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# Aerosol chemical composition during tropospheric ozone depletion at Ny Ålesund/Svalbard

By E. LEHRER*, D. WAGENBACH and U. PLATT, *Institut für Umweltphysik, Univ. Heidelberg, INF 366, D-69120 Heidelberg, Germany*

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ABSTRACT

During spring 1995, aerosol filters were continuously sampled with a temporal resolution of 4–24 h at the NILU Zeppelin Mountain Station (Ny Ålesund/Svalbard) and analysed for bromide, major ions and methanesulfonic acid (MSA). During a strong ozone depletion event at the end of April, a corresponding increase in the non-sea salt $Br^-$ exceeding the typical background level by more than one order of magnitude was observed. Peak f-Br levels (120 ng/m$^3$) were almost equal to results of measurements reported earlier from Alert and Barrow. Less pronounced $O_3$ depletion events occurring in early May were associated with a relatively weak $Br^-$ enhancement. A good correlation of f-Br and simultaneously measured BrO was found ([BrO] = 2 [f-Br] on a per molecule basis), except for situations with near zero $O_3$.

## 1. Introduction

The Arctic troposphere provides an unique natural laboratory for atmospheric research. Due to its distinct seasonal day/night contrast and its remote position far away from continental and industrial sources various processes in atmospheric chemistry may be studied there under ideal conditions. In this context, the Arctic winter and spring are particularly interesting because the phenomena of Arctic Haze and tropospheric ozone depletion, respectively, occur during these seasons.

Tropospheric ozone depletion was reported recently from several Arctic sites, e.g., Barrow, Alaska (Oltmans et al., 1989) and Alert, North Canada (Barrie et al., 1988), Ny Alesund, Spitzbergen (Solberg et al., 1996). After polar sunrise in April the ozone level could drop suddenly from a typical background level of 40 ppb to unmeasurably low values (< 2 ppb).

At Alert, Barrie et al. (1988) found a clear anticorrelation between ozone and filterable bromine (f-Br) (i.e., bromine species sampled by cellulose filters) during spring. The f-Br concentration reached up to 120 ng/m$^3$ during distinct ozone depletions, exceeding the typical level by two orders of magnitude. Such high bromine levels were already reported for the Arctic (Berg et al., 1983), but found nowhere else in the remote troposphere. Measurements of Berg et al. (1983) made at Point Barrow between 1976 and 1980 show springtime bromine concentrations up to 10 times higher than during the rest of the year. Later on a similar seasonal bromine cycle was found at several other Arctic locations, as at Alert by Barrie et al. (1985) and at Ny Ålesund by Maenhaut et al. (1989).

Great progress towards an understanding of the phenomenon was made when Barrie et al. (1988) suggested a chemical mechanism for the observed tropospheric ozone depletion events. A reaction cycle was proposed in which atomic bromine destroys ozone in forming BrO, with Br-atoms subsequently recycled by BrO self-reaction. Meanwhile the role of other reactive halogen species (Solomon et al., 1994; LeBras and Platt,

* Corresponding author.

1995) as well as an additional recycling of reactive halogens by HOBr (McConnell et al., 1992; Fan and Jacob, 1992) was suggested. First experimental evidence for the Br-BrO depletion cycle was obtained during the Alert Polar Sunrise Experiment 1992 by Hausmann and Platt (1994), who detected enhanced levels of BrO by means of differential optical absorption spectroscopy (DOAS) during an ozone depletion event.

The reason for the high bromine levels found during Arctic spring are poorly understood. Currently a chemical mechanism is discussed, suggesting halogen mobilisation in the form of $Br_2$ or BrCl via heterogeneous reaction of sea-salt aerosol with HOBr (Fan and Jacob, 1992; Mozurkewich 1995; Vogt and Crutzen, 1996, Borken et al. 1996). Furthermore emission of organohalogen compounds by sea algae have been proposed by Sturges et al. (1992) to be responsible for the high concentration of spring bromine in the Arctic. For detailed discussion of the sources and reaction cycles of reactive halogen compounds in the Arctic troposphere see Tuckermann et al. (1997).

Open questions remained on f-Br, particularly on its origin, chemical properties, and on its relationship to $O_3$ and related species. Here, we report on measurements of the chemical aerosol composition performed at 500 m above sea level (asl) in Svalbard during the ARCTOC 1995 campaign, which were specifically aimed at the following objectives.

