

DOAS-observation of halogen radical-catalysed arctic boundary layer ozone destruction during the ARCTOC-campaigns 1995 and 1996 in Ny-Ålesund, Spitsbergen

By M. TUCKERMANN, R. ACKERMANN, C. GÖLZ, H. LORENZEN-SCHMIDT, T. SENNE, J. STUTZ, B. TROST, W. UNOLD and U. PLATT*, *Institut für Umweltphysik, Univ. Heidelberg, INF 366, D-69120 Heidelberg, Germany*

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ABSTRACT

During two field campaigns in spring 1995 and 1996, boundary layer concentration levels of BrO, ClO, IO, SO₂, NO₂, HNO₂, CH₂O and O₃, were observed at a time resolution of better than 1.5 h by Differential Optical Absorption Spectroscopy (DOAS). Up to 30 ppt of both, BrO and ClO, were found to coincide with low ozone events (LOE). During periods of normal ozone, average levels of BrO and ClO were close to zero. Average ClO levels during LOE were considerably higher in 1995 (21 ppt) than in 1996 (3.3 ppt). Generally, only upper limits for NO₂ and SO₂ of 50 ppt can be given, however a series of concentration spikes (up to a few ppb) observed are in the case of NO₂ most likely due to local pollution, while the origin of the SO₂ spikes remains unclear. Analysis of the data suggests that the ozone loss is most likely caused by a combination of BrO_x (= Br + BrO)- and BrO_x + ClO_x- catalysed ozone destruction (with the BrO self reaction and ClO + BrO reaction being the rate limiting steps, respectively). The presence of IO at levels exceeding 1–2 ppt and thus its contribution to ozone destruction is unlikely, but cannot be completely excluded. The observed levels of BrO and ClO are sufficiently high to destroy 1–2 ppb O₃ per hour, thus completely eliminating 40 ppb of initial O₃ within 1–2 days. However air mass dynamics is also likely to be important, in particular observed O₃ decrease rates of up to 7 ppb/h can only be attributed to advection of air already depleted in ozone. The Cl-atom and Br-atom concentrations deduced from ClO and BrO measurements and estimates of ClO/Cl and BrO/Br ratios, are compared with data derived from “hydrocarbon clock” observations in the arctic. While both sets of data are compatible for BrO and 1996 ClO data, in 1995 the DOAS ClO data indicate much higher Cl-atom levels than seen by hydrocarbon clock observations.

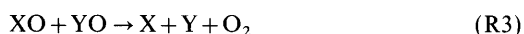
1. Introduction and background

About a decade ago, the phenomenon of complete boundary layer ozone depletion was discovered. Since then sudden, episodic loss of O₃ has been observed at several arctic sites including Alert, Canada (Barrie et al., 1988; 1994; Mickley et al., 1989; Bottenheim et al., 1990); Barrows, Alaska (Sturges et al., 1993), Ny-Ålesund,

Spitsbergen (Solberg et al., 1994; 1996), Thule (Rasmussen et al., 1997), and Søndre-Strømfjord (Rasmussen et al., 1997). Recently a very similar phenomenon was reported from several antarctic stations: Syowa during August, September, and early October of 1989 (Murayama et al., 1992), Neumayer (Wessel, 1996; Frieß, 1997), and Arrival Heights (Kreher, 1996). Apparently ozone depletion episodes only occur after polar sunrise. During these episodes ozone levels drop from the normal 30–40 ppb to mixing ratios unmeasurable

* Corresponding author.

by standard equipment (<2 ppb). Despite many attempts to explain the phenomenon its causes are only partly understood today. Already early observations showed a striking anticorrelation between ozone and levels of filterable bromine (f-Br), i.e. bromine compounds that can be collected on cellulose aerosol filters (e.g., Barrie et al., 1988; Lehrer et al., 1997) leading to the hypothesis of BrO_x (Barrie et al., 1988; Bottenheim et al., 1990; Finlayson-Pitts, 1990), $\text{BrO}_x + \text{ClO}_x$ (LeBras and Platt, 1995), or IO_x (Solomon et al., 1994) catalysed reaction cycles being responsible for the observed ozone destruction. Recently the presence of BrO has been unequivocally verified in the arctic boundary layer (Hausmann and Platt, 1994). All theories have in common that they assume ozone destruction by the reaction sequences:



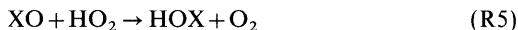
with the net result:



Efficient destruction mechanisms would involve $\text{X}=\text{Y}=\text{Br}$ or $\text{X}=\text{Br}$, $\text{Y}=\text{Cl}$ and possibly $\text{X}=\text{Br}$,

$\text{Y}=\text{I}$ (Table 1). The combination $\text{X}=\text{Br}$, $\text{Y}=\text{Cl}$ or I would be considerably more effective compared to the $\text{BrO} + \text{BrO}$ reaction. While $\text{IO} + \text{IO}$ is believed to lead (at least partly) to a stable dimer and ultimately higher iodine oxides (Jenkin, 1992), likely to be inactive with respect to the ozone budget.

An additional reaction cycle involves the reaction of HO_2 with halogen oxides:



where k_5 (in units of $10^{-11} \text{ cm}^3 \text{ s}^{-1}$) is 0.7, 4.5, and 8.4 for $\text{X}=\text{Cl}$, Br , I , respectively. Followed by:



(or other products).

Together with (R1/R2) the net effect of the cycle (R5, J6, and R7) is also equivalent to (R4), while (R5) usually will be the rate-determining step. In addition the reaction sequence (R5+J6) plays a similar role in the HO_x cycle as the reaction of NO with HO_2 .

We note that the reaction of ozone with HO_2 radicals



is completely negligible as ozone sink. At a HO_2

Table 1. Halogen oxide self- and cross reactions and their potential for tropospheric ozone destruction, data from Atkinson et al. (1992), if not otherwise noted

No. (i)	Reaction $\text{XO} + \text{YO}$	Absolute k_{xi} $10^{-12} \text{ cm}^3 \text{ s}^{-1}$ (at 263K)	Relative $k_{xi}/k_{\text{BrO} + \text{BrO}}$	Remark
1	$\text{ClO} + \text{ClO}$	(0.9)		unstable dimer formed, probably no effect on tropospheric O_3
2	$\text{ClO} + \text{BrO}$	0.01 8.4 ^{a)}	2.6	other products most likely cause for arctic boundary layer O_3 depletion
3	$\text{ClO} + \text{IO}$	6.1 ^{d)}	1.9	probably negligible
4	$\text{BrO} + \text{BrO}$	3.2 ^{b)}	1.0	most likely cause for arctic boundary layer O_3 depletion
5	$\text{BrO} + \text{IO}$	$69 \pm 27^{\text{c)}$	22	potentially very important
6	$\text{IO} + \text{IO}$	108 ^{e)}	34	effect on trop. O_3 unknown

^{a)} There are three product channels: (a) $\text{Br} + \text{Cl} + \text{O}_2$, (b) $\text{BrCl} + \text{O}_2$, (c) $\text{OClO} + \text{Br}$, only channels a and b lead to ozone destruction, thus only $k(a) + k(b)$ is given.

