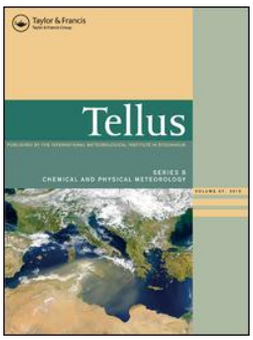

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Occurrence of an ultrafine particle mode less than 20 nm in diameter in the marine boundary layer during Arctic summer and autumn

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ABSTRACT

The International Arctic Ocean Expedition 1991 (IAOE-91) provided a platform to study the occurrence and size distributions of ultrafine particles in the marine boundary layer (MBL) during Arctic summer and autumn. Measurements of both aerosol physics, and gas/particulate chemistry were taken aboard the Swedish icebreaker Oden. Three separate submicron aerosol modes were found: an ultrafine mode ($D_P < 20$ nm), the Aitken mode ($20 < D_P < 100$ nm), and the accumulation mode ($D_P > 100$ nm). We evaluated correlations between ultrafine particle number concentrations and mean diameter with the entire measured physical, chemical, and meteorological data set. Multivariate statistical methods were then used to make these comparisons. A principal component (PC) analysis indicated that the observed variation in the data could be explained by the influence from several types of air masses. These were characterised by contributions from the open sea or sources from the surrounding continents and islands. A partial least square (PLS) regression of the ultrafine particle concentration was also used. These results implied that the ultrafine particles were produced above or in upper layers of the MBL and mixed downwards. There were also indications that the open sea acted as a source of the precursors for ultrafine particle production. No anti-correlation was found between the ultrafine and accumulation particle number concentrations, thus indicating that the sources were in separate air masses.

1. Introduction

Particle production in remote atmospheric regions has been studied recently, both experimentally and theoretically (Covert et al., 1992; Hegg et al., 1992; Clarke, 1993). It is crucial to understand the effect of new particle production in the atmosphere. These particles may play a significant rôle in the radiation balance of the earth and therefore in the climate system. They can backscatter light, directly effecting transmission of sunlight, as well as acting as cloud condensation nuclei which indirectly influence the optical properties of clouds (Charlson et al., 1991). It is believed that particles less than 10 nm in diameter are generated by homogeneous nucleation from precursors, e.g., primarily sulphur gases, such as sulphuric acid (H_2SO_4), which is formed by oxidation of sulphur dioxide (SO_2) in the presence of hydroxyl (OH) radicals. However, homogeneous nucleation is strongly dependent on factors such as temperature, H_2SO_4 vapour pressure, the partial pressure of water vapour (H_2O), and the surface area of pre-existing particles (Seinfeld, 1986; Jaecker-Voirol and Mirabel, 1989).

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1.1. *Modelling of particle production*

There have been several model-supported investigations concerning the conditions for the occurrence of ultrafine particle production ($D_P < 20$ nm) in the marine boundary layer (MBL).

Raes and Van Dingenen (1992) concluded that the process of homogeneous nucleation can occur within 24-h time period and within a homogeneously mixed MBL. This study was performed assuming "realistic" atmospheric conditions of temperature, relative humidity, and average OH and biogenic SO_2 concentrations. In a study by Kreidenweis et al. (1991), best available estimates of the rates of nucleation H_2SO_4–H_2O particles were used to predict the aerosol number concentration. The results of their study indicated that dimethyl sulphide (DMS) can act as a precursor gas for marine aerosol, according to the current limited understanding of DMS oxidation and aerosol forming potential. For a single event, Hegg et al. (1992) related event bursts of ultrafine particles near the sea surface in the size range 3–20 nm to relatively high SO_2 concentrations and low aerosol surface area. These favourable conditions were plausibly attributed to a vertical mixing event which transports air with high SO_2 concentrations and low aerosol surface area to the sea surface.

Ultrafine particles can also be produced in the upper free troposphere (FT) and can be mixed into the MBL. However, according to the model of Raes and Van Dingenen (1992), these ultrafine particles have a long residence and transport time in the FT. By the time they reach the boundary layer, they have grown into the Aitken mode ($20 < D_P < 100$ nm). This is supported by the findings of Clarke (1993). Clarke measures that the upper troposphere is a region where the production and long life time of new particles such as sulphuric acid produced by homogeneous nucleation are favoured. In this region these ultrafine particles can grow to larger sizes.