- To evaluate the f-Br ozone relation already known for the North American sector of the Arctic for the European Arctic as well. Although high Br concentrations during Arctic spring (Berg et al., 1983; Maenhaut et al., 1989) as well as ozone depletion (Solberg et al., 1996) are also observed at Ny Ålesund, the relationship between f-Br and ozone during spring had not been investigated there in detail.
- To achieve a sufficiently high time resolution (fraction of one day) for f-Br sampling in order to resolve the relatively short $O_3$ depletion events and to investigate a possible phase shift between f-Br and $O_3$.
- To evaluate the $O_3$-f-Br relationship above the marine boundary layer. Unlike Alert or Barrow the Zeppelin Station (474 m asl) is not restricted to marine boundary layer air. Although airborne measurements performed by Sheridan et al. (1993) provided a few relevant observations of $O_3$ and f-Br during ozone depletion, no extensive data are available to establish the f-Br-ozone interdependence above the marine boundary layer.
- To scrutinise a possible link between f-Br events (or ozone losses) and other relevant aerosol ionic components associated with different air masses characteristics.
- To evaluate the relation between BrO and f-Br based on continuous BrO measurements made concurrently by Tuckermann et al. (1997). This allows to check for a potential connection between f-Br and ozone.

## 2. Experimental

### *2.1. Sampling and filter preparation*

Collection of aerosol samples was performed at the Norwegian Institute for Air Research (NILU) Air Monitoring Station (Braathen et al., 1990) located 2 km south of the settlement of Ny Ålesund/Svalbard, 484 m asl on an eastern ridge 70 m below the top of Zeppelin Fjellet (the wind direction is controlled by the local topography). Air contamination by the settlement of Ny Ålesund is believed to be negligible (Heintzenberg et al., 1994).

Aerosol sampling closely follows the procedure we routinely applied at the German Antarctic overwintering station (Wagenbach et al., 1988) . To reduce the influence of ice crystal sampling a downward-facing protective cylinder ($\varnothing$ = 320 mm) was attached to the top of a vertical inlet tube ($\varnothing$ = 160 mm), which was continuously ventilated. A stainless steel tube ending in a downward facing bow was used to suck the air from the vertical inlet tube through the filter holder. The typical flow rate of 23 $m^3$/h leads to sample volumes between 100 $m^3$ and 500 $m^3$ at a time resolution between 4 and 24 h.

We used double cellulose filters in series (Whatman W541 $\varnothing$ 90 mm) in order to make the results comparable to those obtained by Barrie et al., 1988 and Berg et al., 1983 on a similar filter media. In addition, the use of dual filters allowed the calculation of the filter efficiency.

Prior to sampling filters were cleaned several times in ultra clean water (18 MΩ) and extracted

by an ultrasonic bath treatment. After drying under clean air they were stored in precleaned polyethylene bags until use. Immediately after sampling the filters were folded and stored again in the original polyethylene bags. To gain information about the overall contamination 25 process blank filters were taken, which were handled identically as the samples, except that they were placed in the filter holder for 20 min without pumping. The filters were stored in the field at about 0°C in a dark place. In total 128 pairs of cellulose filters were collected.

### 2.2. *Chemical analysis*

At the Heidelberg laboratory, the filters were cut in a laminar flow bench. One half of the filter was extracted into 20 ml of ultra pure water (18 MΩ), placed inside a PP-jar in an ultrasonic bath for 10 min. Filter extracts were stored at −18°C before being analysed for major ions by ion chromatography (Minikin, 1994). The anion analyses of MSA, $Cl^-$, $Br^-$, $NO_3^-$ and $SO_4^=$ were performed on a DIONEX DX300 ionchromatograph (AS11 separating column, AG11 precolumn and a 200 µl sampling loop) by applying NaOH eluent gradient procedure. For the cation analysis ($Na^+$, $NH_4^+$, $K^+$, $Mg^+$ and $Ca^+$) we used the DIONEX DX4500i ion chromatograph, equipped with a DIONEX IonPac CG12A pre and separating column, the runs were performed isocratic with a 50 mM MSA eluent. The sample loop was 50 µl.