^{b)} Including the channel leading to Br_2 (ca. 20% of total).

^{c)} Data from Huie et al., (1995); Laszlo et al., (1997).

^{d)} (Bedjanian et al., 1996); there are three product channels: (a) $\text{I} + \text{Cl} + \text{O}_2$, (b) $\text{ICl} + \text{O}_2$, (c) $\text{OClO} + \text{I}$, only channels a and b lead to ozone destruction, thus only $k(a) + k(b)$ is given.

^{e)} (Jenkin, 1992), higher oxides are formed, 26% of reactions lead to $\text{I} + \text{I} + \text{O}_2$.

level of 10^7 cm^{-3} (R8) would result in an ozone lifetime in excess of two years.

It is interesting to note that the halogen oxide self- and cross reaction mechanism (R3) as well as the HO_2 mechanism (R5 + J6) are of zero order in O_3 as long as the ozone concentration does not become too low. This is due to the fact that reaction 3, the rate of which is independent of O_3 , is rate limiting (rather than R1). As an approximation one can assume, that the rate of ozone destruction is independent of the ozone concentration, if the $[\text{XO}]/[\text{X}] \gg 1$ (eq. (2)). On the other hand as the O_3 concentration approaches zero $[\text{XO}]/[\text{X}]$ drops to a point where $[\text{XO}] \ll [\text{XO}_x]$ ($\text{XO}_x = \text{XO} + \text{X}$) then (R1) will be rate limiting. As a consequence $[\text{XO}]$ becomes proportional to $[\text{O}_3]$ (see eq. (2), neglecting reactions of halogen atoms with hydrocarbons and HO_2) and $d[\text{O}_3]/dt \propto [\text{XO}]^2 \propto [\text{O}_3]^2$, thus kinetics will shift from zero order to second order in ozone. At $[\text{XO}]/[\text{X}] \approx 1$, for instance the rate of ozone destruction will only be 25% of its initial value. Judging from eq. (2) this point will be reached at ozone levels of the order of 1 ppb in the case of $\text{X} = \text{Br}$ and at several ten ppt for $\text{X} = \text{Cl}$, respectively.

The total ozone loss rate-limited by the self- and cross reactions of halogen oxides (Table 1) is therefore given by:

$$-\frac{d}{dt}[\text{O}_3] = 2 \sum_i ([\text{XO}] [\text{YO}]) k_{xi} + \sum_j [\text{HO}_2] [\text{X}_j\text{O}] k_{sj}, \quad (1)$$

Where i denotes the XO-YO pairs as given in Table 1, while j refers to the different halogens. Thus a XO-catalytic mechanism with 30 ppt BrO could reduce the ozone to levels below the detection limit of commercial ozone monitors (of ≈ 2 ppb) within roughly two days, while a hypothetical first order loss of O_3 with $\tau_{\text{O}_3} \approx 2$ days would require about one week to reduce O_3 levels even below 2 ppb.

The most important questions regarding the presence of reactive halogen species (RHS) in the lower troposphere involve their sources, a possible influence by human activities, and the fraction of total tropospheric halogen being present as RHS. In the following we briefly review the reaction cycles of RHS in the troposphere pertinent to the phenomenon of Arctic tropospheric ozone loss

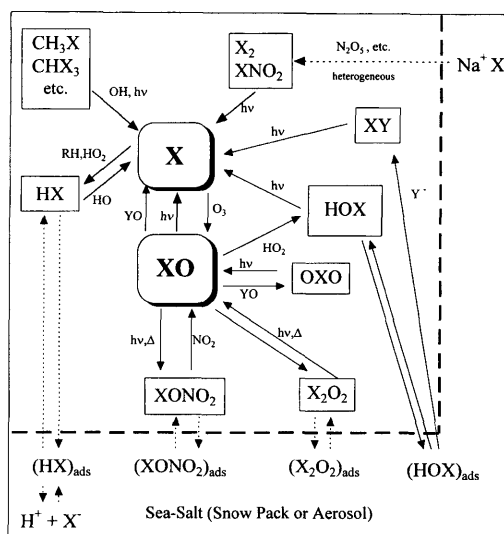


Fig. 1. Simplified scheme of the inorganic halogen reactions in the boundary layer ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) after Wayne et al., (1995). Sources are release from sea-salt (aerosol or deposits) or photochemical degradation of organohalogen species. Important questions concern the XO/X interconversion and recycling from hydrogen halides (HX).

(Fig. 1), more information can be found for instance in Platt and Janssen, (1996), and in the review of Wayne et al., (1995).

Following release from various sources (as discussed below) reactive halogen species are converted to halogen atoms (X), which are (at normal O_3 levels) most likely to be oxidised to XO (by R1). The alternative is reaction with hydrocarbons, aldehydes, or HO_2 leading to conversion of X-atoms to HX. In particular Cl-atoms react readily through hydrogen abstraction leading to the formation of hydrogen halides,



while Br-atoms may add to the $\text{C}=\text{C}$ double bond of olefins, but can only abstract hydrogen atoms from HO_2 or aldehydes,



I-atoms are even less reactive. Because of the decreasing reactivity of the heavier halogens towards H-containing compounds to form HX, the fraction of halogen atoms being converted to

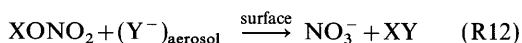
XO by reaction with atmospheric ozone (R1) is roughly 50% for Cl, about 99% for Br, and essentially 100% for iodine (Wayne et al., 1995; Platt and Janssen, 1996). Hydrogen halides may be irreversibly lost or recycled to the RHS reservoir (see below).

Unlike the stratosphere, where the dominating source of RHS is photochemical degradation of fully halogenated compounds (like CF_2Cl_2 etc.), in the troposphere reactive halogen species can only be released from less stable precursors.