There is also a hypothesis suggesting that ultrafine particle production is associated with marine clouds, especially in the cloud top. It is assumed that such layers are the result of in situ, photochemical particle production (Hegg et al., 1990).

Besides sources of ultrafine particles, there are also natural sink processes. The main sink for ultrafine particles is growth by coagulation or condensation to larger sizes rather than removal from the atmosphere. If the number concentration of aerosol particles is high ($N > 1000$ cm^{-3}), losses by coagulation, most likely with accumulation mode particles, are relatively rapid (Friedlander, 1977). In the remote marine boundary layer, coagulation is only likely to be significant immediately after a production burst when the ultrafine particle number concentration is high. Otherwise, in remote areas with very low particle number concentrations ($N < 300$ cm^{-3}), the particle-particle coagulation process is very slow. However, if well-mixed boundary layer air is intermittently mixed into a cloud, ultrafine particles are efficiently scavenged by cloud droplets due to particle-droplet coagulation. The coagulation rates between 10 nm particles and: 100 nm, 1 μm, and 10 μm particles are respectively 2.3, 25, and 238 times faster than the coagulation between 10 nm particles (Hinds, 1977).

If enough condensable material, e.g., H_2SO_4, is present, particles in the ultrafine mode can grow by homogeneous or heterogeneous condensation into the Aitken mode. However, there is no general agreement on estimations of the time scales of these growth processes and no experimental evidence exists for it.

Another apparent "sink" is the reduction of the ultrafine particle concentration due to transport phenomena. If ultrafine particles are produced in bursts under locally favourable conditions, then these high number concentrations of ultrafine particles are naturally diluted during transport.

1.2. *Ultrafine particle measurements*

A large number of size distribution measurements in remote marine areas have been made in the past using different instrumentation. Over the North Atlantic, Hoppel et al. (1990) found a bimodal aerosol distribution in the size range $D_P > 17$ nm using a Differential Mobility Particle Sizer (DMPS). For measurements in the mid-Pacific and Atlantic, peaks in the bimodal size distribution were obtained approximately at 40 and 150 nm (Quinn et al., 1993; Covert and Heintzenberg, 1993).

On the other hand, only a few size distribution measurements were performed in the size range down to 3 nm. Ito (1980), measured with a diffu-

sion battery, bimodal size distributions below 100 nm in diameter over remote islands in the North Pacific (1000–2000 km away from Japan). These measurements produced size distributions consisting of one peak at approximately 40 nm in diameter, and also another peak at about 8 nm which was not always detected. Ito (1993) measured also a separate ultrafine mode with the same instruments in the Antarctic. DMPS measurements over the tropical and South Pacific by Hoppel and Frick (1989) showed strong variability in the size range below 60 nm in diameter. This was interpreted as a result of new particle production with a subsequent growth into the observation range of the DMPS. Covert et al. (1992) compared the total number concentration of an Ultrafine Condensation Particle Counter (UCPC) ($D_P > 3$ nm) with the number concentration of the aerosol size distribution measured with a DMPS ($20 < D_P < 570$ nm). Here, an increase in the UCPC concentration was observed while the total aerosol surface area in the DMPS size range rapidly fell. This is indicative for new particle formation.