The IC detection limits for all measured ions were always below the respective levels in the process filter blanks, which in turn control the overall detection limit defined as the $3\sigma$ blank variability. Because of the insignificant blank contribution no corrections (i.e. subtraction of the mean field blank contributions from the sample concentrations) were necessary. For typical 100 $m^3$ air samples the overall detection limit corresponds to atmospheric concentrations of 12, 7.0, 0.8, 0.12, 3.6 and 0.36 $ng/m^3$ for $Cl^-$, $Na^+$, $SO_4^=$, $Br^-$, $NO_3^-$ and MSA, respectively.

Although air volumes of 100 $m^3$ and more were collected the $Br^-$ concentration in filter extracts were found to be at the lower end of the useable range of the method. Therefore evaluation of the $Br^-$ peak was performed individually by computer aided visual inspection of the IC chromatogram. Subsequently, applying a background stripping method the analytical $Br^-$ detection limit could be improved by approximately a factor two.

### 2.3. *Sampling artefacts*

The inlet system designed to avoid sampling of snow crystals on the filters proved to be successful, except in the case of two filters, sampled on 22 April during a heavy snow storm, which became blocked by a 1–2 cm thick ice crystal layer. In Figs. 1, 2 and 4, these filters are marked by upward directed arrows. The results of the two affected filters showed significantly lower concentrations for $Na^+$, $SO_4^{2-}$ and $NO_3^-$. Therefore, we assume that these two data points represent lower limits (i.e. the actual concentration should be higher than measured) for all presented ions, including bromide.

The filter efficiency calculated from the ion concentrations sampled on either filter of the pair varied, probably due to changing relative humidity, aerosol acidity, and different sampling times. The average fraction of $Cl^-$, $Na^+$, $SO_4^=$, $Br^-$, $NO_3^-$ and MSA found on the first filter was 58, 84, 92, 69, 79 and 85% respectively. The relatively low efficiency for $Cl^-$ and $Br^-$ may be due to revolatilisation of HCl and HBr from the filter media. The final aerosol concentrations were calculated by adding the theoretically determined missing fraction, that passed both filters, to the amount sampled by the front and backup filter, respectively.

## 3. Results and discussion

### 3.1. *Non-bromine species*

In order to document the variable influence of sea salt as well as of anthropogenic and biogenic aerosol sources during the observational period at the Zeppelin Station in Fig. 1 the time series of sodium, nitrate, (nss) sulphate and methansulfonic acid (MSA) during 16 April to 15 June, 1995 are presented along with ozone (Norwegian institute for air research NILU data).

*Ozone.* As shown in Fig. 1 a strong ozone depletion event occurred in late April. Several minor ozone depletions down to concentrations of about 20 ppb were found later on in May. In the following we shall refer to the case of an almost total ozone loss, as observed from 20 to

