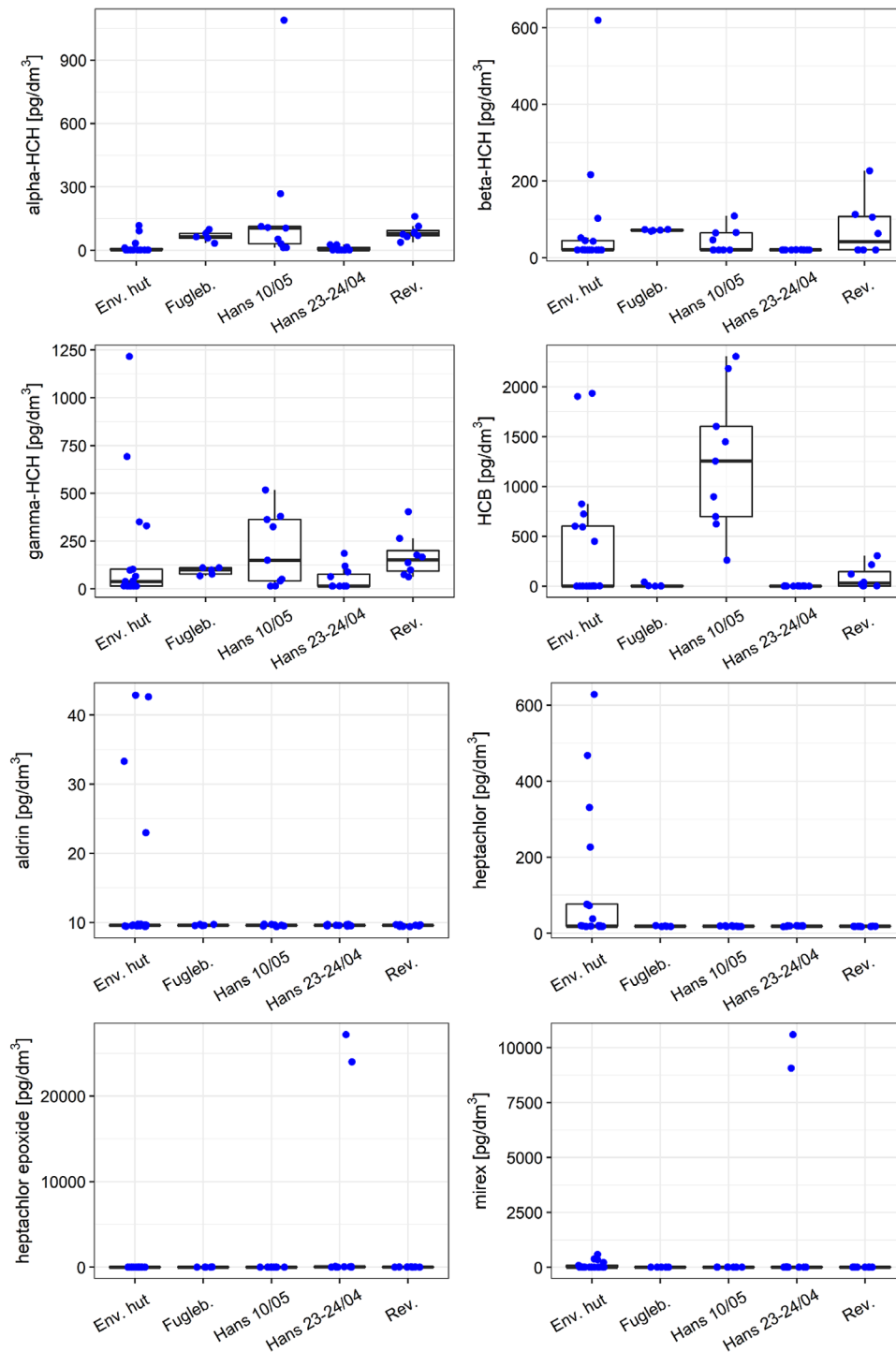
FIGURE 5 Continued

interpreting data on regional variability. However, the comparison has also proven that regional variability in snow concentrations of organochlorine POPs may be successfully detected in spite of the large sampling error resulting from the local differences in snow composition. The regional variability was also more pronounced for PCBs than for OCPs in our dataset from southern Svalbard, and it seemed connected to an elevation-dependent process. Hexachlorohexane

