

AMAP CORE – ATMOSPHERE

Scientific Report from DCE – Danish Centre for Environment and Energy

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Data sheet

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Abstract:	This report describes the results obtained in the Danish contribution to the atmospheric part of the Arctic Monitoring and Assessment Program (AMAP). It includes results of measurements at Villum Research Station, Station Nord from 1990 to 2019 and is an update of the previous report from 2017 (Skov et al. 2017). A series of climate-relevant particle parameters as well as particle bound compounds and gasses relevant for determining the anthropogenic impact on the sensitive Arctic environment have been measured. The results have been used to improve the parameterisation of the Danish Eulerian Hemispheric Model (DEHM) as well as to constrain the model. The results are all reported to AMAP, EMEP and to WMO-Global Atmospheric Watch and have been a significant contribution to AMAP assessment reports on Mercury, Short Lived Climate Forcers (SLCF), as well as Persistent Organic Pollutants (POPs) and Chemicals of Emerging Arctic Concern (CEACs). The data have been analysed statistically for significant trends, and the connection between emissions and observed concentrations was investigated using a combination of models and measurements. The assessment reports are used to support policy-making and legislative work in the Arctic Council as well as international conventions, such as the Stockholm and Minamata Conventions.
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1 Introduction

This report is an update of (Skov et al. 2017) and represents 30 years of monitoring of air pollutants in Greenland. The long time series of key pollutants provides the basis for understanding the connection between source regions, chemical and physical transformation and long-range transport for final observed levels in Greenland. The work has provided the Danish Kingdom with key information applied in national reporting e.g. Skov et al. (2017) and international reporting, e.g. to the Arctic Monitoring and Assessment Programme (AMAP), where recently, summaries for policy makers and technical reports have been published on persistent organic compounds (POPs) and chemicals of emerging Arctic concern (CEACs), on mercury and short lived climate forcers (SLCF) including ozone, methane, black carbon and atmospheric particles (see <u>Arctic Monitoring and Assessment Programme | AMAP</u>) (AMAP 2021a; 2021b; AMAP 2022).

More specifically, we have contributed with measurement data, model projections and data interpretations to several AMAP assessment reports to the Arctic Council. Contaminant monitoring data have been included in recent AMAP reports on persistent organic pollutants (POPs) and chemicals of emerging Arctic concerns (CEACs), i.e. POP time trends (AMAP 2016) and CEAC assessments (AMAP 2017). Both POP data and modelling results are included in the assessment report "POP and Chemicals of Emerging Arctic Concern: Influence of Climate Change" (AMAP 2021b). Furthermore, mercury data from Greenland represent a significant contribution to the AMAP assessment report on Hg (AMAP 2021b). Finally, we have been very active with six participants from AU-DCE working on the upcoming SLCF assessment report.

In the present report, we present new data of potentially noxious species in order to obtain knowledge about potential threats to the vulnerable Arctic system for example of the load of these species arriving from long-range transport and the interaction with climate. We present updated results of our monitoring activities that provide information for policy makers, which can be included in decision processes at the local, regional and global level, addressing contaminant transport to, and accumulation in, Greenland. These decisions can contribute to the future development of Greenland in a sustainable way.

The Greenlandic population is exposed to high concentrations of heavy metals and persistent organic pollutants (POPs) depending on the fraction of their diet originating from mainly marine mammals (e.g. AMAP 2004, 2011, 2017, 2018). The majority of heavy metals and POPs enter the Arctic through longrange atmospheric transport and sea currents from mid-latitudes to Greenland (e.g. Lange et al. 2018; Kamp et al. 2018; Carbone et al. 2018; Nielsen et al. 2019; Skov et al. 2020). Transport of contaminants to the Arctic environment is dependent on source strength and source areas as well as interacting complex hydrological and meteorological processes including climate factors. Following atmospheric deposition and ocean transport, the contaminants are taken up into the food web through algae, copepods and benthic fauna. In general, POPs and mercury are recalcitrant to metabolisation and therefore increase up through the Arctic food web (biomagnification).

Acidifying and eutrophying compounds like SO_2 , SO_4^{2-} , NO_3^{-} and NH_4^{+} are known to represent limiting factors for biological growth and, furthermore, they are important ingredients of Arctic Haze (Skov et al. 2017; AMAP 2006).

The power, robustness and thus also importance of the temporal trends of Arctic pollutants increase with length of the time series. The trends are an important tool to evaluate the effect of changing sources due to abatement strategies and variation in economic level and factors like receding ice-cover and increasing human activities potentially affecting the dynamics of contaminants in the Arctic, i.e. from emissions to accumulation in the Arctic environment.

The AMAP Core programme was initiated in 1994 and has continued since then. It was an update of an earlier Arctic programme SAGA that started in 1990. This report extends the time series to include in particular the results from the years 2018 and 2019 but for some cases, we will focus exclusively on those two years. The measurements are performed at Villum Research Station at Station Nord (Villum) and model calculations using the Danish Eulerian Hemispheric Model (DEHM) were made in parallel using the integrated monitoring approach (Hertel et al. 2007). In this way, information on the processes behind an observed trend can be identified and the geographical variations described. The AMAP data obtained at Villum are reported to EBAS and are available not only for the AMAP program but also for EMEP and WMO-GAW. Lately, Villum became part of "The Aerosols, Clouds and Trace gases Research Infrastructure" (ACTRIS), where most of the high-ranked and high scientific level research institutions in Europe working on atmospheric chemistry and physics are members. This will increase the visibility of our work presented in this report and together with our peer reviewed articles it will ensure that we deliver measurement results, knowledge and scientific advice at the highest possible scientific level.