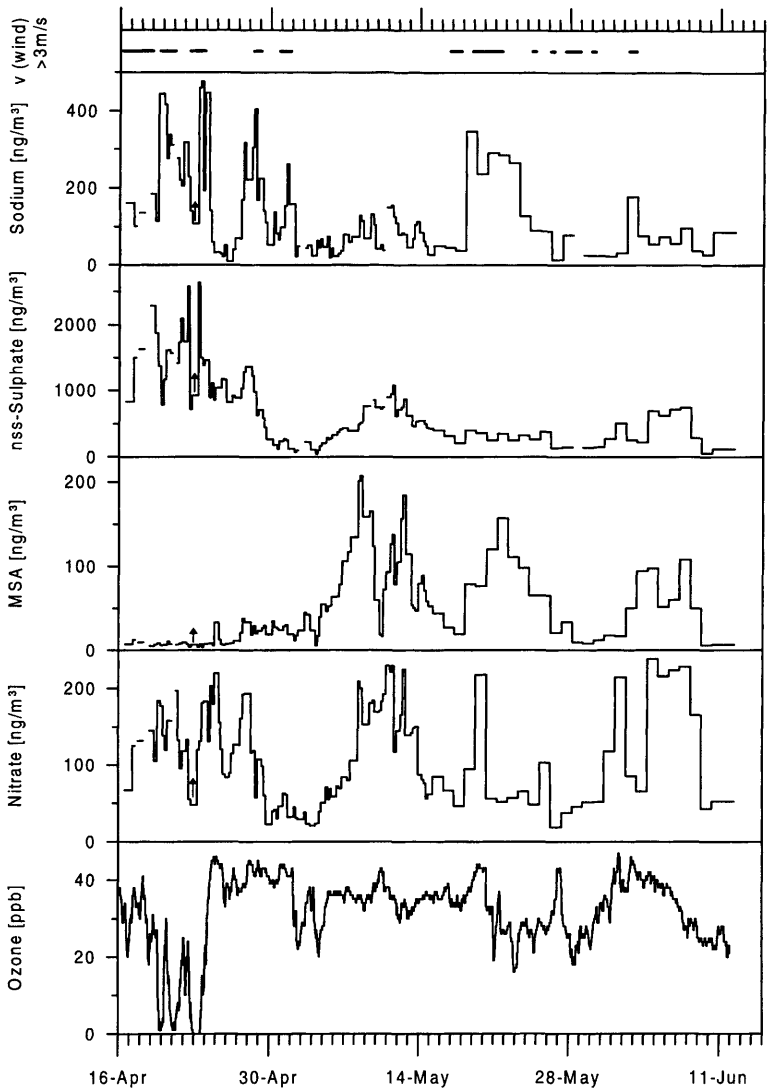


*Fig. 1.* Record of ionic aerosol compounds and ozone at Zeppelin Station (periods of average windspeed >3m/s are indicated on top panel) during the ARCTOC campaign in 1995. The upward directed arrows mark two samples which represent lower limit values due to obstructing snow on the filter media. (see text).

24 April as primary ozone depletion and to the case of slight ozone depletion down to levels of about only 20 ppb (e.g., on 2 and 4 May) as secondary ozone depletion. Outside the primary and secondary ozone events the ozone background level was near 40 ppb with a tendency to decrease to the typical summer background of about 30 ppb towards the end of the observation period.

*Sea salt aerosol.* The average sodium concentration during the campaign was 116 ng/m$^3$. This concentration is in the range of former spring measurements at Ny Ålesund, but significantly lower than at the North American stations Barrow and Alert (see Table 1), probably due to the higher elevation of the station. Sodium concentrations larger than 150 ng/m$^3$ coincide with periods of high average wind speed as expected. This is consistent with the fact that production of sea salt

Table 1. *Average concentrations of sulphate, methanesulfonic acid, nitrate and sodium at different Arctic sites for different seasons*

| Site | Season | Total-$SO_4^=$ [ng/m$^3$] | MSA [ng/m$^3$] | $NO_3^-$ [ng/m$^3$] | Na [ng/m$^3$] |
|---|---|---|---|---|---|
| Ny Ålesund[1] | winter (16 Oct–15 May) | 1440–2300 | 5.8 | n.a. | 84 |
| Ny Ålesund[1] | summer (16 May–15 Oct) | 394 | 18.3 | n.a. | 31 |
| Alert/Canada[2] | spring (22 Feb–26 April) | 1820 | n.a. | 70 | 235 |
| Barrow/Alaska[3] | late winter (17 Mar–7 May) | 1040 | 11.5 | 125.9 | 677 |

[1]Heintzenberg et al., 1994 (out of cloud data).
[2]Bottenheim et al., 1990 ($SO_4$ + particulate $NO_3$).
[3]Li and Winchester, 1989 (fine + coarse particle data).
n.a.: not analysed.

is mainly a function of wind speed. In Fig. 1 the high wind speed periods are indicated at the top of the plot.

Except for a period between 18 and 22 May, when trajectory calculations show air masses to be advected straight across the Barents Sea from Scandinavia, the sodium concentration is generally lower after 1 May, than before (90 versus 180 ng/m$^3$) (Table 2).