The 1991 International Arctic Ocean Expedition (IAOE-91) provided a platform to study the occurrence and size distribution of ultrafine particles in the MBL during the Arctic summer and autumn. Measurements of both aerosol physics, and gas/particulate chemistry were taken aboard the icebreaker *Oden* during 13 separate time periods (atmospheric chemistry stations). Measurements were also made at other times when atmospheric sampling was possible (Leck et al., 1996). We found three separate submicron aerosol modes: the ultrafine mode ($D_p < 20$ nm), the Aitken mode ($20 < D_p < 100$ nm), and the accumulation mode ($D_p > 100$ nm), with geometric mean diameters of 13 nm, 43 nm, and 165 nm, respectively (Covert et al., 1996). There were clear minima between the modes that appeared at 20–30 nm, and at 60–110 nm. The Aitken mode and accumulation mode were detected nearly 100 % of the time while the ultrafine mode appeared only about 65 % of the sampling time. The highest number concentrations were generally found in the Aitken mode (40 %) and in the accumulation mode (45 %). The number concentration and geometric mean diameter of the ultrafine mode showed the greatest variabilities. The physics of the coarse mode ($D_p > 1\ \mu$m) was beyond the scope of this study. In this investigation, meteorological, air chemistry, and aerosol physics data were used in multivariate statistical methods to explore correlation with ultrafine particle number concentration and the ultrafine mean diameter.

2. Aerosol size distribution measurements

Four different instrumental methods were used for measuring ultrafine particle size distributions in the size range 3–20 nm in diameter: A DMPS that was designed for ultrafine particle classification (UDMPS), a diffusion battery that was optimised for ultrafine particle sizing, an Ultrafine Condensation Particle Counter (UCPC) with a variable condenser (T:UCPC), and an UCPC with pulse height analysis (PHA:UCPC). In all cases, a UCPC was used as the particle detector. This limited the lower detection size to 3 nm in diameter. However, the UCPC permitted single particle detection, which made it possible to measure very low number concentrations (Wiedensohler et al., 1994). In addition, a second DMPS measured the size distribution of aerosol particles in the size range $20 < D_p < 500$ nm.

A fitting algorithm (Distfit®, TSI) was used to parameterise hourly size distribution data from the UDMPS and DMPS according to the best fit to bimodal or trimodal lognormal distribution functions (Covert et al., 1996). The fitting algorithm produced three parameters for each fitted mode: the integral number concentration in the mode, the geometric mean diameter of the mode, and the geometric standard deviation. A bimodal fit was selected in cases when a trimodal fit produced unrealistic parameters. In the multivariate statistical evaluation, only the integral number concentration and the geometric mean diameter of these bimodal or trimodal fits were used.

3. Results and discussion

3.1. *Principal component analysis*

Several multivariate statistical evaluation algorithms were applied to the hourly *Oden* data set. The objective was to elucidate relationships

Table 1. *Acronyms for the measured physical, chemical, and meteorological parameters used in the multivariate statistical analysis*

parameter	acronym
ultrafine mode number concentration	N_{uf}
Aitken mode number concentration	N_{Ait}
accumulation mode number concentration	N_{acc}
ultrafine mode surface area	A_{uf} (derived from N_{uf} and D_{uf})
Aitken mode surface area	A_{Ait} (derived from N_{Ait} and D_{Ait})
accumulation mode surface area	A_{acc} (derived from N_{acc} and D_{acc})
ultrafine mode geometric mean diameter	D_{uf}
Aitken mode geometric mean diameter	D_{Ait}
accumulation mode geometric mean diameter	D_{acc}
radon concentration	radon
ozone concentration	O_3
DMS concentration	DMS
absolute humidity	abshum

between the properties of the ultrafine mode (i.e., ultrafine number concentration, surface area, and geometric mean diameter) and the other measured atmospheric parameters listed in Table 1.

The surface areas of the three aerosol modes were added to the data set to find indications of possible chemical reactions which are related to the particle surface area. The total surface areas were analytically calculated from the number concentrations and geometric mean diameters from the respective modes. The absolute humidity was derived from the measured ambient temperature and relative humidity. Because of the wide spread of values for all variables, except for absolute humidity, the logarithm of the variables were used. Furthermore, the variables were standardised (zero mean and unit variance) prior to the multivariate statistical evaluation. Three outliners were excluded: two high accumulation mode number concentrations during a station in early August and one ultrafine mode number concentration in the beginning of October.

The analysis was done for two subsets of the data using: (i) all 1-h average sampling periods of the 13 air chemistry stations except those for which the number concentration of any of the modes was zero (183 out of 287 cases); (ii) only 1-h averages from stations 4–10 sampling periods (ship in pack-ice) except those for which the number concentration of any of the modes was zero (87 out of 287 cases).