The results have provided us with a strong basis for participation in AMAP assessment reports on atmospheric mercury, SLCFs and POPs as well as on climate effects as already mentioned. The results of measured and modelled activities are used together with observations from stations in other Arctic countries as well as other atmospheric models, as outlined above. Both measured data and model contributions as well as scientific expertise for circumpolar data interpretations and assessments are included. An update of air monitoring trends in a circumpolar context, including results from Villum Research Station, was recently published (Wong et al. 2021; Skov et al. 2020) and additional papers on particles, sulfate and ozone are in preparation.

1.1 Villum Research Station

Villum is located at the military base; Station Nord, see Figure 1.1.



Figure 1.1. Location of Villum Research Station in Northeast Greenland.

The Base Station of Villum consists of three buildings with living quarters, laboratories and storage rooms (Skov et al. 2017). It provides a platform for joint studies of air pollution, climate, geology, and biological processes in ecosystems near Station Nord. The atmospheric measurements are made in the Air Monitoring Laboratory located 2 km south of Station Nord. The dominant wind direction is from southwest and thus the Air Monitoring Laboratory is upwind of the station most of the time minimizing the effect of even the limited emissions of pollutants from Station Nord.

The details on instrumentations and special inlets for sampling of both particles and gases are described elsewhere (Skov et al. 2017) and will not be part of this report.

1.2 The DEHM model

DEHM covers the Northern Hemisphere (Brandt et al. 2012; Christensen 1997; Heidam et al. 2004) on a polar stereographic projection true at 60°N. An important global reanalysis dataset from ECMWF for the years 2018-2019 has been retrieved, and the meteorological weather forecast model, WRF, has been run for 2018-2019 in order to make the necessary meteorological gridded data with high spatial and temporal resolution for the DEHM model system as input.

DEHM has been used in the field of Arctic air pollution for many years and in many published articles and has contributed to several assessment reports in the AMAP program since the first assessment in 1998. In this study, the model was set up with two nested model domains with 300 × 300 grid points. A mother domain was used with a resolution of 75 km × 75 km, covering the entire northern hemisphere, and a nested domain was also used covering the Arctic down to approximately 500N with a resolution of 25 km × 25 km. The North Pole was used as the centre for both model domains.

The basic version of DEHM includes three different possibilities for setups: The basic chemical setup in DEHM includes 80 different species. It is based on the scheme by Strand and Hov (Strand and Hov 1994), and has been extended with e.g. a detailed description of ammonia chemistry and a Volatility Basis Set (VBS) scheme to describe the formation of Secondary Organic Aerosols (SOA). Reactions concerning the wet-phase production of sulphate have also been included. The setup describes concentration fields for 59 photochemical compounds (including NO_X , SO_X , VOC, NHX, CO, O_3 etc.), 12 species for the SOA scheme and several classes of particulate matter, of which one class is related to BC (Thomas et al. 2022). The two other setups are a mercury chemistry setup (with 7 components), and a setup with Persistent Organic Pollutants (3 HCH isomers, 11 PCB congeners and D5) and both setups are mainly used together with the basic chemical setup.

Furthermore, it is possible to add tracers in DEHM without or together with the setups describes above.

2 Results

2.1 Sulfate and potassium

2.1.1 Measurements of inorganics at Villum

A custom-built filter pack sampler (FPS) is operated at Villum, to collect weekly bulk aerosol particle samples from 1990 onwards. In the present report we present sulphate (SO₄²⁻) and potassium (K) as examples. Sulfate was measured with ion chromatography and potassium was measured by proton-induced x-ray emission (PIXE) from 1990 to 2010 and by inductively coupled plasma–mass spectrometry (ICP-MS) from 2010 onwards.

A statistical analysis was performed with the aim of investigating long-term trends in the data. Data was pre-whitened to remove serial autocorrelation using the method outlined by (Coen et al. 2020). Trends were determined using the Mann-Kendall test (Sen 1968) at the 95th % confidence level (CL) and the associated Theil Sen's slope (Theil 1950) on weekly concentrations in each month separately.