*Sulphate.* Sulphate in the Arctic has 3 main sources. (1) Especially in the Arctic spring and summer dimethylsulfide (DMS) oxidation leads to MSA and biogenic sulphate. (2) During Arctic winter, when the polar front is moving south towards the industrialised areas of Eurasia and North America anthropogenic $SO_2$ is transported to the area north of the Arctic circle [Barrie and Hoff, 1984]. After polar sunrise the $SO_2$ is quickly converted to sulphate. (3) Some of the sulphate originates from the sea salt particles. Using the $SO_4^=/Na^+$ ratio of 0.252 in sea salt given by Wilson (1975) we obtained the (non-sea salt) sulphate (nss$-SO_4^=$) concentration as:

$$nss^-SO_4^= = SO_{4_{aerosol}}^= - \left(\frac{SO_4^=}{Na^+}\right)_{seasalt} \cdot Na^+_{aerosol}$$

During our measurements, the sea salt fraction accounts only for 6% on average (maximum 15%) of the total sulphate (1160 ng/m$^3$). High (nss$-SO_4^=$) levels were found mainly in late April, in contrast to a significantly lower average concentration of 400 ng/m$^3$ after May.

Algae blooms during spring and summer lead to the production of DMS, which is oxidised to MSA and $SO_2$. From our measurements we can deduce the start of the algae bloom to be around mid April, because the MSA concentration is increasing rapidly in early May reaching concentrations of more than 100 ng/m$^3$.

The MSA concentrations found in earlier measurements at Ny Ålesund, Alert and Barrow are listed in Table 1, and are significantly lower than

Table 2. *Average aerosol composition for 2 main periods during the ARCTOC 95 measuring campaign*

| Ions [ng/m$^3$] | Late winter 16 April–1 May | Early summer 1 May–15 June |
|---|---|---|
| sodium | 180 | 90 |
| total sulphate | 1160 | 400 |
| — as sea salt | ≈60 | ≈30 |
| — biogenic | ≈40 | ≈190 |
| — anthropogenic (nss-nbio) | ≈1060 | ≈180 |
| nitrate | 115 | 105 |

our data. An explanation could be, that our measurement covers the MSA spring peak, whereas the referenced data are averages over a longer period.

Using a linear regression through the lower envelope of the nss sulphate versus MSA plot (compare Lehrer, 1995), the MSA/biogenic sulphate branching ratio may be estimated. We found a MSA/biogenic sulphate ratio of 0.34, which is consistent with the findings of Heintzenberg et al. (1994) and Li and Barrie (1993).

The fraction not explained by the sea salt or the DMS derived sulphate will therefore be called nss-nbio sulphate and we believe that the main source of this remaining sulphate fraction is mainly due to anthropogenic emissions. During the first half of the measuring period, until 1 May, this anthropogenic fraction represents most of the total sulphate (Table 2).

We assume that the enhanced concentrations during the first period are due to the polar sunrise oxidation of the winter time reservoir of anthropogenic $SO_2$, while afterwards about half of the atmospheric sulphate load is due to biogenic DMS emission from the Arctic ocean.

*Nitrate.* The separation into two different time periods suggested by the sulphate and MSA records is not obvious in the nitrate record. The nitrate concentration does not differ significantly between the time before and after 1 May (compare Table 1).

A separation of the measuring campaign into two time periods is possible for all observed ionic tracers except of for nitrate. The late winter period when primary ozone depletion down to unmeasurable ozone concentrations occurs stands out mainly by the distinct anthropogenic influence, but also by relatively high sea salt concentrations. The onset of marine biogenic activity seen in the atmospheric MSA was observed after 1 May. In this early summer period the anthropogenic influence became less dominant.

### 3.2. *Bromide*

Bromide, plotted in Fig. 2, shows high concentrations of up to 120 ng/m$^3$ in the end of April. This level exceeds the typical background of about 2 ng/m$^3$ during the campaign by two orders of magnitude. Referring to the two periods mentioned before, we find an average f-Br concentration of 15 ng/m$^3$ during the late winter period which is much higher than the average concentration of 2 ng/m$^3$ associated with the early summer period.

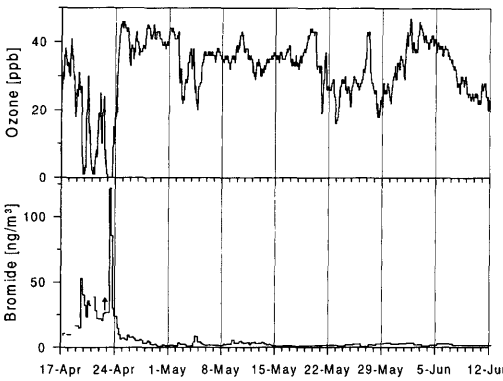


*Fig. 2.* Bromide and ozone concentration measured at the Zeppelin research station/Ny Ålesund. The upward directed arrow marks two samples which represent lower limit values due to obstructing snow on the filter media (see subsection 2.3).