(a) Partially halogenated organic compounds, e.g., methyl halides (CH_3X) or other halocarbons, as well as polyhalogenated species such as bromoform, CHBr_3 or CH_2Br_2 (Cicerone, 1981; Oertel, 1992; Sturges et al., 1992; Schall and Heumann, 1993; Khalil et al., 1993), are particularly emitted from the polar oceans. On the other hand the lifetime of CH_3X is of the order of years and even CHX_3 species have several days lifetime (Wayne et al., 1995; Yvon et al., 1996; Davis et al., 1996), in particular under arctic springtime conditions. At the levels of e.g. bromoform found in the arctic (a few ppt) at most a liberation of several ppt of Br atoms per day can be assumed. Thus the known halocarbon emission from the arctic Ocean is unlikely to be the cause for the extremely high RHS concentrations in the Arctic (and Antarctic). It is, however, possible, that even less stable halocarbon species are also emitted, which perhaps — due to their instability — have yet escaped detection.

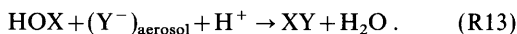
(b) Salt aerosol or sea salt deposits on sea-ice constitute a large reservoir of halogens. Sea salt contains (by weight) 55.7% Cl, 0.19% Br, and 0.00002% I. Here the depletion of the halogen content (Cl and Br) of marine aerosol relative to bulk seawater (i.e. X/Na ratios) indicates a net flux of Cl and Br to the gaseous phase (Cicerone, 1981).

In principle reactions of the nitrogen oxides NO_2 , NO_3 , or N_2O_5 with NaX contained in sea salt aerosol can lead to the formation of XNO or XNO_2 , respectively, as demonstrated in several laboratory studies for $\text{X}=\text{Cl}$ and Br (Finlayson-Pitts and Johnson, 1988; Zetzsch and Behnke, 1993; Behnke et al., 1992; 1993). Also there are other potentially important reactions leading to heterogeneous conversion of halides contained in sea salt (aerosol or deposits) to halogen molecules:

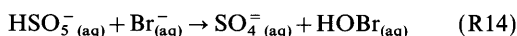


(X, Y = Cl, Br), and where BrONO_2 is formed by (R18). On the other hand, ozone depletion is only observed after Arctic sunrise i.e. in permanent sunlight where NO_3 levels and consequently N_2O_5 concentrations are extremely low. Thus all reactions involving N_2O_5 or NO_3 are unlikely to play a role in halogen liberation in polar spring.

An interesting reaction cycle involves HOX species (McConnel et al., 1992; Fan and Jacob, 1992)



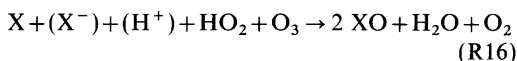
The required H^+ could be supplied by strong acids, such as H_2SO_4 and HNO_3 originating from man made or natural sources. In more detail, dissolution (in the aqueous fraction of aerosol particles or at the ice pack surface (Tang and McConnel, 1996)) of gas-phase HOBr or liquid phase formation of HOBr (Mozurkewich, 1995)



was proposed. Then reaction with halides (Br^- or Cl^-) (R13) would lead to Br_2 or BrCl formation, perhaps via Br_2Cl^- ions (Vogt et al., 1996; Borken, 1996; Kirchner et al., 1997). The halogen molecules are rapidly photolysed (time constant below one minute in the case of Br_2 at arctic springtime) to form halogen atoms.



Finally, reaction with O_3 (R1) will convert the halogen atoms to XO radicals. Thus a reaction sequence involving (R13, J15, R1, and R5) would constitute an autocatalytic cycle releasing halogen atoms from sea salt (aerosol or deposits) according to the net reaction:



(Fan and Jacob, 1992; Sander and Crutzen, 1996; Borken, 1996; Vogt et al., 1996) effectively converting one reactive gas phase halogen molecule (or atom) into two. Once a reaction cycle of the above type has started there would be exponential growth of the RHS concentration as long as the halide supply in the liquid phase lasts. The time constant of the reaction ("doubling time") would be given by the conversion of XY to HOX (by reactions J15 and R5) followed by surface uptake of HOX . If (R5) is assumed to be rate limiting (which is well possible, at least in the case of $\text{X} =$

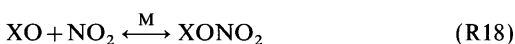
Br), a RHS doubling time of about 20 minutes (at $10^7 \text{ HO}_2 \text{ cm}^{-3}$) would result, leading to an increase of RHS by three orders of magnitude within 3 hours (this exponential growth in RHS could be referred to as "Bromine Explosion").

The fate of hydrogen halides resulting from (R9 to R11) is important when assessing stationary state RHS concentrations. Since HX is highly water soluble it is likely to be irreversibly removed from the atmosphere by wet or dry deposition. The only other important gas phase removal mechanism of HX is reaction with OH,



which will return the halogen atom to the RHS reservoir. Reaction 17 is endothermic for $\text{X}=\text{F}$, also $\text{F} \rightarrow \text{HF}$ conversion is extremely rapid in the troposphere (because the $\text{F} + \text{H}_2\text{O}$ reaction is exothermic), so essentially any reactive F species will be quickly and irreversibly converted to HF. Other reactions of F-atoms are therefore not considered here.

Another RHS reservoir (besides HX) is XONO_2 :



which is assumed to be quite stable in the case of $\text{X}=\text{Cl}$ and Br. On the other hand NO_2 levels were found to be very low in the arctic boundary layer, so the role of XONO_2 is probably limited. Ultimately a halogen atom produced in reaction (R3) or (R19) will either react with O_3 (R1) or with a VOC- (R9), HO_2 - (R10), or HCHO - (R11) molecule. Therefore, the extent of ozone destruction will not only depend on the magnitude of the primary source of reactive halogen species, but at least as sensitively on the efficiency of mechanisms (like a reaction sequence of the type summarised as R16) reconverting hydrogen halides and HOX to XO_x . In fact a simple estimate comparing the rates of reactions R1 with the sum of R9 to R11 shows that XO has to be recycled several 10 times ($\text{X}=\text{Br}$) to several 100 times ($\text{X}=\text{Cl}$) from HX/HOX before 40 ppb O_3 are destroyed.

While homogeneous recycling (R17) of HCl and HBr would be slow at the low OH concentrations assumed for Arctic sunrise, heterogeneous reactions (e.g. R16) are assumed to be very efficient.