isomers are characterized by a lower value of the octanol–water partition coefficient and a lower soil adsorption coefficient value, and they are more volatile than the other compounds analyzed here. As a result, HCHs may become more evenly distributed in the environment through equilibration with the atmospheric air, leading to a small difference between the local and regional CoVs. On the other hand, PCBs exhibit higher values of the octanol–water partition coefficient and
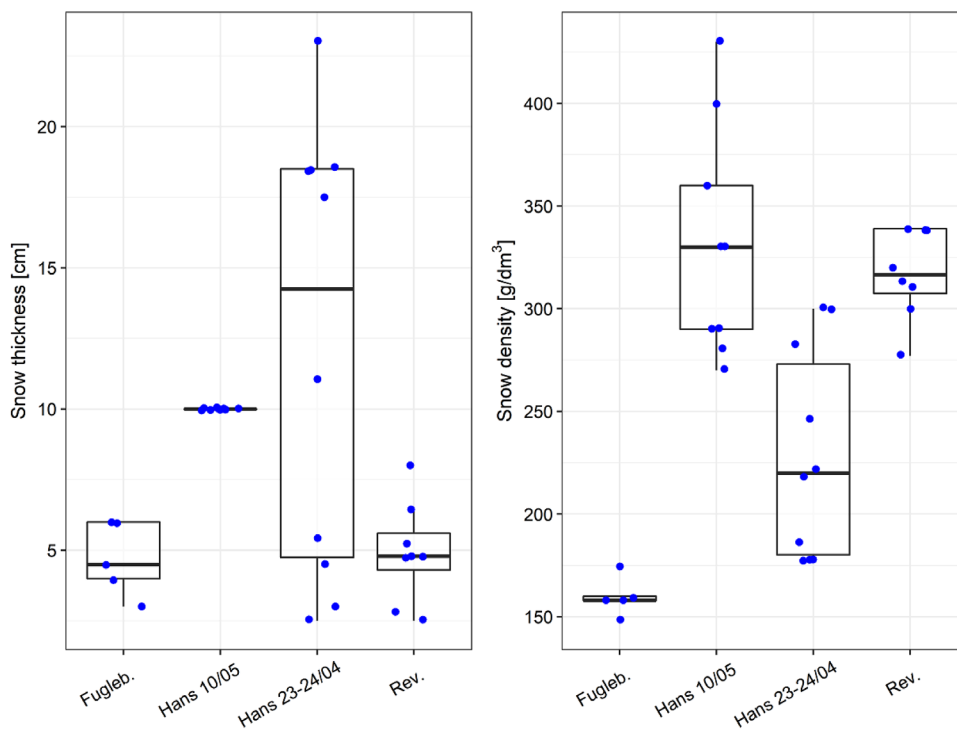
FIGURE 6 Variability in the physical properties of snow across the regional transects: Env. hut, the Environmental hut, next to the Polish Polar Station (showing variability within a time series); Fugleb., Fugleberget slope; Hans, the Hans glacier; Rev., Revdalen, a nonglaciated valley). HCB, hexachlorobenzene; HCH, hexachlorocyclohexane

soil adsorption coefficient, which may result in their more stable deposition in the snow (e.g., through trapping in snow particulate matter).

3.5 | Implication for large-scale studies: Hemispheric comparisons

The influence of local variability should be taken into account in comparisons of PCB and OCP contents in snow between different geographic areas, including the hemisphere-wide studies. Figure 8 shows the content of ΣHCHs, ΣDDXs, and ΣPCBs in snow in various glaciated regions in the Northern Hemisphere. We can distinguish three regions: the Alps, the Himalayas, and the Arctic. A lower ΣPCB content can be observed in the Himalayas; however, the peculiarly low content and the assessment based on only one publication cannot be conclusive. In the case of ΣHCHs and ΣDDXs, there are no clear differences between the comparable regions. The only noticeable trend is the decrease in the content of ΣHCHs and ΣDDXs in snow over the years in the Northern Hemisphere, related to the introduced restrictions on the use of these compounds, consistent with previous studies' conclusions on atmospheric concentrations trends (e.g., AMAP, 2016; Berg et al., 2004).