*Connection to sea salt aerosol.* It is well known from earlier measurements (Berg et al., 1983; Barrie and Hoff, 1985), that the collected f-Br is far in excess to the expected sea salt bromide. Using sodium as sea-water reference element and a respective Br/Na mass ratio of 0.00625 (Wilson, 1975) we found that for primary and secondary ozone depletion events less than 10% (range, see Fig. 3) of the total f-Br on each filter set is made up by sea salt bromide. However, the nss $Cl^-$ record (based on Na) shows periods with $Cl^-$ enrichment but also with $Cl^-$ depletion. There is a slight tendency for a general $Cl^-$ enrichment during the late winter period. Thus, unlike $Br^-$ which always exhibits a large positive excess, chloride does not differ substantially from the expected sea salt chloride (Fig. 3). The occasional slight deviations of $Cl^-$ from the sea salt abundance may simply be explained by sampling atmospheric HCl formed in reactions of sea salt particles with acidic species, or by mobilisation of HCl from the filter media (see subsection 2.3), respectively.

*Connection to anthropogenic species.* High bromide concentrations clearly coincide with high anthropogenic (i.e. nss-nbio) sulphate levels indicating that an "acidic environment" may be one of

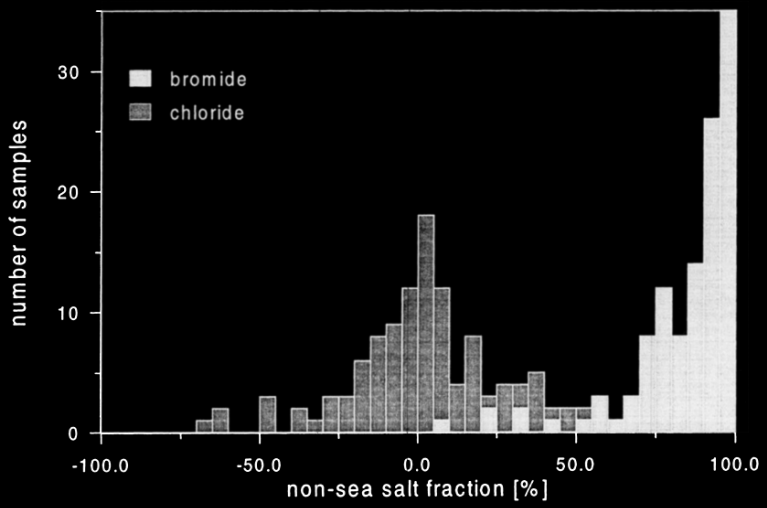


*Fig. 3.* Frequency distribution of the non-sea salt fraction of $Cl^-$ and $Br^-$ for all filter samples during the ARCTOC '95 campaign at the Zeppelin station/Ny Ålesund. While nss-$Cl^-$ is zero on average, bromide is dominated by nss-$Br^-$.

the prerequisites for bromine events and for tropospheric ozone depletions, respectively. Indeed high resolution (up to one hour) data from the ARCTOC '96 filter measurements (Langendörfer, 1997) show an increase of the sulphate and nitrate background levels during periods at significantly decreasing ozone.

*Connection to the marine biosphere.* Another possible contribution to the nss-$Br^-$ peak during Arctic spring could be obtained by inspection of the concurrently measured MSA concentration. If we relate the relevant onset of the algae bloom with the emission of DMS precursors to the atmosphere by the Arctic sea algae and consequently with the local atmospheric MSA level, we find such algae bloom occurs significantly later than the first, distinct filterable bromide increase during spring. Or to conclude in another way, if algae activities provide atmospheric precursors to reactive bromine compounds that initiate ozone depletion, these algae species should be different from the algae producing relatively large amounts DMS.