The temporal characteristics for sulphate and potassium are displayed in Figure 2.1. The time series from 1990 to 2019 for monthly medians of sulfate and potassium are presented in Figures 2.1a and b, respectively. The gap from mid-2002 to late 2007 is due to measurements being temporarily moved from Villum to Nuuk at the west coast of Greenland. The annual cycles of median sulfate and potassium concentrations (calculated using weekly values for each month) for the periods 1990-2002 (solid lines) and 2007-2019 (dashed lines) are presented in Figures 2.1c and d, respectively. Sulfate peaks in spring due to transport of anthropogenic emissions from the mid-latitudes combined with inefficient removal processes (wet deposition) during the so-called Arctic haze period (Hirdman et al. 2010). In the summer, sulfate reaches a minimum due to increased wet deposition and decreased transport from anthropogenic source regions. For potassium, maximum values are observed in the winter and spring due to anthropogenic and marine sources, while natural sources (biomass burning and suspension from bare soils) become more important during the summer (Heidam et al. 2004). Trends in each month for sulfate and potassium for the periods 1990-2002 (bars with solid outlines) and 2007-2019 (bars with dashed outlines) are presented in Figures 2.1.e and f, respectively. Blue bars indicate trends that are statistically significant on the 95th % CL, while white bars are not statistically significant. For sulfate, no statistically significant trends were observed for either periods under investigation. While the concentrations are, in general, lower during 2007-2019 compared to 1990–2002, there is considerable variability especially during the early and later years compared to the middle segment. This variability is the likely reason for no statistically significant trends. For potassium, statistically significant increasing trends are observed for April and November during 1990-2002 while statistically significant decreasing trends are observed for January and April during 2007-2019. This is an interesting pattern and one that will require more investigation to elucidate fully the processes and mechanisms that are responsible for these changes.



Figure 2.1. Temporal characteristics for sulfate (panels on the left) and potassium (panels on the right). Time series for a) sulfate and b) potassium for 1990–2019. Annual cycle of c) sulfate and d) potassium for 1990–2007 (solid lines) and 2007–2019 (dashed lines). The monthly trends for e) sulfate and f) potassium for 1990–2007 (bars with solid outlines) and 2007–2019 (bars with dashed outlines). The blue bars indicate trends that are statistically significant on the 95th % CL; white bars are not statistically significant. Error bars showing the 95 % confidence interval (CI) for the monthly trends were omitted for clarity.

2.2 DEHM model results

The DEHM model system has been run for the period 2018-2019 with basic the SOx-NOx-Ozone chemistry setup.



Figure 2.2. The daily mean concentrations of sulfur dioxide calculated by the DEHM model for the period 2018-2019 at VRS.

In Figure 2.2. the calculated daily mean concentrations of sulfur dioxide are shown for Villum. The model results show that there is a strong seasonal variation with highest concentrations during the dark winter months from late November to March, where the chemical lifetime of sulfur dioxide compared to sulfate is long due to reduced oxidation. In Figure 2.3 the calculated daily mean concentrations of sulfate are shown for Villum. This figure also shows the seasonal variation of pollution with higher concentrations in the winter season. This observation is explained by pronounced transport in the lower part of the troposphere close to the surface from sources at mid-latitudes to Villum. The maximum levels appear in general in the spring and are explained by the photooxidation of sulfur dioxide to sulfate after polar sunrise but in the present period, a maximum is observed in January and February 2018 due to long range transport episodes.



Figure 2.3. The daily mean concentrations of sulfate calculated by the DEHM model for the period 2018-2019 at VRS.

2.3 Comparison of modelled and measured α-HCH

Technical HCH was one of the most applied organochlorine insecticides worldwide and the major component is α -HCH (Li, Scholtz, and van Heyst 2000). Technical HCH was added to the Stockholm convention on POPs in 2009 after its use was banned in several countries starting in the late 1970s and onwards. Due to the long lifetime in soil and the large amounts applied, residues from previous year's usage are still emitted to the atmosphere.

We measured α -HCH concentrations at Villum and compared them with results from a simulation with the DEHM model (with the POP setup) covering the period from 1989 to 2020. The emission estimates until 2000 are from Li et al. (2000). The emissions from 2000 and onwards are estimated to be exponentially decreasing with an e-fold time of 10 years. An initial field in ocean water based on measurements (Hansen et al., 2004) and an initial field in soil based on a long-term spin-up simulation (Hansen et al., 2008) was applied to account for α -HCH deposited from usage in the years prior to 1989.



Figure 2.4. Measured weekly average α -HCH concentrations (black dots) and daily averaged modelled concentrations (red curve) and modelled concentrations averaged over same periods as measurements (blues triangles).

The DEHM model predicts similar levels of α -HCH as measured in summer, whereas the predicted winter concentrations are much lower (Figure 2.4.). The seasonal variation is much stronger and the peak appears earlier in the summer in the simulated concentrations compared to the measurements. This is in line with previous results, which indicate that the surface description of the DEHM model is not adequate to describe the seasonal variations in detail when the primary source to atmospheric concentrations is re-volatilisation from the ocean (Skov et al. 2017). This result has consequences for the atmospheric lifetime of α -HCH and the higher measured values indicate that it might have a longer environmental lifetime than hitherto believed.

2.4 Measured organochlorines, brominated- and fluorinated compounds

2.4.1 Organochlorines (OCPs)

Trend in air concentrations of OCPs and fluorotelomer alcohols (FTOHs) presented in (Skov et al. 2017) and (Wong and 2021) have been updated with the data from 2016 to 2019, now covering the time range 2008-2019.

As shown in Figure 2.5, decreasing trends have been confirmed for HCB, α -HCH and endosulfan using classical regression analysis on annual mean concentrations. Endosulfan was not detected in any samples in 2019, confirming that the phasing out of this pesticide is consistent with our observations. No decreasing or increasing trend is observed for lindane (γ -HCH).



Figure 2.5. Temporal trends of annual median concentrations for HCB, α -HCH, γ -HCH and endosulfan 2008-2019.

