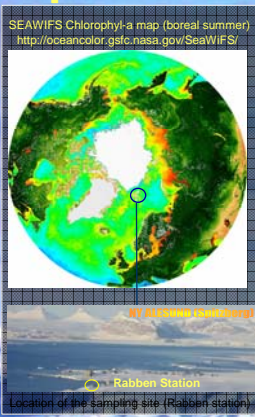


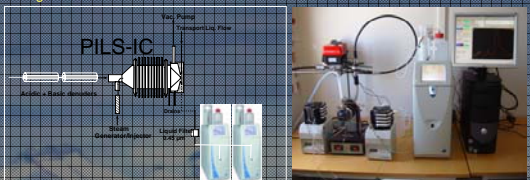
Real-time measurements of fine / ultrafine sulfate aerosols in the Arctic atmosphere during summertime: Insights to Cloud Condensation Nuclei (CCN) sources

Experimental

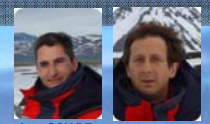


MOTIVATIONS

A 2-week campaign has been performed at Ny Alesund (Spitzberg) within the IPEV-AEROBIPOLAR program in order to document fast changes in the chemical composition of fine/ultra-fine aerosols at sea levels. A set of instruments dedicated to number size distribution (CPC-DPS & OPC GRIMM), optical properties (absorption, light scattering) and chemical composition (ions & carbon) were deployed in the field in order to better document the physical, chemical, and optical of tropospheric Arctic marine aerosols during summertime.



A novel instrument (PILS-IC) has been deployed during this campaign and set to perform fast (6min) measurements of the major anions (Cl⁻, SO₄²⁻, NO₃⁻) within 2 fractions Fine (AD<0.8µm) and ultra-fine (AD<0.2µm). (See figures above)
 A sequential program (30 min for fine, 30 min for ultra-fine) was then adopted in order to document these 2 size fractions with a single PILS-IC instrument.



SHORT CV (J. SClARE)

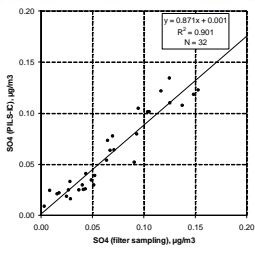
June 2008: PI of the IPEV-AEROBIPOLAR program (biogenic sulfate aerosols in the Arctic Ocean, 2-week field experiment at Ny Alesund (Spitzberg)).

1995-2007: PI of the IPEV-AEROTRACE program (Aerosols and atmospheric Tracers in the Austral Ocean) and co-PI of IPEV-CESOA program (Biogenic sulfur cycle and mid- and high latitudes). Long-term observations of atmospheric DMS and size-segregated aerosol composition at Amsterdam Isl., Crozet Isl., and Cape Point (south Africa).

SELECTED PUBLICATIONS ON BIOGENIC MARINE AEROSOLS

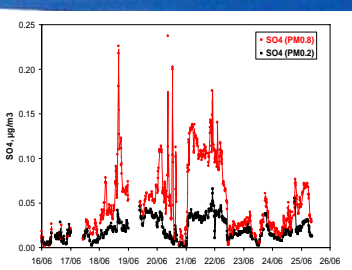
1. SClare et al., Interannual variability of atmospheric dimethylsulfide in the Southern Indian Ocean, J. Geophys. Res., 105, 26,369-26,377, 2000
2. SClare J., et al., Short-term variations of dimethylsulfide and its oxidation products at Amsterdam Island during summer months, Atmos. Chem. Phys., 3, 281-302, 2003
3. Boucher, O., J. SClare, et al., DMS atmospheric concentrations and sulphate aerosol indirect radiative forcing: a sensitivity study to the DMS source representation and oxidation, Atmos. Chem. Phys., 3, 49-65, 2003
4. SClare J., et al., Seasonal variations of carbonaceous aerosols in the Austral Ocean: Evidence of a marine biogenic origin, J. Geophys. Res., submitted, 2008
5. Spracklen, J. SClare, et al., Globally significant oceanic source of organic carbon aerosol, Geophys. Res. Lett., in press, 2008
6. Arnold, S. R., J. SClare et al., Global estimates of oceanic isoprene emissions from speciated phytoplankton and impacts on marine organic carbon, Atmos. Chem. Phys., in press, 2008

Validation of PILS-IC data



A comparison was performed between PILS-IC anion measurements and filters sampled in parallel.
 By the mean of a R&P Partisol equipped with a PM1 cut-off URG cyclone. Quartz filters were sampled every 3 hours and analysed for their anion/cations contents.
 Results are reported here and show a good agreement ($r^2=0.90$) and a slope close to 1 (0.87).
 The lower cut-off diameter applied to the PILS-IC (AD<0.8µm) can probably account for the lower values of PILS-IC data (13% lower compared to filter data).

Temporal variations of Fine & Ultra-Fine aerosols

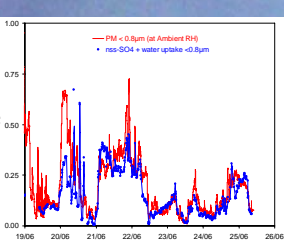


Fine and ultra-fine sulfate have been measured for a 10-day period (16-26/06/2008) totaling more than 800 datapoints for each size fractions. Surprisingly, Chloride concentrations in these 2 size fractions were systematically in the values of the blank (low levels supported from filter IC analyses).