*Connection between f-Br and ozone.* In Fig. 4 the bromide (f-Br) concentration is plotted on a logarithmic scale to clarify the variability of the bromide concentration during times outside the high peak. During all the observed ozone decreases presented in Fig. 4 there is good correspondence between ozone depletion (primary and secondary) and $Br^-$ level enhancement. At our time resolution we could not determine a phase shift between the f-Br - ozone variability. However, after May bromide level remains near the background value although secondary ozone depletions still occur.

In Fig. 5 f-Br and $O_3$ are shown in a scatter plot to illustrate their interrelation for different cases. As indicated by the different symbols in Fig. 5, we distinguish 3 different regimes. (a) During primary and secondary ozone depletion events in the late winter period, a strong anticorrelation ($r^2 = 0.89$, thin line) was observed. (b) However, for post-total ozone depletion (i.e., periods immediately subsequent to unmeasurable low values, marked in Fig 5 with "×") we found maximum bromine levels which do not match the f-Br/ozone relation of case (a). (c) From early May onwards (during the early summer period defined above), the bromide level is relatively constant at near background and any relation to the still appearing secondary ozone depletion is absent.

The obtained picture shows a striking similarity to the results from the Alert Polar Sunrise Experiment Measurements in 1992 (Barrie et al., 1992). If we compare the two datasets we find almost the same maximum bromide, respective bromine, concentration of about 120 ng/m$^3$, and

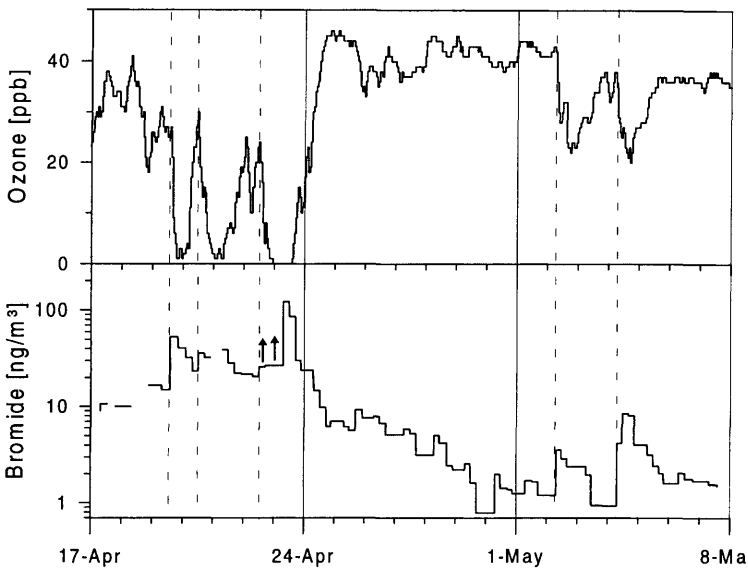


*Fig. 4.* Ozone and bromide records during the late winter period of the ARCTOC '95 campaign at the Zeppelin research station. The upward directed arrows mark two samples which represent lower limit values due to obstructing snow on the filter media (see subsection 2.3).

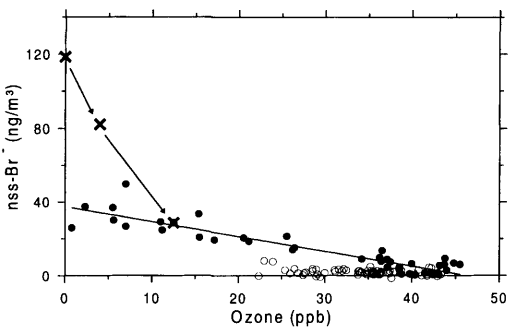


*Fig. 5.* nss-Br versus ozone concentration (○-early summer period; ●-late winter period; ×-post total ozone depletion; the connecting arrows represents subsequently following data points).

the same quantitative relation between depleted ozone and f-Br.

Differences between the two before mentioned cases of (a) primary and secondary ozone depletions and (b) post total ozone depletion in the f-Br ozone interrelation are seen as well in the BrO- ozone interrelation. Here the common anticorrelation between the latter two species observed during moderate ozone depletion events is changed to a correlation (covariance) starting at near total ozone loss, suggesting that BrO is destroyed during this particular period (Tuckermann et al., 1997). The obvious f-Br excess over the normal f-Br/ozone ratio in case b) may be interpreted therefore to be a reaction product of atomic Br, which could not react anymore with ozone to form BrO. From modelling simulations (Borken, 1996) HBr is expected to be the most likely Br species, which may be formed in the case of extremely low ozone levels. Consequently we expect the extremely high bromine (bromide) levels found at the Polar Sunrise Experiment 1992 and during the ARCTOC 95 campaign to be HBr.