Annual median concentrations of FTOHs showed an increasing trend between 2016 and 2019, whereas the trend was decreasing between 2010 and 2015, see Figure 2.6. As we do not have emission inventories, it is not possible to explain the behaviour at the moment.



Figure 2.6. Temporal trends of annual median concentrations for HCB, α -HCH, γ -HCH.

2.4.2 PCBs

PCBs have been added to the monitoring program starting from 2016. The analytical program includes 15 congeners that are analyzed in the same samples as OCPs and Polybrominated diphenyl ethers (PBDEs). The average monthly concentrations of the detected congeners from 2016 to 2019 are shown in Table 2.1. Only those congeners detected for 100% of the total samples are shown. The heavier congeners such as PCB-180, PCB-170, PCB-194, PCB-206 and PCB-209 and PCB-114 were only sporadically detected (PCB 114, PCB-180 and PCB-170) or never detected (PCB-194, PCB-206 and PCB-209).

Table 2.1. Median monthly concentrations (pg/m3) of selected PCB congeners in the period 2016-2019.

	PCB-3	PCB-8	PCB-28	PCB-52	PCB-101	PCB-118	PCB-153*	PCB-138
Jan	0.58	23.30	25.81	54.33	23.09	2.96	0.07	5.79
Feb	0.87	16.22	40.28	30.02	11.78	1.40	0.00	3.21
March	0.88	14.30	47.43	30.08	12.05	1.50	0.00	3.74
April	0.13	5.82	13.89	11.91	9.70	1.30	0.00	2.73
Мау	0.30	7.45	25.96	13.00	8.56	1.96	0.00	4.37
June	0.51	7.26	29.39	18.62	16.22	3.44	0.00	8.21
July	0.64	8.33	36.34	23.18	20.48	4.18	0.00	10.15
Aug	0.31	9.37	20.06	16.61	10.18	2.29	0.07	5.04
Sept	0.13	5.30	12.59	9.57	8.53	1.60	0.00	3.17
Oct	0.05	2.01	7.58	6.65	5.11	1.17	0.00	2.39
Nov	0.19	2.08	11.63	6.54	6.24	1.48	0.03	2.65
Dec	0.27	2.79	3.78	1.60	0.78	0.19	0.00	0.39

*The many zero values are for results below detection limit.

2.4.3 HBCDD

Hexabromocyclododecane (HBCDD) is an aliphatic brominated flame retardant (FR), which is mainly used as an additive FR in polystyrene for the insulation of buildings. Unlike the PBDE FRs, HBCDD, see Figure 2.7, was mainly used in Europe. The technical FR consists of three major diastereo isomers, with α -HBCDD, β -HBCDD and γ -HBCDD accounting for approximately 10-13, 1-12 and 75-89%, respectively. HBCDD was added to the Stockholm Convention on POPs in 2013.



Figure 2.7. 2-D projection of the chemical structure of Hexabromo cyclododecane (HBCDD). The major diastereomers are α -HBCDD, β -HBCDD and γ -HBCDD.

HBCDD monitoring has been included by analysing weekly filter samples collected monthly at Villum since 2012. First results were reported previously (Skov et al. 2017). Owing to the low levels of HBCDD in the samples, which generally have been close to or below detection limits, the monitoring of HBCDD will be stopped in July 2021. Instead, a selection of other organic contaminants will be included in the POP monitoring programme, which were identified as relevant Arctic air pollutants in the AMAP assessment on Chemicals of Emerging Arctic Concern (AMAP 2017).

Due to the low levels of HBCDD and the omnipresence of FRs, for example in dust, particular attention was paid to quality assurance/quality control (QA/QC) in the HBCDD measurements. All analyses included reagent blanks and/or non-used filters to determine a potential HBCDD background. In the 2018 measuring campaign, a variety of additional field blanks was included to ensure that the concentrations of HBCDD in the filter samples were no false positives. These additional QA/QC samples did not indicate significant HBCDD sources during sampling, transport, storage or analysis, as most blanks were below the limit of detection.



Figure 2.8. Annual mean concentrations and standard deviations for HBCDD in filter samples from Villum (2012-2019). Concentrations below detection limits were replaced with zero.

Figure 2.8 shows the annual mean concentration of Σ HBCDD (i.e. sum of α -, β - and γ -HBCDD) during the monitoring phase. The annual mean concentrations indicate a maximum in 2016, but due to the large standard deviation, i.e. large variation in the concentration throughout the year, this value is connected with large uncertainty. Each year with data includes several individual samples with concentrations below detection limits.

The low levels of HBCDD are in line with measurements at Zeppelin (Svalbard) and Alert (Canada), as recently summarised (Wong et al., 2021). The detection frequency was only 3-14%, depending on the diastereo isomer, at Zeppelin, while it was 29% for Σ HBCDD at Alert, covering the time periods of 2006-2017 and 2002-2017, respectively. Median Σ HBCDD concentrations were 0.012 and 0.044 pg/m3 at Alert and Zeppelin, respectively (for 2015-2017), while the median value for our data was 0.016 pg/m3 (2012-2019; concentrations below detection limits were replaced with zero). Only considering the time period from 2015-2017, the median value at Villum is 0.022 pg/m3, i.e. similar to the other Arctic measurements. Because of the limited number of quantifiable data points, it is not possible to derive time trends of HBCDD at the Arctic monitoring stations, including Alert, Zeppelin and Villum (Wong et al., 2021).