This distinction was used to study separately the ultrafine particle occurrence over the central Arctic Ocean pack ice area, far away from continental and marine sources. Principal component analysis is a multivariate statistical method which aims at describing the multivariate data set to facilitate its interpretation. The pattern of covariation between the observed parameters (the variables) is effectively revealed as the original variables are transformed into fewer new variables (the components) while retaining a maximum amount of the information (variance) contained in the original data.

SUBSET 1

The VARIMAX rotated solution for data subset 1 which retained four principal components (PC) is given in Table 2a. The bold numbers emphasise the parameters with the strongest correlation which are the basis of that component. Loadings are the coefficients of correlation between the variable and the PC in question. The commonalties give the fraction of variance for each variable explained by the PC model. The amount of variance accounted for each PC is also given.

In the first PC, the number concentration of the accumulation mode is strongly correlated with the Aitken mode number concentration and with the ozone concentration. The strong coupling between the accumulation and Aitken mode number concentration is probably due to cloud processing. The major part of the accumulation mode and Aitken mode could be transported into the Arctic from polluted areas. This could be sup-

Table 2. *VARIMAX rotated PC solution for subset 1 (2a) and subset 2 (2b)*

(a)

Variable	Component 1	Component 2	Component 3	Component 4	Communality
N_{uf}	0.08	−0.03	**0.96**	−0.12	0.94
N_{Ait}	**0.71**	0.42	0.47	−0.02	0.91
N_{acc}	**0.90**	0.17	0.13	−0.20	0.90
A_{uf}	0.16	0.42	**0.71**	−0.20	0.75
A_{Ait}	**0.80**	0.29	0.36	0.16	0.88
A_{acc}	**0.89**	0.19	0.09	0.09	0.85
D_{uf}	0.15	**0.69**	−0.32	−0.13	0.63
D_{Ait}	0.47	−0.20	−0.14	0.50	0.53
D_{acc}	0.09	0.12	−0.15	**0.87**	0.81
radon	0.22	0.45	−0.03	−0.45	0.45
O_3	**0.67**	−0.20	−0.27	0.13	0.57
DMS	−0.01	**0.85**	0.42	0.04	0.90
abshum	0.12	**0.84**	0.34	0.07	0.84
variance	3.54	2.71	2.33	1.39	9.96

(b)

Variable	Component 1	Component 2	Component 3	Component 4	Communality
N_{uf}	0.39	−0.10	**−0.75**	−0.42	0.91
N_{Ait}	**0.86**	0.29	−0.01	−0.22	0.88
N_{acc}	**0.87**	0.09	0.24	−0.05	0.83
A_{uf}	0.56	0.02	−0.35	−0.55	0.75
A_{Ait}	**0.91**	−0.04	0.01	0.10	0.85
A_{acc}	**0.87**	0.12	0.11	0.27	0.85
D_{uf}	0.23	−0.18	0.55	−0.18	0.43
D_{Ait}	0.15	**−0.79**	0.05	0.21	0.69
D_{acc}	−0.07	−0.02	−0.29	**0.78**	0.69
radon	0.17	0.19	**0.80**	−0.11	0.71
O_3	0.17	−0.42	0.09	**0.65**	0.62
DMS	−0.01	**0.81**	0.01	−0.15	0.74
abshum	0.12	**0.75**	0.04	0.13	0.72
variance	3.88	2.21	1.80	1.78	9.66

The four PC model accounts for 75% (9.96 units for the variance) in subset 1 and for 75% (9.73 units for the variance) of the total data set variance in subset 2. The behaviour of ultrafine particle number concentration is largely described by the 3rd PC. The bold values represent these parameters with the strongest loading in the components.

ported by the positive correlation to the concentration of tropospheric ozone. This correlation could, however, also be interpreted as a support for vertical downward mixing if the aerosol in the free troposphere is aged. The vertical transport could occur either due to subsidence in an entire region of high-pressure circulation or due to some intermittent overturning of the boundary layer which has been found to bring down higher ozone concentrations from aloft.