Inspection of the f-Br record immediately following ozone depletion events revealed apparent atmospheric f-Br lifetimes of $\tau = 1$ to 2 days (after primary/secondary events) and $\tau = 6$ h (immediately after events leading to total $O_3$ loss). In the case of primary and secondary events $\tau$ is certainly attributed to aerosol removal and air mass changes (dilution). The much shorter $\tau$ during post-total ozone depletion periods suggests that additional chemical degradation of f-Br may occur. Following Fan and Jacob (1992) this chemical sink might operate via the mobilisation of bromide by HOBr from air born (aerosol) particles.

In Fig. 6 BrO, concurrently measured by DOAS during the campaign at ground level (40 m asl) near the Ny Ålesund airfield (Tuckermann et al., 1997), and f-Br (Zeppelin data) are shown in a scatter plot.

The symbols used for this scatter plot are the same as the ones of Fig. 5. Excluding again the two data points during absolute f-Br maximum, we found a good correlation between the two datasets ($r^2 = 0.88$). The linear regression leads to a BrO/f-Br mole ratio near 2.0. However for the post total ozone depletion period, f-Br appears to be enhanced relative to BrO. Here, the BrO concentrations are almost comparable with maximum concentrations up to 30 ppt(v). It is believed, that BrO was converted completely into HBr which is captured by our cellulose filters.

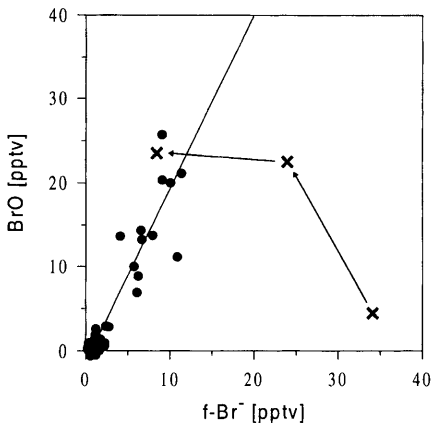


*Fig. 6.* Bromine oxide versus filterable bromide concentration (expressed in pptv) / symbols same as in Fig. 5 (●-late winter period; ×-post total ozone depletion; the connecting arrows represents subsequently following data points).

## 4. Conclusions

In total, 128 aerosol were sampled at a temporal resolution of 4–24 h during spring 1995 at Ny Ålesund/Spitsbergen, which were subsequently analysed for bromide, major ions and methanesulfonic acid. On the base of relevant ionic aerosol records we were able to characterise the different chemical air mass climatology during the campaign. From our aerosol chemical data a separation into two main periods was obvious, distinguished by (1) dominance of the anthropogenic influence in the late winter (until 1 May) and (2) a markedly increasing biogenic activity in the early summer (after 1 May). During the first period we observed the major ozone depletion events and the concurrent increases of f-Br. Combining our data with observations made during the PSE (Barrie et al., 1994) an almost identical concentration range of f-Br and a striking similarity in the relation between f-Br and ozone depletion becomes apparent. It is therefore likely, that these findings are representative for the entire Arctic sector. At our time resolution in the range of a few hours no significant phase shift between f-Br and ozone during ozone depletion periods could be found.

At the Zeppelin station situated over or at least at the top of the marine boundary layer, we found significantly lower sodium concentrations, but no difference in the bromide levels (up to 120 ng/m$^3$), if compared to other sea level Arctic sites (e.g., Alert or Barrow). Comparison between f-Br and the concurrently observed BrO shows a clear positive correlation, except for the time after total ozone depletion, suggesting that in those cases total BrO may be converted to HBr (which is then collected by cellulose filters).

The experience of this work suggested that a further improvement of the time resolution is possible and would yield further information. Therefore, during the ARCTOC '96 measurements we successfully established a temporal resolution of one hour (Langendörfer, 1997). Future work should concentrate on the investigation of source and chemical nature of f-Br.

## 5. Acknowledgements

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