In addition photolysis of XO can be a source of halogen atoms for $\text{X}=\text{I}$, Br, and to a minor

extent Cl:



Where $J_{19} \approx 3 \times 10^{-5} \text{ s}^{-1}$, $4 \times 10^{-2} \text{ s}^{-1}$, 0.2 s^{-1} for $\text{X}=\text{Cl}$, Br, I, respectively under arctic spring noontime conditions. While this process does not lead to ozone destruction it will (slightly) reduce the $[\text{XO}]/[\text{X}]$ ratio. Another $\text{XO} \rightarrow \text{X}$ conversion mechanism is reaction with NO:



Ultimately the $[\text{XO}]/[\text{X}]$ ratio is determined by reactions (R1, R3, R20, reaction of X with VOC/ HO_2 , R9 — R11, J19), and heterogeneous reactions involved in recycling and autocatalytic release of X-atoms. The stationary state $[\text{XO}]/[\text{X}]$ -ratio can be calculated:

$$\frac{[\text{XO}]}{[\text{X}]} = \frac{k_i[\text{O}_3] + k_{\text{VOC}}[\text{VOC}] + k_s[\text{HO}_2]}{k_{19}[\text{NO}] + 2k_i[\text{XO}]_i + \sum_{\text{YO} \neq \text{XO}} k_i[\text{YO}]_i + J_{18} + f_{\text{het}} k_{\text{het}}[\text{HO}_2]}, \quad (2)$$

where k_i denotes the rate constants for XO self- and cross reactions leading to the formation of X-atoms as in eq. (1 — (Table 1). The term ($f_{\text{het}} k_{\text{het}}[\text{HO}_2]$) summarises the heterogeneous reaction channels following (R5) and leading to the autocatalytic release of halogens from sea salt. Therefore f_{het} may range between zero (if there is no formation of HOX and further reactions in the aerosol phase) and two, if the autocatalytic release is ideal. The $[\text{XO}]/[\text{X}]$ ratios depend sensitively on the O_3 -concentration, according to calculations of Platt and Janssen, (1996), and especially Borken, (1996), $[\text{XO}]/[\text{X}]$ ratios may range from < 5 ($\text{X}=\text{I}$), 5–50 ($\text{X}=\text{Br}$), to 100–2500 ($\text{X}=\text{Cl}$).

2. Experimental

Measurements of the halogen oxide radicals were performed by Long Path Differential Optical Absorption Spectroscopy (LP-DOAS) observing the strongly structured absorption bands of ClO and BrO in the near UV and of IO in the blue spectral region. In addition the concentrations of O_3 , SO_2 , CH_2O , OCIO , NO_2 , and HONO were determined by the same technique.

The measurements were carried out in the Arctic at Ny-Ålesund, Svalbard (78.9°N , 11.8°O). The station is located at the southern shore of the

Kongsfjörd. To minimise contamination of the measurements by local air pollution, the experimental set up was installed in a laboratory located about 1.5 km to the west of the small settlement (less than 100 inhabitants) of Ny-Ålesund (Fig. 2) at an elevation of about 50 m above sea level. During the period described here from April 18 the sun was above the horizon all day.

A new design of a DOAS spectrometer (Stutz, 1996; Unold, 1995), based on the principle of Platt and Perner, (1983), was used, it incorporates a unit of two coaxial arranged Newton type telescopes (Axelson et al., 1990; Hausmann et al., 1992) to send and receive the light beam. The light of a Xe-short-arc lamp was formed into a beam by the transmitting section of the telescope, reflected by a retroreflector array mounted in the field and recollected by the receiving section of the telescope. The spectrometer was coupled to the telescope by a quartz fibre, which also performed the task of a mode mixer as described by

Stutz and Platt, (1997). Spectra in the UV and visible were recorded at a resolution of about 0.3 nm by a Czerny-Turner spectrograph with a focal length of 0.5 m ($f=6.9$, 1200 gr/mm grating, thermostated to $+10 \pm 0.3^\circ\text{C}$) in combination with a photodiode array detector (RETICON RL 1024R, thermostated to $-30 \pm 0.3^\circ\text{C}$). In 1996 the thermostating of the spectrograph and detector was changed to $+15 \pm 0.3^\circ\text{C}$ and $-35 \pm 0.3^\circ\text{C}$, respectively.

The DOAS light path length for optimum signal to noise depends on the visibility (Platt, 1994), in order to be able to use a close to optimum light path length the telescope combination could be pointed to either of three retroreflector arrays mounted at different distances in the field (Fig. 2). The telescope/spectrometer unit and the mast carrying the retroreflector-array of light path 2 (see below) were set up at slightly different locations (separation of the order of a few 100 m, not noticeable in Fig. 2) in both years. The full length of the folded light path (the distance between telescope and array is half as long) in 1995 and 1996, respectively were:

- (1) 3560 m/3418 m in north-westerly direction, running over land in its full length (retroreflector array at Brandalpynten);
- (2) 5672 m/6226 m in westerly direction, running over land in its full length (retroreflector array at Knudsenhaia)
- (3) 11646 m/11646 m in northerly direction, running across the Kongsfjörd during most (ca. 10000 m) of its length to Blomstrandhalvøya peninsula.

Due to changing visibility conditions the light paths had to be changed frequently at times, the length of the path actually used is indicated at the bottom of Figs. 3, 4, respectively. Spectra were taken in four wavelength ranges selected for optimum detection of ClO, BrO, NO₂, and IO (Table 2). Bands of NO₂ and O₃ could be observed in several of the regions. In addition bands of HONO (1995 only), H₂O, SO₂, and oxygen dimers (O₄, 1995 only) were detectable (Table 2). During the 1996-campaign the spectral range C was skipped, thus giving up the evaluation of HONO and O₄.

The DOAS measurements employed the Multi-Channel-Scanning Technique (MCST) (Knoll et al., 1990; Brauers et al., 1995; Stutz, 1996), it

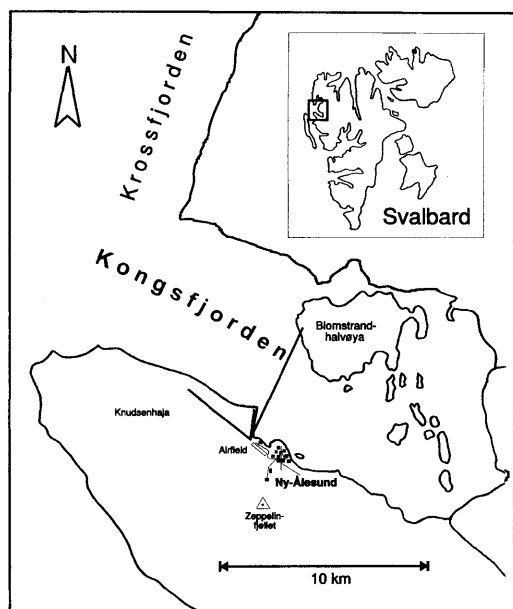


Fig. 2. Measurement site at Ny-Ålesund, Spitsbergen (Svalbard). The three alternatively used DOAS light paths (short light path (1) (≈ 3.5 km) in northerly direction; (2) intermediate light path (≈ 6 km) in westerly direction, running over land in its full length (Knudsenhaia); (3) long light path (11.6 km) in northerly direction, running across the Kongsfjörd for most of its length) are marked.