Average HBCDD composition in filter samples



The average HBCDD composition was dominated by γ -HBCDD and was thus relatively similar to the technical composition of HBCDD (Figure 2.9). However, it has to be noted that standard deviations were > 100% for all isomers in calculations of HBCDD composition, i.e. the individual samples varied considerably in their composition. Wong et al. (2021) reported that α -HBCDD was the most frequently detected diastereomere at Zeppelin. In our dataset, 15% of all samples had a predominance of α -HBCDD. γ -HBCDD was detected most frequently, i.e. in 77% of the samples, while α -HBCDD was detected in 51% of all samples.

Although HBCDD was globally banned in 2013, much later than legacy organochlorine such as PCBs and HCB, its air concentrations at Villum have been relatively low in agreement with its very low vapour pressure and smaller global used amounts (UNEP, 2011). As concentrations are expected to decrease further, following the worldwide ban of HBCDD, the measurement efforts at Villum will focus on other compounds in the future as already stated.

2.5 Acid PFASs in snow

Surface snow samples are collected from October to May every second month. Samples are collected with a metal shovel into a plastic bag. The snow is slowly melted and transferred from the bag into five litre plastic buckets. The samples are then shipped to Denmark, where they are analysed.

The mean concentrations of PFAS in snow over the period 2008-2019 are summarized in Figure 2.10. Half of the detection limit was used in case of nondetected compounds for calculating the average concentrations.



Figure 2.10. The mean concentrations of acid PFAS in for the period 2008-2019. The error bars indicate the standard deviations of the measured concentrations of the entire period.

PFHpA (polyfluorinated heptanoic acid) is the dominant compound followed by the other polyfluorocarboxylic acids with decreasing average concentrations as the number of carbon atoms increases from C6 to C12. PFHpA was the only compound detected in all samples during sample years (Figure 2.11) but the highest level was found for PFNA in 2013 at 1.88 ng/L (Figure 2.12). In 2015, a maximum concentration of PFHpA at 1.46 ng/L was observed.



Figure 2.11. Frequency % of detection for PFAS in snow between 2008 and 2019.

The annual mean concentrations of selected compounds in the period 2008-2019 are shown in Figure 2.12.



Figure 2.12. Trend of annual mean concentrations in ng/L between 2008 and 2019 for PFOS, PFHpA, PFOA, PFNA and PFDA.

PFOS was not detected between 2015 and 2018 with only three samples detected in 2019 (38% detection frequency), confirming the general low level of this compound in the environment after retractions and regulations in production as well as use by US-EPA and EU. PFHpA is the most abundant compound as already stated (but dominated by observations in one particular year). This compound is most probably a product from photo-oxidation in the atmosphere of the more volatile 6:2 fluorotelomere alcohol (FTOH), which is the most abundant FTOHs found in the atmosphere at Villum (Bossi, Vorkamp and Skov, 2016). In 2016 very high concentrations of PFHpA (2.29 ng/L in May/June) were found, probably because of transport episodes of the corresponding alcohols. Besides these episodes, the concentrations of these two perfluorocarboxylic acids and the other longer chained PFAS (PFDA, PFUnA, PFDoA) have remained more or less constant as a result of their unregulated use in industrialized countries.

2.6 Hg in Snow

Snow samples have been collected since 2013 and analysed for mercury concentrations. Sampling was not done systematically in the first years but recently, snow samples have been collected after each new snowfall or at least once per month. The levels are in general low around detection limits but levels up to 8 ng/L have been observed, see Figure 2.13.



Figure 2.13. Hg in surface snow measured from 2013 to 2019.

Interestingly, the yearly average concentration of Hg in snow samples is 1.03 ng/L. Whereas for the spring month, April and May, it is 2.14 ng/L and for the rest of the year, it is 0.56 ng/L as an average. The latter is very close to the limit of detection (LoD) of 0.5 ng/L. The higher level in spring thus indicates that mercury depletion has an increasing effect on the Hg concentration in surface snow, though the high concentrations observed at Barrow (Brooks, Saiz-Lopez et al. 2006) are not seen at Villum so far.

2.7 Black Carbon measurements and model results

We present here for the first time a MAGEE AE33 aethalometer used for measuring black carbon (BC). It has been operated at Villum since July 2017 to measure equivalent black carbon (eBC). The aethalometer is an absorption photometer that measures light attenuation through a filter with sampled aerosol and converts this to an eBC concentration using a standard mass-absorption cross-section of 7.77 m2 g-1 at 880 nm wavelength (Drinovec et al. 2017). An Arctic harmonization factor was used to account for the known overestimation of absorption coefficients by the aethalometer in the Arctic environment (Weingartner et al. 2003; Backman et al. 2017) which was also applied in the latest AMAP report on SLCF (AMAP 2021a).

DEHM with the basic chemical setup has been used to simulate black carbon (BC) concentrations at Villum, of which the major source region is primarily northern Eurasia (Massling et al. 2015). In Figure 2.14 results from DEHM are compared to measurements of the aethalometer eBC at Villum.



Figure 2.14. Comparison of aethalometer eBC measurements with modelled BC concentrations from DEHM, shown as monthly means. The error bars indicate the spread of the measurements as 1 std. dev.