Field observations of contaminant concentrations in snow may be used to ground-truth snow wet deposition models, and indeed a shortage of data for this purpose was commu-
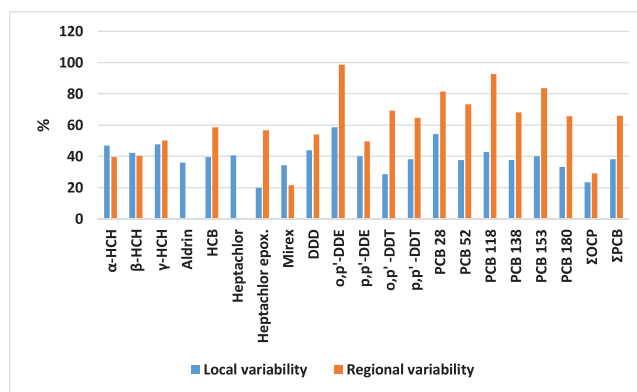

FIGURE 7 Comparison of local and regional variability in individual organochlorine pesticide (OCP) and polychlorinated biphenyl (PCB) concentrations in snow, calculated as coefficient of quartile variation. DDD, dichlorodiphenyldichloroethane; DDE, dichlorodiphenyldichloroethylene; DDT, dichlorodiphenyltrichloroethane; HCB, hexachlorobenzene; HCH, hexachlorocyclohexane

nicated by the modelling studies in the first decade of this century (e.g., Hansen et al., 2006, 2008). The uncertainty in the observational data will limit the extent to which models can draw from field data in attempts to improve performance. Currently, the model performance for large scale (e.g., Arctic-wide) estimations of organochlorine POP deposition falls within the range of 500-2,000% (Hansen et al., 2006, 2008),
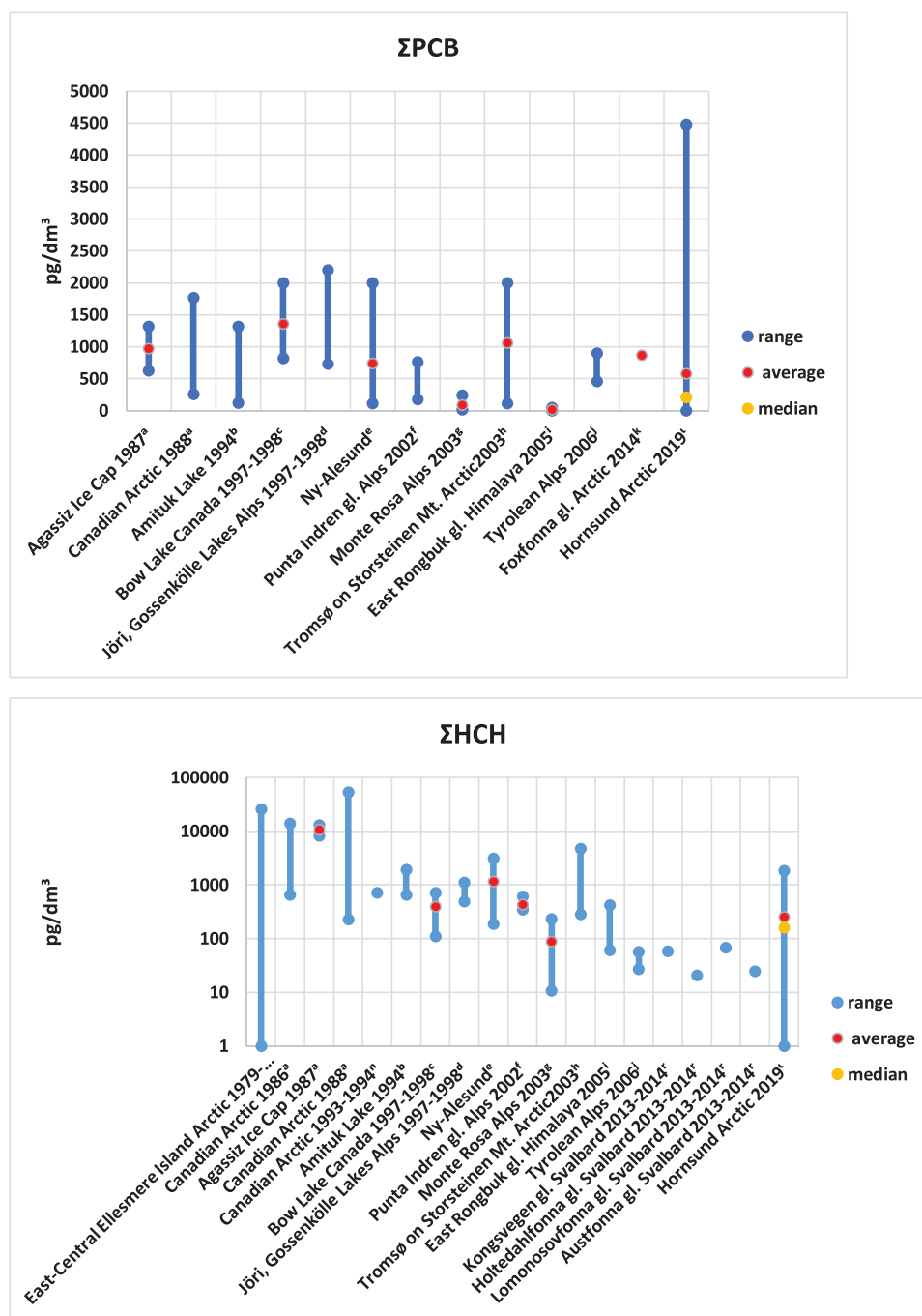
FIGURE 8 Range of (a) polychlorinated biphenyl (ΣPCB), (b) hexachlorocyclohexane (ΣHCH), and (c) ΣDDX concentrations, i.e., a sum of DDD, DDE and DDT concentrations (all as pg dm^{-3} of melted snow water) in snow in various glaciated regions worldwide. References: [a]Gregor and Gummer (1989), [b]Murray et al. (1995), [c]Lafrenière et al. (2006), [d]Carrera et al. (2001), [e]Herbert et al. (2005), [f]Herbert et al. (2004), [g]Finizio et al. (2006), [h]Herbert et al. (2005), [i]Kang et al. (2009), [j]Arellano et al. (2014), [k]Koziol et al. (2017), [l]this study, [m]McNeely and Gummer (1984), [n]Boyd-Boland et al. (1996), [o]F. Wang et al. (2007), [r]Hermanson et al. (2020)