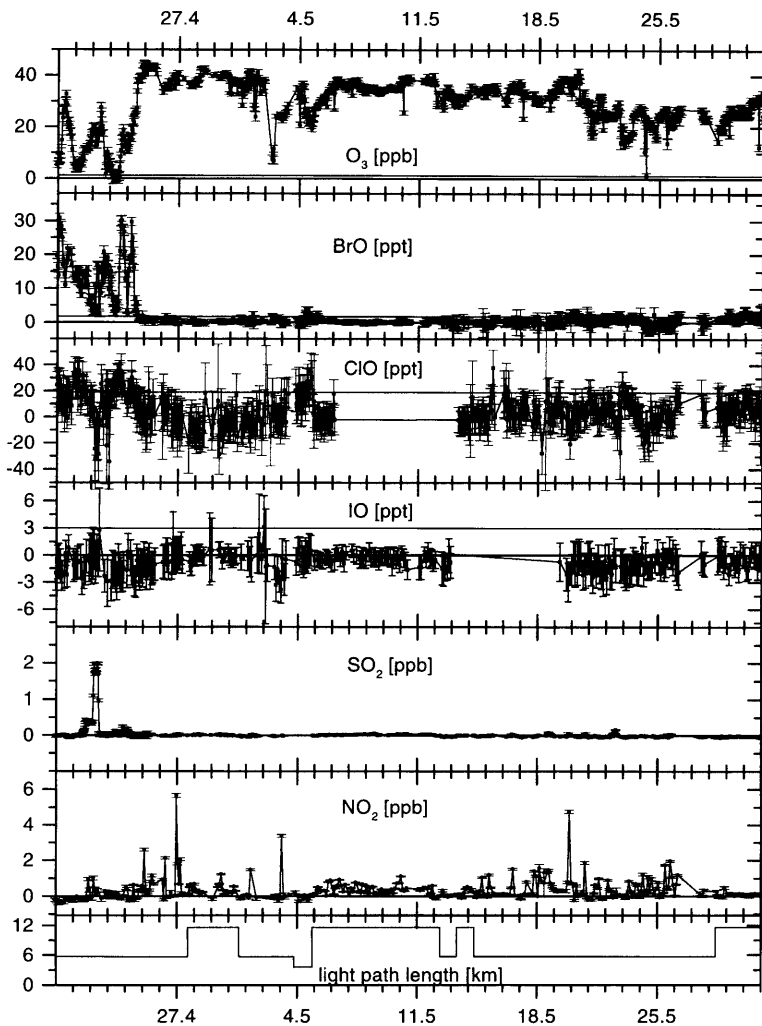


Fig. 3. Time series (20 April–31 May) of the halogen oxides ClO, BrO, IO, O₃, NO₂, and SO₂ during the entire period of the 1995 campaign. The graph at the bottom indicates the DOAS light path length of the individual measurements.

was implemented by taking spectra in the following sequence.

(1) The intensity returning from the path was maximised by an automatic telescope aligning routine.

(2) The desired spectrum was recorded at an integration time of 120 s for the 275–305 nm range and 30 s for the other spectral ranges in 1995, while in 1996 all spectra were recorded at an integration time of 30 s.

(3) In the following step, the light source was blocked to record a background spectrum.

(4) A wavelength calibration was performed by recording the spectrum of a Hg-lamp.

(5) Steps 2 to 4 were repeated with advancing the wavelength by 0.4 nm, thus recording a total of 9 spectra slightly shifted in wavelength with respect to each other.

In addition, Xe-lamp spectra were taken in every fifth measurement sequence. The evaluation

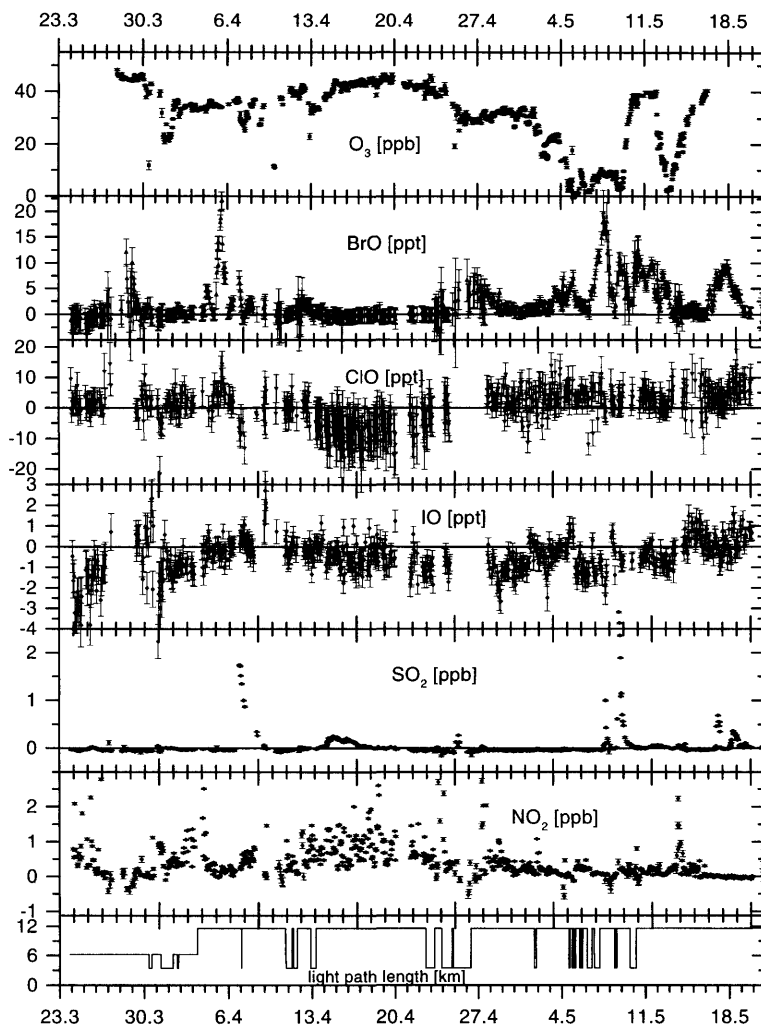


Fig. 4. Time series (27 March–18 May) of the halogen oxides ClO, BrO, IO, O₃, NO₂, and SO₂ during the entire period of the 1996-campaign. The ClO and IO data from the short light (3418 m) path are omitted due to their large errors, otherwise, except for single points on the intermediate light path (6226 m), only the long light path (11646 m) was used.