PC 2, the DMS concentration and absolute humidity can be linked to air masses from the open sea. The geometric mean diameter of the ultrafine mode seems to be correlated to DMS and absolute humidity. This finding indicates an aged ultrafine mode, probably produced over the ocean a few days before it reached the ship location.

Fortuitously, the number concentration of the ultrafine mode only has significant loadings on PC 3, which facilitates the interpretation of the interdependence between ultrafine particle concentration and the other variables. The dependence of

the ultrafine mode number concentration on the other variables was found to be weak. In particular, no anti-correlation was observed between the ultrafine and accumulation mode number concentrations and the accumulation mode surface area, which otherwise was expected according to the model scenarios and the results of Hegg et al. (1992) and Clarke (1993). This implies that the accumulation mode observed at the sampling site was not present at the location of ultrafine particle production, and that its concurrence is the result of mixing of two air masses, one of them maybe from aloft. In Nilsson (1996), breaking waves and the radiation of shear induced gravity waves are suggested to be the cause of sudden changes of number concentration for $D_p > 20$ nm on a time scale less than 1 h. Mixing from the free troposphere could explain the weak positive correlation with the Aitken mode number concentration. Furthermore, it was found that the ultrafine particle concentration anti-correlates with the ultrafine diameter. This can be explained by a combination of dilution and condensational growth during transport and ageing of the ultrafine particles. The older the ultrafine mode was, the more material condensed on the particles and the more diluted it became. Thus, producing a larger mean diameter and a lower number concentration.

The fourth PC, the geometric mean diameter of the accumulation mode has a positive correlation with the geometric mean diameter of the Aitken mode and an anti-correlation with the radon concentration. This correlation pattern indicates an aged air mass which was not recently in contact with a land mass.

SUBSET 2

The VARIMAX rotated solution for data subset 2 retaining also four PCs is given in Table 2b.

Here, the first PC gave again a strong coupling of the Aitken and accumulation mode number concentrations. However, in contrast to subset 1, no correlation with the ozone concentration was observed. Furthermore, a weak correlation with N_{uf} was found. It seems to be that the Aitken and accumulation mode number concentrations are always closely coupled. The ultrafine mode is often, but not always coupled to the other modes independent of the source. This indicates that all modes are transported to the ship position due to an air mass change.

The second PC is loaded most strongly with the variation of DMS concentration, absolute humidity, and the Aitken mode mean diameter. D_{Ait} is inversely related to the other two, however. Furthermore, there is a weak anti-correlation between N_{Ait} and D_{Ait}. If the first component represents a particle source from polluted areas then the second component represents another source, probably the open sea. This is primarily a source of fresh Aitken mode particles produced over open water, which have grown during the transport into the central Arctic.

PC 3 is dominated by a strong anti-correlation between N_{uf} and the radon concentration. It seems that a possible ion-induced homogeneous nucleation of ultrafine particle was not connected to the existence of radon. Furthermore, this anti-correlation indicates that the ultrafine particle mode did not occur when air from continental origin or from islands and coasts within/around the Arctic ocean was directly transported over the pack ice. On the other hand, sudden decreases in radon concentration were used in Bigg et al. (1996) as indicators of downward mixing within the Arctic stable MBL. This is based on the crustal source of radon which generally will result in upward decreasing vertical radon profiles such that a downward mixing would cause a decrease in radon. Ultrafine particles could be transported due to this process to the ship location. N_{uf} anti-correlated again with D_{uf} as seen in subset 1. Since N_{uf} did not correlated with marine air (PC 2) or continental air (PC 3), ultrafine particles could have been produced in other stable levels of the MBL or in the top level of the MBL connected to cloud processes. Furthermore, there is no correlation to N_{Ait} as found in subset 1 which would indicate intermitted mixing from the free troposphere.

The accumulation mode diameter and ozone comprise the fourth PC. When D_{acc} is large, the aerosol is aged and probably represents (as PC 1 from subset 1) transportation into the Arctic.