whereas an investigation of atmospheric bulk deposition observations across Central Europe shows differences within the range of 140–450% PCB content as significant and below 100% for the OCPs as insignificant (Nežiková et al., 2019). The uncertainty of snow deposition models remains larger than in the case of atmospheric air concentration models. For

example, Hansen et al. (2004) report an uncertainty of 200-300% in an atmospheric concentration model, whereas Wang et al. (2020), in a simpler model, report uncertainty of up to 500%. The high contrast between model predictions and observations of POP deposition in snow partially stems from the fact that both snow models and observations are scarce
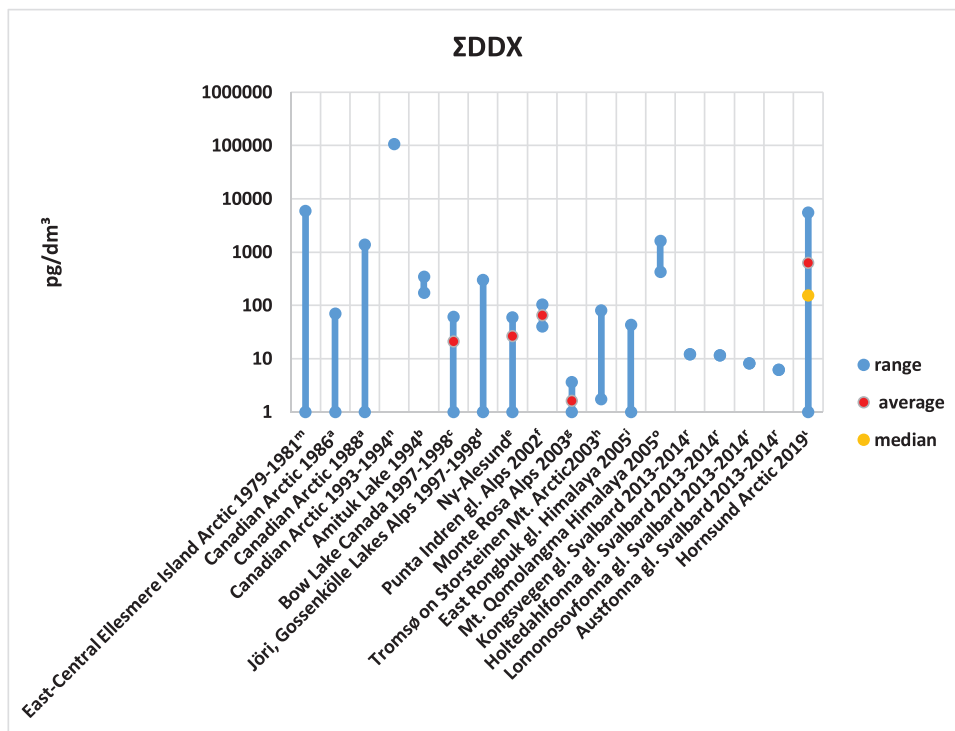
FIGURE 8 Continued