It can be seen that the Arctic haze period with elevated BC/eBC levels in the winter and spring is reproduced well by the model and by the measurements; though there is disagreement between DEHM results and observations in the haze period from late 2017 to mid-2018. A closer agreement between DEHM and observations is seen onwards. In addition, DEHM seems to show an overestimation of BC concentrations in the summer, between the Arctic haze periods. The concentration levels in summer originate predominantly from biomass burning contributions (contributing between 60 and 100% of the total BC), and this discrepancy is attributed to uncertainties in biomass burning emissions generated from satellite data.

2.8 Monitor results; CO, Ozone and GEM

2.8.1 CO

CO is a key compound in the atmosphere. Besides being toxic at high concentrations, it is an important compound as its oxidation leads to formation of ozone and a significant contribution to CO_2 . Furthermore, it is also important as an indicator for incomplete combustion of either fossil fuel or biomass.

We tested and calibrated a new CO monitor (based on absorption of IR light) in our monitor laboratory, where we got the expected values. Thereafter, it was set up at Villum, where we got very unstable readings and results that were discarded. We tried again after repair and we repeated this a few times with unsuccessful results at each trial. Therefore, we have decided to replace the instrument with a new CO monitor from Picarro, which was bought in November 2021. It has been successfully tested and is now measuring continuously at Villum.

2.8.2 Ozone

Ozone has been measured at Villum since 1996 with a break between June 2002 and June 2007, see Figure 2.15. The aim of these measurements is to obtain a deeper insight into the general chemistry of the Arctic atmosphere that



determines the fate of many pollutants and to assess the dynamics of this toxic compound.

Figure 2.15. Time series of ozone mixing ratio at Villum.

A distinct seasonal pattern of ozone mixing ratios is evident in Figure 2.15 and 2.16. A maximum ozone concentration is observed during winter, and in spring, a highly perturbed period during ozone depletion episodes (ODEs) is observed leading to a minimum in May. Thereafter, a local maximum is seen in June and another minimum in July and August. This seasonality is demonstrated clearest in Figure 2.16, where the monthly medians of all the years are shown together with the quartiles spread on values.



Figure 2.16. Monthly median concentrations at Villum for the years 1996 -2000 and 2012-2019, respectively (Based on Law et al. 2023).

The late spring minimum is due to the depletion of ozone that is observed at Arctic coastal stations (AMAP 2021a) and is connected to the depletion of ozone and mercury called ozone depletion events (ODEs) occurring together with mercury depletion events (MDEs) (Skov et al. 2020; Brooks et al. 2006; Skov et al. 2004; Wang et al. 2019). It is now proven that the occurrence of ODE

at times is due to catalytic degradation of ozone by reaction with Br (Wang et al. 2019):

 $O_3 + Br \rightarrow BrO + O_2$ $2BrO \rightarrow Br_2 + O_2$ $Br_2 + hv \rightarrow 2Br$

These processes give a different seasonal behaviour than at continental, higher altitude localities or more southern sites (AMAP 2021a).

The source of bromine is a more open question. The most common hypothesis is that Br₂ is released to the atmosphere by heterogeneous reactions from refreezing leads or produced from windblown snow containing marine salt and the first attempts have been made to model ODEs including these sources (Yang et al. 2020).

Yearly median concentrations of ozone do not show a significant trend looking at all data from 1997 until today, see Figures 2.17 and 2.18, though there is a significant monthly increase on a 95 confidence interval during winter (except February) and March. In Figure 2.16, the median from 1996 to 2000 is compared to the median from 2012 to 2019. We have chosen a relatively short second period in order not to have it too strongly weighted compared to the data available in the first period.

However, from 2007 and until today there is a significant increase in the yearly average concentrations, especially during the winter half year except February (see Figure 2.18).



Figure 2.17. Seasonal Sen slopes of ozone monthly median concentrations calculated by de-seasoned Mann-Kendall test for the available data from 1996 to 2019 including 95% confidence interval. Months with significant trends are in blue and non-significant trends are in grey (Based on Law et al. 2023).

For this period (2007-2019), the increase in the ozone mixing ratio is significant for all months but April and May, where the ODE's occur. In the spring, the special halogen chemistry might be the reason for this lack of increase. The increase in ozone has been explained previously by decreasing emission of NOx, since removal of ozone by reaction with NO is also reduced. In the summer (June, July and August), the lower increase might be explained by the



retreating sea ice and greening of the Arctic that leads to faster deposition of ozone (as the surface resistance decreases) and the photochemical formation of O3 is lowered due to the smaller anthropogenic NOx emission.

Figure 2.18. Seasonal Sen slopes of ozone monthly median concentrations calculated by de-seasoned Mann-Kendall test for 2007 to 2019, including 95% confidence interval. Months with significant trends are in blue and non-significant trends are in grey (Based on Law et al. 2023).

The results from Villum are part of the next AMAP report on SLCF as mentioned earlier and more scientific papers as spin-off of this work.

2.8.3 GEM

The long time series of gaseous elemental mercury (GEM) measurements and modelling results at Villum with a focus on observed inter-annual and seasonal trends as well as the likely explanations for these in terms of sources, transport patterns and dynamics are presented in this section.