3.2. *Partial least square (PLS) regression*

To further elucidate the covariation between the ultrafine number concentration and the other variables (excluding the surface areas of the three modes), a direct multivariate PLS regression was performed (Geladi and Kowalski, 1986). This PLS is a regression of N_{uf} (dependent variable) on the other variables listed in Tables 3 (independent

Table 3. *PLS regression solution for subset 1 (3a) and subset 2 (3b)*

(a)

Variable	PLS1 loadings	PLS2 loadings	Regr. coeff.
N_{Ait}	**0.48**	−0.24	**0.24**
N_{acc}	**0.31**	−0.31	0.01
D_{uf}	0.04	**−0.69**	**−0.41**
D_{Ait}	−0.18	−0.24	−0.15
D_{acc}	−0.16	−0.21	**−0.19**
radon	**0.28**	−0.30	−0.05
O_3	−0.04	−0.26	−0.10
DMS	**0.52**	−0.20	**0.21**
abshum	**0.51**	−0.26	0.12
variance of N_{uf} (%)	19	11	constant = 10.8
variance of independent variables (%)	26	11	

(b)

Variable	PLS1 loadings	PLS2 loadings	Regr. coeff.
N_{Ait}	**0.51**	−0.21	**0.35**
N_{acc}	**0.35**	−0.26	0.07
D_{uf}	**−0.32**	**−0.39**	**−0.35**
D_{Ait}	**−0.37**	0.23	−0.07
D_{acc}	−0.20	0.12	−0.13
radon	−0.09	**−0.57**	**−0.40**
O_3	−0.19	0.003	−0.08
DMS	**0.37**	**−0.40**	0.02
abshum	**0.38**	**−0.43**	0.02
variance of N_{uf} (%)	12	14	constant = 8.9
variance of independent variables (%)	38	9.2	

The bold values represent these parameters with the strongest loading.

variables). Unlike multiple linear regression (MLR), PLS extracts only the number of dimensions from the independent data block that are relevant in explaining the covariation between data blocks i.e., the dependent variable (N_{uf}) and the independent variables. The number of dimensions is determined by observing the decreasing amount of variances of the dependent variable and the independent data block explained by each PLS component in combination with a cross-validation technique (Wold, 1978).

The prominent feature of the PLS regression results from the *Oden* data, is that the degree of the variance in N_{uf} is rather low (37% and 47% for subsets 1 and 2, respectively). These two-component PLS models are based on only 30% and 25% of the variance in the independent variables. In other words, somewhat more than a quarter of the information contained in the independent variables can be linearly related to N_{uf} and, in doing so, account for less than half of the variation in N_{uf}. Thus, the dependence of the ultrafine number concentration on the other measured parameters is rather weak. Other phenomena which were not directly observed could explain the behaviour of the ultrafine mode, e.g., sink function for N_{acc} and N_{uf}, cloud physics and other meteorological parameter, and intermittent mixing from aloft. The extraction of only two PLS components (out of nine possible as in MLR) is equivalent to a noise reduction, which will give more stable predictions of N_{uf} based on the independent data.

Once the number of PLS components has been established, an attempt can be made to interpret the components as physical/chemical/meteorologi-

cal factors controlling the variation in N_{uf}. This interpretation is based on the PLS loadings. Alternatively, regression coefficients showing the summed influence of all relevant PLS components can be calculated.

SUBSET 1

Here, the PLS regression result is similar to the interpretation of the third factor of the PC analysis for this subset. This is because the third PC (Table 2a) has a very high loading for the ultrafine number concentration. For this subset, the ultrafine number concentration covaries most strongly with (arranged in order of decreasing relevance) the ultrafine mode geometric mean diameter (negative correlation; $-$), the Aitken mode number concentration (positive correlation; $(+)$, the DMS concentration $(+)$, and the accumulation mode geometric mean diameter $(-)$.

Results from a PLS regression of the ultrafine number concentration of subset 1 on the other nine variables are listed in Table 3a (most significant in bold). The scaled regression coefficients give the combined influence of each variable on N_{uf} summed over the two PLS. The loadings are a measure of how much each variable enters the model (0:weak, 1:strong) (Geladi and Kowalski, 1986).