compared with those of atmospheric observation, and thus the compared values do not directly match by location or time period. At the same time, various models predicting change in environmental concentrations of POPs with climate change agree on the effect mostly within 200% (Hansen et al., 2015). Therefore, decreasing the model uncertainty against observation would be of interest for prediction purposes. To summarize, with field data suffering from sampling-related uncertainty at the level of 20–58% (depending on the compound), there is promise in ground-truthing models with such observational data. The field sampling uncertainty is, however, an important threshold to consider in order to avoid overfitting models to randomness in the data.

The uncertainty we quantified has possible implications for ice core studies (Fuoco et al., 2012; Villa et al., 2006; X. P. Wang et al., 2008), although it remains to be proven whether the ice cores formed from snow are characterized by the same level of sampling-related uncertainty as the fresh snowfall. In fact, they are more likely closer to the uncertainties exhibited by the annual snow cover profiles (Hageman et al., 2010). For logistical reasons, usually one ice core is collected in a given glacier, which means that the composition analysis is for one point, which might not be very representative. Therefore, even more than with snow samples, the uncertainty of sampling needs to be considered when interpreting the results, especially when the content of POPs in ice cores from two different places is compared (Hermanson et al.,

2021). Taking the uncertainty level into account as it pertains to snow would mean that significant differences between the ice cores collected worldwide are fewer than mentioned in the literature.

Descriptions of compliance with the quality assurance/quality control standards in the presented publications relating to snow mainly relate to the analytical procedure used and whether they meet the strict requirements imposed on them. The description of snow sampling in the cited publications includes a description of the tools with which they were taken, but in most cases it does not contain information about the surface area from which they were taken or homogenization across several subsamples, which suggests that they were taken from one point with a specific area (and that this surface area may not have been repeated throughout the study). We indentify this as a limitation in the interpretation of data on heterogeneous solid media such as snow.

Because the concentrations of chlorinated POPs in snow may differ significantly over a small area, we would suggest to test new ways of sampling in the future. For example, one could sample exhaustively a certain surface area covered by snow (and note it) or collect several point samples (five if possible) and mix them in equal proportions for the final analyzed sample. Furthermore, in situations where only point measurements are possible (e.g., drilling a deep firn core, using a direct deposition sampler), the uncertainties calculated here may be applied as error estimations.

4 | CONCLUSION

This study presents a new look at representative snow sampling in terms of chlorinated POP content. The currently available data on snow content of OCPs and PCBs, generated through snow sampling at a single point per sample, have inherent limitations preventing the interpretation of relatively small spatial and temporal differences. The heterogeneity of snow at local scale results in an uncertainty at the level of 23–38% in terms of sums of several compounds concentrations and up to 58% in single-compound concentrations (as measured by CoV). In our opinion, more detailed repeatable sampling protocols need testing in the future to enable interpretation of smaller spatial differences. The compounds that may be better suited for the study of spatial changes are DDE, DDD, DDT and PCBs. Especially for PCBs, both regional and hemisphere-wide differences may be observed beyond the error brackets determined by the local variability in snow samples. However, all the studied organochlorine POPs were subject to errors from snow heterogeneity. At the same time, the uncertainty in field data, including the uncertainty related to sampling, remains much lower than the atmospheric deposition model accuracy, and thus observational snow concentration data can be successfully used as means of ground-truthing such models. Quantifying the sampling errors and contrasting them with spatial and temporal differences detected in snow data, as well as deposition models, would increase the confidence in the interpretations of POPs atmospheric deposition patterns in the future.

AUTHOR CONTRIBUTIONS

Filip Pawlak: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Validation; Visualization; Writing – original draft; Writing – review & editing. Krystyna Anna Koziol: Conceptualization; Formal analysis; Funding acquisition; Investigation; Methodology; Project administration; Resources; Software; Validation; Visualization; Writing – original draft; Writing – review & editing. Klaudia Kosek: Conceptualization; Data curation; Investigation; Writing – original draft; Writing – review & editing. Zaneta Polkowska: Conceptualization; Resources; Supervision; Writing – original draft; Writing – review & editing.

CONFLICT OF INTEREST
The authors declare no conflict of interest.

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