The measurements of GEM 1999 to 2019 are shown in Figure 2.19.



Figure 2.19. Time series of GEM at Villum from 1999 to 2019.

A seasonal pattern is observed for each year, see Figure 2.20. In January and February, the level of ozone and GEM is rather stable. After the polar sunrise, the concentration starts to fluctuate strongly, and ozone and GEM are depleted quickly (within 2 to 10 hours).



Figure 2.20. Monthly mean concentrations from 1999 to 2019 showing seasonal behaviour of GEM. From Skov et al. 2020.

Figure 2.21 shows the variations of the measured yearly average GEM concentration and the average for the winter season between 1999 and 2019, where only periods with more than 50% data coverage have been included. The annual averages show a negative trend, however not significant at a 90% confidence level. The autumn (September-October-November) and the winter months show both negative trends that are significant at a 90% confidence level (only the winter months and yearly average are shown in the figure). The trends, in percentage of the average measured GEM concentrations during these periods, are -1.7%/yr for the winter period and -1.4%/yr for the autumn period (Skov et al. 2020).



Figure 2.21. Red squares show yearly mean GEM concentrations together with red Sen's slope line. Black squares are average concentrations for the period December, January and February together with blue Sen's slope line. From Skov et al. 2020.

The DEHM model with Hg as a simple tracer, using variable anthropogenic emissions, shows a slightly decreasing concentration trend, -0.7% per year. However, this direct anthropogenic input, assuming a GEM relaxation time (the time from which an emission change will lead to change in atmospheric concentration) of 12 months, only accounts for between 14 and 17% of the observed GEM concentrations, (Figure 2.22). Including also the impact of sea emissions and the model boundary conditions, the model predicts an annual average GEM concentration of 1.40-1.43 ng/m3, i.e. in agreement with the measured average in the period of 1.46 ng/m3, although the measured data covers a larger range of values (1.2-1.8 ng/m3). When applying longer or shorter GEM lifetimes, the model results deviate more from the measured concentrations and thus the best relaxation time of GEM in the Northern Hemisphere is 12 months. The chemical lifetime of GEM in the atmosphere is shorter according to the theoretical and experimental evidence (Skov et al. 2020; Goodsite, Plane and Skov 2004; Goodsite, Plane and Skov 2012) (and references therein). Therefore, the deposition of HgII species appears to be followed by a reduction and reemission of Hg0 (Brooks et al. 2006; Kamp et al. 2018; Saiz-Lopez et al. 2020). Thus, relaxation time seems to be a more appropriate name than lifetime for GEM. This is supported by a study on the photo-reduction of HgII in cloud droplets, which was found to be much slower than the one used in models, leading to the conclusion that deposition and reemission are involved in the dynamics of atmospheric mercury (Saiz-Lopez et al. 2018). The sea emissions were found to account for 20-21% of the GEM concentration at Villum, and the boundary conditions of 1.5 ng/m3 explained 62-65%, while emissions from wildfires contributed 1% during the years of the measurements.



Figure 2.22. Model calculations with variable emissions of the source apportionment of annual average GEM at Villum. The DEHM model was used for 2 years (1990 and 1991) to spin up the model. In the model, re-emissions from the ocean and contributions from boundary conditions at the Equator are included. Source regions: Russia – Russia; EEU – eastern Europe; WEu – western Europe; China – China; Africa – Africa; SAm – South America; Bound – boundary condition; Ocean – ocean; Fire – wildfire. Unit: ng/m³. From Skov et al. 2020.

In test calculations with DEHM, it was found that emissions from China had larger relative importance during the summer compared to the winter season; however, this difference was only significant when applying relatively short (less than 1 year) atmospheric relaxation lifetimes of GEM.

3 Conclusion

This report describes the results obtained in the Danish contribution to the atmospheric part of the Arctic Monitoring and Assessment Program (AMAP). We have contributed to several new AMAP assessment reports:

- 2021 POPs and Chemicals of Emerging Arctic Concern: Influence of Climate Change.
- 2021 AMAP Mercury Assessment.
- 2022 Impacts of Short-lived Climate Forcers on Arctic Climate, Air Quality, and Human Health.

(see <u>www.amap.no</u>.)

Thus, this report has to be seen as an addition to this work to highlight the Danish contribution.

The longest data series we have, goes back to 1990 and is on elements, and salts as well as sulfur dioxide. Ozone measurements were initiated in 1995, GEM in 1999 and most of the other measurements (e.g. POPs) started in 2008. These data series form a strong base for evaluating trends, yearly differences and seasonal patterns.

We are using the integrated monitoring strategy, where measurements and models are performed following the same strategy in order to obtain most information from the funded activities. Focus is on process understanding in order to evaluate the consequences of abatement and legislative initiatives and potentially enable optimization of these. Some of the main findings and conclusions from this report are highlighted below.

3.1 SOx

The main source of sulfur dioxide and sulfate at Villum is anthropogenic emissions at mid latitudes. The main reasons for observations of changed pollution levels in the Arctic atmosphere are still the changes in anthropogenic emission for most species.