	Sulfate (0.8µm)	Sulfate (0.2µm)	Ratio Sulfate Ultra-Fine / Fine
unit	ng/m ³	ng/m ³	%
Average	40.8	17.3	51.1
Standard deviation	38.0	12.0	31.0
Detection limit	-3.4	-2.4	-
Number of valid values	859	867	253
period of measurements	1406 - 2506 (112 days)		

As a result the role of sea-salt sulfate could be neglected, and SO₄ measurements reported here could stand for nss-SO₄. Levels of SO₄ in both fractions were particularly low (41 & 18ng/m³ for the fine & ultra-fine fractions, respectively). Due to sequential sampling, ultra-fine-to-fine SO₄ ratios were averaged every 30 min and show high variability with values ranging typically from 30 to 70%. Variability in this ratio is not related to RH changes (that could explain a shift in the accumulation mode). Changes in this ratio are discussed below.

Sulfate aerosols : A major contributor to CCN ?



PM below 0.8µm (at ambient RH) was derived from OPC measurements (GRIMM model 1.108) and was calculated from the number size measurements performed by the instrument between 0.3 and 0.8µm. A calibration factor (f) was used to convert the integrated volume concentration into mass concentrations and was derived from a direct intercomparison with R&P TEOM-FDMS. Note that this PM values should include water uptake onto particles (which is RH dependent). Sulfate mass concentration were corrected with water uptake following the thermodynamic equations given by the AIM model
<http://www.aim.gov.uk/aim/model3/model3a.php>

The good agreement between the 2 dataset suggests that most of the PM below 0.8µm is composed of sulfate aerosols. These findings are different to those reported for the North Atlantic Ocean (O'Dowd et al., nature, 2004) at the station of Mace Head (Ireland) where marine organic aerosols have been identified as the main contributor of PM₁. Our findings support the idea that sulfate is the main contributor of CCN at this period of the year in the Arctic atmosphere.

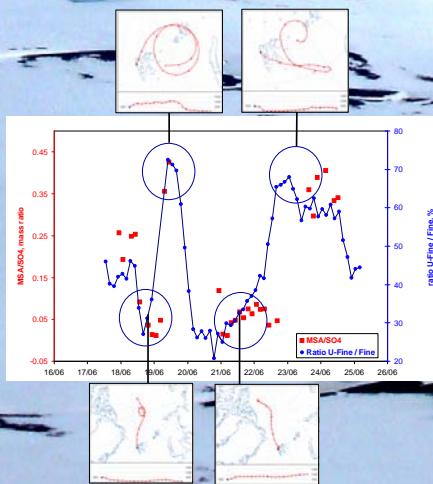
Insights to sulfate (CCN) sources: (biogenic vs anthropogenic) ?

The ultrafine-to-fine mass ratio (R) was plotted here together with the MSA/SO₄ ratio calculated from the filter sampling (in PM₁).

This figure shows a very strong variability of the R-ratio with values ranging from 20% to more than 70%. This result points out the fact that sulfate measurements in PM₁ are not sufficient to properly describe sulfate contribution to smaller size fractions which comprise most of the CCN.

Of particular interest, the highest R-ratios do correspond to the highest MSA/SO₄ ratios. This latter ratio can be used as a surrogate to estimate a contribution of anthropogenic sulfate. In other words, high MSA/SO₄ ratios will reflect an almost exclusive biogenic (DMS) origin. This ratio will be lowered by any additional (anthropogenic) source of sulfate.

The lowest MSA/SO₄ ratios (e.g. probably the highest anthropogenic contribution) are observed for air masses originating from the North pole region. They correspond to a low mass contribution of ultrafine sulfate (relatively to fine sulfate). On opposite, the highest MSA/SO₄ ratios (e.g. biogenic origin) do correspond to air masses originating from marine (open sea) regions surrounding spitzbergs. They correspond to the highest mass contribution of ultrafine sulfate (relatively to fine sulfate).



Conclusions

Real-time measurements of Fine and Ultra-Fine ion composition of Arctic aerosols have shown that **sulfate was the major contributor to the fine aerosol mass** and most probably **the major contributor to CCN**. This result would suggest that **marine organic aerosols are likely to play a non significant role as CCN in the Arctic atmosphere** during summertime. This is supported by the fact that 1) production mechanism of marine organics are similar to sea salt aerosols, 2) sea salt aerosols were almost inexistent in the fine size fraction (<0.8µm).

The ratio of UltraFine-to-Fine sulfate has shown a strong variability (20 to 70%), that is not connected to RH (e.g. growth to water uptake onto sulfate particles). This high variability points out the fact that sulfate in the fine fraction (AD<0.8µm) is not sufficient to properly account for CCN concentrations. This variability has shown to be in accordance with the MSA/SO₄ ratio, which ratio could be used as a surrogate to trace the contributions of biogenic vs anthropogenic sulfate. The results presented suggest that, in the Arctic atmosphere (and during summertime), **biogenic sulfates (originating from DMS) are likely to be a major source of CCN.**

Future studies

Future studies will be proposed to AWIPEV in order better document the origin of CCN in the marine Arctic atmosphere. The following measurements will be proposed for 2010 at Ny Alesund:

+ Real-time (5-min) measurements of ions⁺ & OC⁺ into the CCN fraction (below 140nm) by the mean of a cascade impactor coupled an aerosol concentrator (equipment to be purchased by LSCE in 2009).

+ Looking for collaborators to provide size resolved CN and CCN measurements, indirect measurements of sulfate / ammonium sulfate (VHTDMA) & any useful information to better separate the relative contributions of anthropogenic vs biogenic species.

Acknowledgements:

We gratefully thank IPEV for fundings (AEROBIPOLAR program), and AWIPEV staff for their helps in the field (E. Larmanou, A. Le Trestoler, ...). A special thank to F. Delbart who did a great job to make this campaign successful.

⁺ Ions = Sulfate, Nitrate, Chloride, MSA, Sodium, Ammonium, Potassium, Magnesium, Calcium.
⁺ OC = EC-OC Sunset Field instrument