followed the principles of DOAS evaluation (Platt, 1994; Stutz and Platt, 1996) in addition employing the MSCT to correct for the diode-to-diode variation in detector sensitivity. The concentrations of the trace gases were then deduced by least-squares fitting a linear combination of reference spectra with known column-densities plus a polynomial to the measured spectrum. A non-linear least squares fitting technique allowed to model

spectral shift and slight changes in the dispersion of the instrument (Stutz, 1996; Stutz and Platt, 1996). In some spectral intervals Xe-lamp emission structures were present, most of these could be removed by including lamp spectra in the fit; in a few cases the spectral regions around strong Xe-lines were excepted from the fitting procedure.

The reference spectra were obtained by (1) convoluting literature data for the absorption

Table 2. Spectral intervals used for the DOAS measurements in Ny-Ålesund and list of species observed in the particular interval, absolute values of the differential cross sections were taken from the literature as indicated

Spectral interval (nm)	Species	Wavelength of prominent band (nm)	Mean detection Differential absorption cross section (10^{-20} cm ² /molec)	limit (ppt)		Source of absorption cross section
				1995	1996	
A: 275–305	ClO ₂	280	353 ^a	19	8.5	Simon et al. (1990)
	O ₃	281.5	10	1200	800	Bass and Paur (1985) ^{a)}
	SO ₂	291	68	40	30	Brassington et al. (1981)
B: 310–340	BrO	328	1040	1.7	1	Wahner et al. (1988) ^{a)}
	O ₃	320	0.6			Bass and Paur (1985) ^{a)}
	CH ₂ O	326	6.2		700	Cantrell et al. (1990) ^{a)}
	OCIO	336	980		1.3	Wahner et al. (1987) ^{a)}
	NO ₂	333	7			Schneider et al. (1986)
						Coquart et al. (1996) ^{a)}
C: 350–380 (1995 only)	BrO	355	410		—	Wahner et al. (1988) ^{a)}
	NO ₂	356	8.7		—	Schneider et al. (1986)
	HONO	352	41	60	—	Bongartz et al. (1991) ^{b)}
	O ₄					
D: 420–450	IO	427	1700	2.5	0.9	Himmelmann et al. (1986)
	NO ₂	430	17	100	60	Schneider et al. (1986)
						Coquart et al. (1996) ^{a)}

^{a)} Data were regarded to our resolution and used to scale relative laboratory spectra.

^{b)} Data corrected, U. Schurath, personal communication.

cross-sections to the dispersion and the spectral resolution of our spectrometer. (2) By recording relative spectra with our instrument and scaling the data to literature values (references are given in Table 2). The reference spectra of BrO and O₃, were recorded with the spectrometer itself. This was done by placing a quartz cell filled with the respective trace gas in front of the entrance of the quartz fibre. The absolute absorption cross-sections of these reference spectra were determined by scaling them to literature spectra (Wahner et al., 1988; Bass and Paur, 1985; respectively). The temperature dependence of the absorption cross sections of BrO and O₃ were taken into account. Because of the variability of the air temperature path (252°K to 268°K) along the absorption path, a remaining uncertainty of the BrO and Ozone cross-sections of $\pm 3\%$ has to be assumed. In the case of NO₂ the room temperature data were used, leading to an error of less than 5%. In 1996 NO₂ cross-sections for low temperatures had been available (Coquart et al., 1996).

The measurements are subject to systematic and

statistical errors. The main systematic errors are the uncertainty of the literature values of the cross-section of the trace gases (3%–10%) and the systematic error caused by the instrument itself (due to, e.g., stray light or uncertainties in the instrument function, amounting to about 3% (Stutz, 1996)). The statistical error is caused by photon-statistics, detector-noise and random residual structures in the spectra. The statistical error of the measurements is calculated by the fitting procedure following the principles of Stutz and Platt, (1996). The detection limit of an individual measurement largely depends on the statistical error and is in this work referred to as twice the 1σ error of the measurements.

3. Results

Summarising the experimental results of the spring 1995- and spring 1996-campaigns the time series of ozone together with the halogen oxides BrO, ClO, IO, NO₂ and SO₂ are given in Figs. 3, 4, respectively.

During both years, pronounced episodes of ozone loss occurred. These low-ozone episodes, 19 to 24 April in 1995 and 24 April to 14 May in 1996, are shown in detail in Figs. 5, 6, respectively. During LOEs BrO levels are clearly enhanced and there are indications for elevated ClO-levels.

During the remaining periods (25 April to 31 May in 1995 and 27 March to 24 April in 1996) brief drops in ozone were also recorded, sometimes coinciding with BrO-peaks. Otherwise

BrO-, ClO- and IO-levels remained low, though ClO and IO signals are rather noisy. From ozone sonde launches it can be seen, that low ozone periods always coincide with strong temperature inversion layers at 1000–1500 m height. Above the temperature inversion ozone is still at background levels (Platt, 1997). The trace gases NO₂ and SO₂ show a few (SO₂) or frequent (NO₂) spikes. In more detail the following observations can be made from the data:

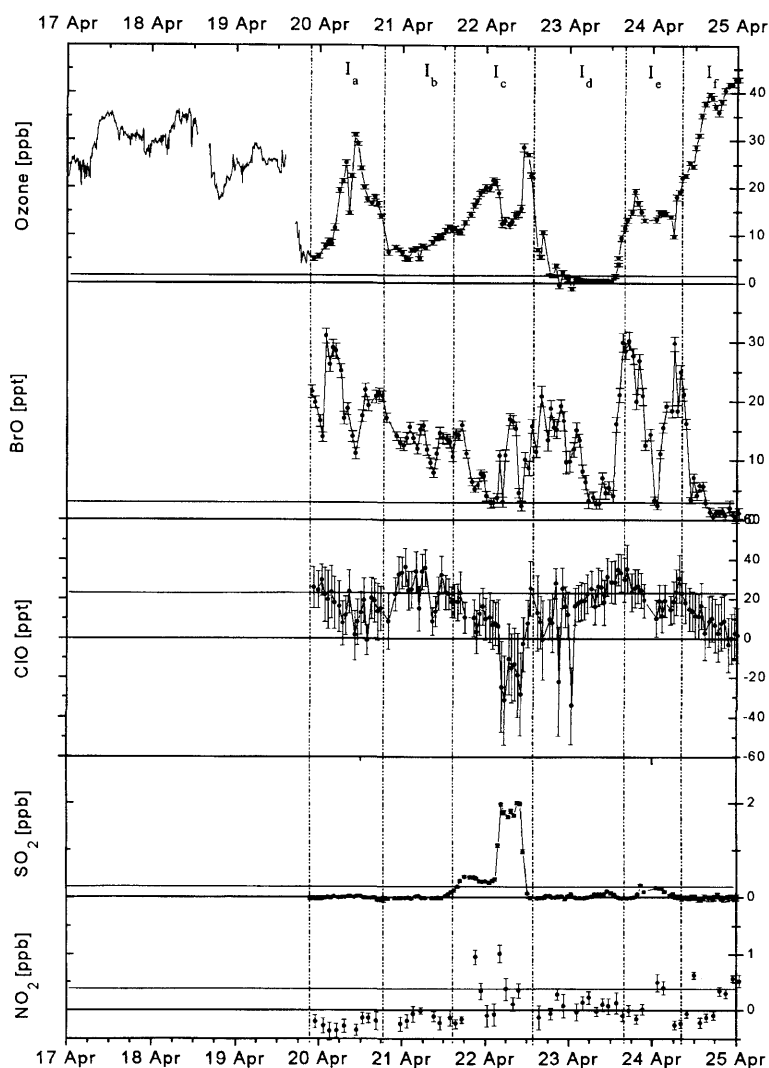


Fig. 5. Time series of O₃, BrO, ClO, SO₂, and NO₂, during the 1995 ozone depletion event (19–25 April). DOAS measurements started on 19 April 1995.

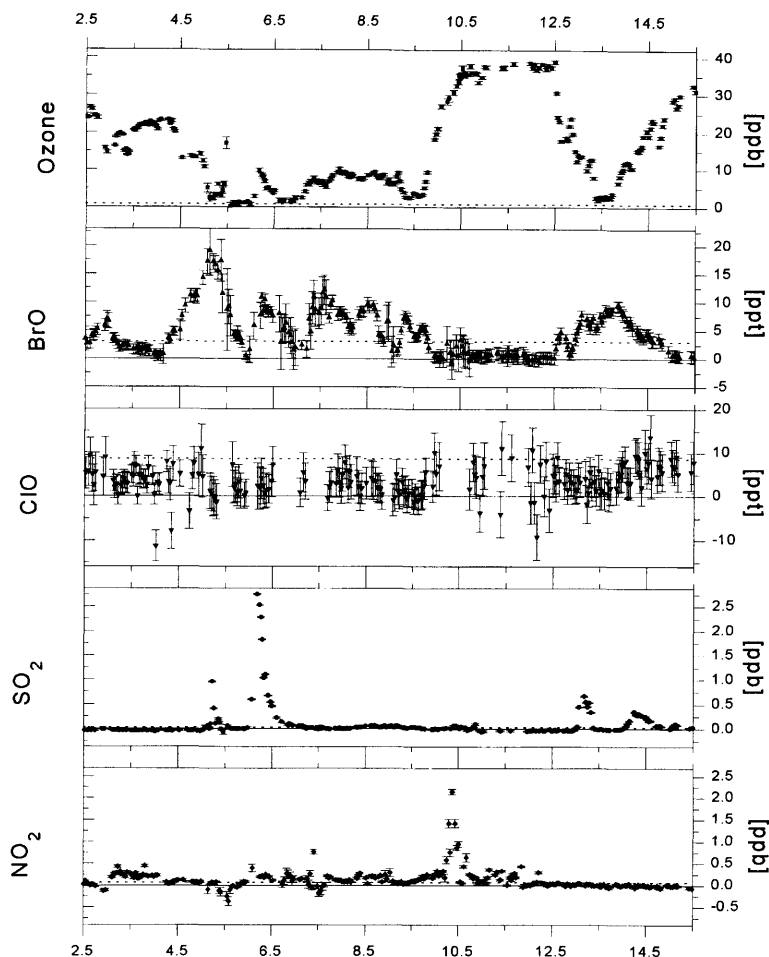


Fig. 6. Time series of O_3 , BrO, ClO, SO_2 , and NO_2 , during the low ozone period in 1996 (24 April to 17 May).

3.1. BrO-data 1995

It is obvious from Figs. 3, 5, that BrO levels up to 30 ppt clearly exceed the detection limit of ≈ 2 ppt (for an individual measurement, see Table 3) during the low-ozone event (LOE) of 19 to 24 April. Throughout the remaining period until 31 May BrO levels only exceeded the detection limit on 5 May, when about 4 ppt were recorded. This latter peak in BrO also coincided with a dip in O_3 , though not the strongest seen in the post-LOE period (Fig. 3). For the entire post-LOE period (24 April to 31 May) the average BrO level was 0.5 ± 0.04 ppt (error of the mean), showing an essentially normal distribution (Fig. 7).

3.2. BrO-data 1996

Fig. 4, 6, show BrO-levels up to 20 ppt, rising by a factor 20 above the average detection limit of an individual measurement of 1 ppt. During the second event from 12 to 14 May a peak-level of only 11 ppt BrO is reached, which is also clearly anticorrelated to O_3 and furthermore coincides with higher wind-speeds. The remaining period shows some smaller dips in the O_3 -levels with corresponding peaks in BrO, up to 7 ppt. Note that on 7 April a BrO-peak with maximum 21 ppt occurs (the highest measured level during campaign 1996) while O_3 just shows a rather moderate decrease. A statistical analysis (see frequency-plots Fig. 8), separated in a non-LOE-period (27 March