The concentrations of sulfur dioxide and sulfate are still interesting because sulfate aerosols serve as transport container for many compounds. Modelling of sulfate demonstrates that DEHM describes the transport of anthropogenically emitted species at mid-latitudes very well. Looking more into details there are still discrepancies between modelled and measured concentrations of sulfur species. The discrepancies are due to the uncertainty in emission inventories of anthropogenic emissions of mainly sulfur dioxide and the parameterisation of sea salt sulfate, DMS and other natural sulfur sources.

The appearance of the seasonal behaviour is explained by the position of the polar front over the year, the variation in source strength and by the appearance of polar sunrise in the end of February. With the polar sunrise, photochemical processes start oxidizing sulfur dioxide to sulfate and the solar heat creates more turbulence in the atmosphere leading to faster deposition of pollutants that eventually also removes the sulfate aerosol.

3.2 Organochlorines, brominated and fluorinated compounds

Long series of POPs have been measured since 2008, establishing levels of several persistent compounds in the Arctic atmosphere. In general, we can explain the observed levels and trends from the emissions, source areas and the properties of the compounds. Emission inventories are only available for few of the compounds, which limits the possibilities of modelling the atmospheric transport using DEHM or other models. Although the measured time series are relatively short, significant trends have been observed for many of the compounds.

Very low levels of HBCDD were observed over the monitoring period of 2012-2019. HBCDD was banned in 2013 and thus used more recently than legacy POPs such as PCBs and HCB. As concentrations are expected to decrease further following the worldwide ban on HBCDD, the measurement efforts at Villum will focus on other compounds in the future (e.g. Heksachloro-1,3-butadiene).

The number of potentially persistent compounds emitted to the environment due to human activities is increasing (<u>Homepage - ECHA (europa.eu)</u>). As some of these compounds have low environmental concentrations, measurements and modelling can be challenged and further complicated by limited availability of emission inventories.

All legacy POPs pose the modelling challenge that no anthropogenic primary emissions occur, since most legacy POPs are totally banned worldwide (with very few exceptions, such as the restriction of DDT, instead of its ban), the only source is reemission from soil and water surfaces. This became apparent for α -HCH. The comparison between measured and modelled concentrations of α -HCH shows that a new parameterization will be needed to describe the levels and trends in order to capture important noxious environmental effects.

3.3 Black carbon

Black carbon concentrations have been reported to AMAP and are an important part of the AMAP assessment report on SLCF (AMAP 2021a). The sources of BC are dominated by long-range transport of pollution from mid latitudes and are mainly connected to combustion of fossil fuel. A lot of attention has been towards biomass burning as a source of BC, but its contribution to Arctic BC concentrations is minor during most parts of the year. However, during summer biomass burning contributes significantly to the general low concentrations of BC at Villum.

Fossil fuel contribution to BC is well described by DEHM, whereas this is not the case for biomass burning. The latter is explained by the large uncertainty in wildfire emission inventories.

3.4 Ozone

The depletion of ozone is following the one for GEM. The variability of ozone is large and thus there is no trend in the appearance and duration of ODE. Ozone has no significant trend from 1990 to 2019, though an increased level is seen during the winter months. A significant trend is observed when looking at the later years from 2007 to 2019 in all months, except the spring months April and May that have highly perturbed levels due to ODE. The work on

ozone contributes significantly to the AMAP assessment on SLCF (AMAP 2021a).

3.5 Mercury

The measurements of GEM have been carried out since 1999. Measurements show a decreasing trend during autumn of 0.03 ng m-3 year-1, whereas no trend in the appearance or change in the beginning and end of mercury depletion episodes can be observed. The decreasing trend in autumn and winter can be explained by changes in transport patterns to the Arctic and by changes in removal processes. However, direct transport constitutes only about 20% of the total concentrations at Villum where the remaining major part can be attributed to background levels of mercury and reemission from oceans (Skov et al. 2020).

3.6 Snow samples

3.6.1 Hg

In general, the measured mercury concentrations at Villum are low. In spring 2016 higher levels of mercury were observed though they were still a factor of 10 lower than e.g. found at Point Barrow in Alaska.

The yearly average concentration in surface snow of Hg at Villum is 1.03 ng/L, whereas, for the spring months April and May, it is 2.14 ng/L and 0.56 ng/L as an average for the rest of the year, indicating that mercury depletion increases Hg concentrations in surface snow.

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AMAP CORE - ATMOSPHERE

This report describes the results obtained in the Danish contribution to the atmospheric part of the Arctic Monitoring and Assessment Program (AMAP). It includes results of measurements at Villum Research Station, Station Nord from 1990 to 2019 and is an update of the previous report from 2017 (Skov et al. 2017). A series of climate-relevant particle parameters as well as particle bound compounds and gasses relevant for determining the anthropogenic impact on the sensitive Arctic environment have been measured. The results have been used to improve the parameterisation of the Danish Eulerian Hemispheric Model (DEHM) as well as to constrain the model. The results are all reported to AMAP, EMEP and to WMO-Global Atmospheric Watch and have been a significant contribution to AMAP assessment reports on Mercury, Short Lived Climate Forcers (SLCF), as well as Persistent Organic Pollutants (POPs) and chemicals of emerging Arctic concern (CEACs). The data have been analysed statistically for significant trends, and the connection between emissions and observed concentrations was investigated using a combination of models and measurements. The assessment reports are used to support policy-making and legislative work in the Arctic Council as well as international conventions, such as the Stockholm and Minamata Conventions.

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