SUBSET 2

For this subset, N_{uf} is significant in more than one of the PCs of the five principical-component solutions, which makes a direct comparison with the PLS results more difficult. Nevertheless, the PLS regression for subset 2 gives PLS component loadings and regression coefficients which are quite similar to those of subset 1 (Tables 3). The major difference were found for radon and DMS. For subset 2, the ultrafine number concentration covaries most strongly with (arranged in order of decreasing relevance) the radon concentration (negative correlation; $-$), the ultrafine mode geometric mean diameter $(-)$, and the Aitken mode number concentration (positive correlation; $+$). The coefficients for the remaining variables are low.

The regression coefficients for both subsets show that the accumulation mode number concentration has no influence on the ultrafine number concentration. Similar results were obtained using ordinary multiple linear regression and stepwise linear regression. As mentioned previously, the PLS component loadings can be used to interpret the PLS components as underlying factors controlling the variation in N_{uf}. Used in this sense, PLS provides us with the insight (to an otherwise overly complex data set) to formulate a hypothesis regarding the nature of the sources and sinks of the ultrafine particle mode. Further data or model calculations are needed to validate the interpretation.

The first PLS component is most positively correlated to the Aitken and accumulation mode number concentrations, the DMS concentration, and the absolute humidity for both subsets. This component might be interpreted as a source of ultrafine particles since the correlation to the number concentration is positive. However, the particle production could have taken place far from the measurement site. Notice the change from subset 1 to 2 in the importance of DMS and radon to explain the variance in the ultrafine number concentration. Due to the half-life of the measured radon products, the influence of radon is more pronounced when the stations closest to the continent are included in the data set. The average transporting time of the air over the pack-ice was about 50 h (Nilsson, 1996).

3.3. *Discussion*

If the production of ultrafine particles took place near the cloud top of the marine boundary layer (Hegg et al., 1990) and air above the MBL had an aged Aitken mode from the upper troposphere (Raes and Van Dingenen, 1992), then mixing from the free troposphere would cause a correlation of the ultrafine particle number concentration with the Aitken mode number concentration. Since ultrafine particle production occurs preferentially during specific conditions, a strong correlation is however, not to be expected. This is supported by the PC analysis in that a weak correlation between Aitken mode and ultrafine mode concentrations was seen. Furthermore, we must take into account that the PLS model used here is based on linear relationships, while ultrafine particle production certainly is a non-linear process. Nevertheless, the presence of DMS and absolute humidity on the PLS 1 component indicates that the open sea might be an important source of precursor gases

such as SO_2 and H_2SO_4 for ultrafine particle production.

The second PLS component is most clearly related to the ultrafine mode geometric mean diameter in such a way that an increase in N_{uf} concurs with a decrease in the mode geometric mean diameter of this mode. This PLS component can therefore possibly be interpreted as an ageing and dilution term.

4. Conclusions

The occurrence of the ultrafine, Aitken and accumulation particle modes were analysed using PC analysis and partial least square regression to find correlation to precursor gases and meteorological observations. A rather weak relationship was found between the ultrafine mode variables and the other variables. Nevertheless, the ultrafine number concentration can be linked to two sources. First, ultrafine particles can be mixed downwards from the free troposphere into the MBL or from the cloud tops of the upper part of the stable MBL. A weak correlation between the number concentrations of ultrafine particles and Aitken mode particles support this hypothesis. Second, the open sea could be identified as a source of ultrafine particles, represented by a component with DMS and absolute humidity. In the most cases, the observed ultrafine particles were probably not produced nearby the ship site. This hypothesis can be supported by the anti-correlation between DMS/absolute humidity and geometric mean diameter of the ultrafine mode.

The mean geometric diameter of the ultrafine particle mode can be taken as indicator of the age of the ultrafine mode. The older the ultrafine particles are, the larger the mean diameter. This relationship variation can be explained by a combination of dilution and condensational growth, or the oxidation of soluble gases on/in the particle. No ultrafine particle sink could be attributed to the accumulation and Aitken modes, probably since the available surface area was too small.

Other parameters, such as UV-irradiation, SO_2 concentration with a high time resolution, and vertical mixing processes between the marine boundary layer and the free troposphere, which were not directly observed might explain better the occurrence of the ultrafine particle mode.

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