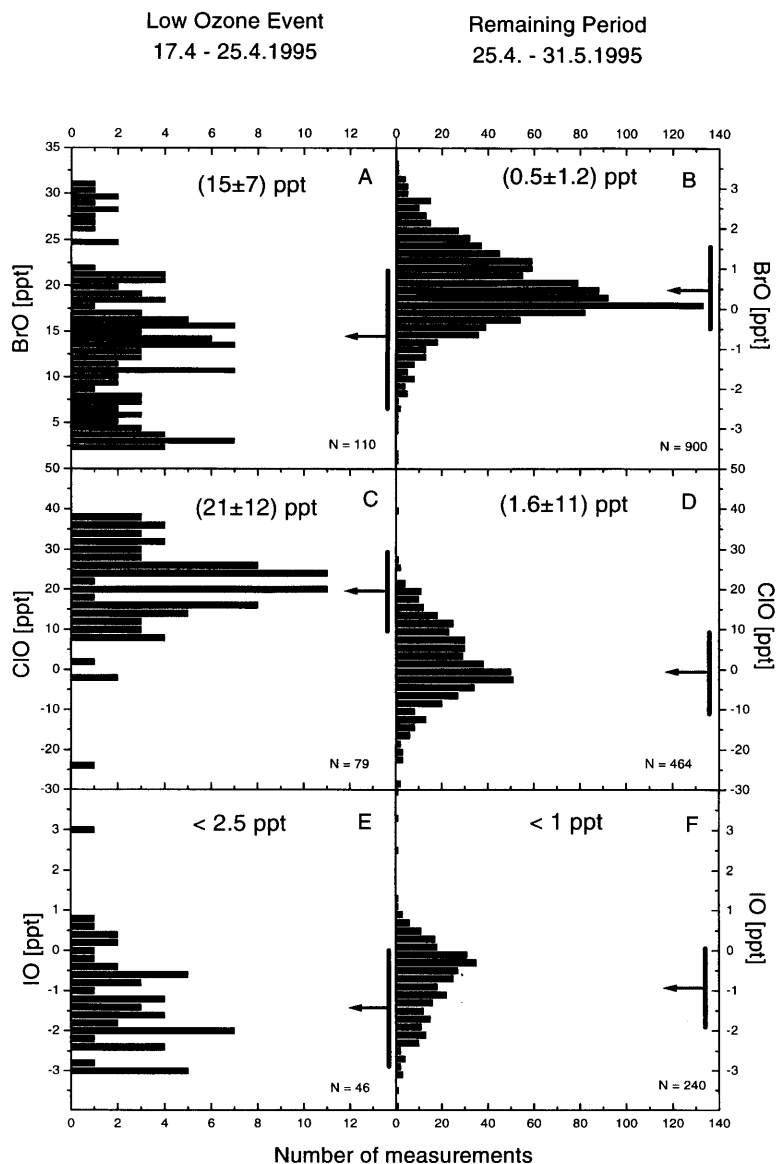


Fig. 7. Frequency distribution in 1995 of: (A) BrO during the low ozone event (17–25 April 1995); (B) BrO during the remaining (non-LOE) period (25 April to 31 May 1995); (C) ClO during the LOE; (D) ClO during the remaining period; (E) IO during the LOE; (F) IO during the remaining period. Horizontal arrows and vertical bars indicate mean and variance (S) of the data, respectively. Numbers in the diagram give mean and standard deviation (STD) of the mean ($S/\sqrt{N}$), N = number of individual measurements. Note that the distributions of the three species are approximately of Gaussian shape in the non-LOE period, indicating constant levels (of essentially zero) within the sensitivity of the instrument.

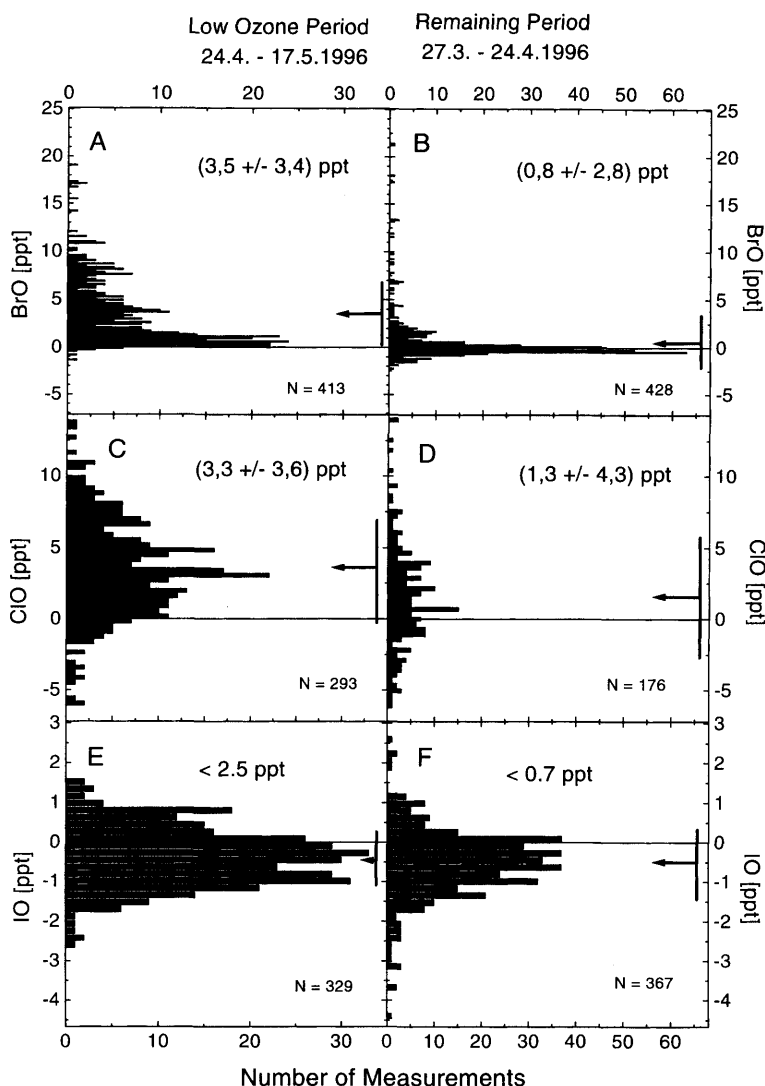


Fig. 8. Frequency distribution in 1996 of: (A) BrO during the low ozone period (24 April to 17 May 1996); (B) BrO during the high ozone period (27 March to 24 April 1996); (C) ClO during the LOE; (D) ClO during the remaining period; (E) IO during the LOE; (F) IO during the remaining period. Indication of mean, variance, STD and number of measurements as in Fig. 7.

to 24 April) and a period when LOEs occurred- (24 April to 17 May), shows mean BrO mixing ratios of 3.5 ± 0.2 ppt for the LOE period with obvious systematic deviations from a normal distribution, while the non-LOE-period, showing a fairly normal distribution, and 0.8 ± 0.1 ppt (errors given are the standard deviation of the mean). The correlation-plot of BrO- and O_3 - mixing-

ratios (Fig. 9) reveals a drop in BrO at very low O_3 -levels.

3.3. ClO-data 1995

In the case of ClO the uncertainty of the individual measurement is ≈ 20 ppt. Therefore the signatures of ClO are difficult to see in individual

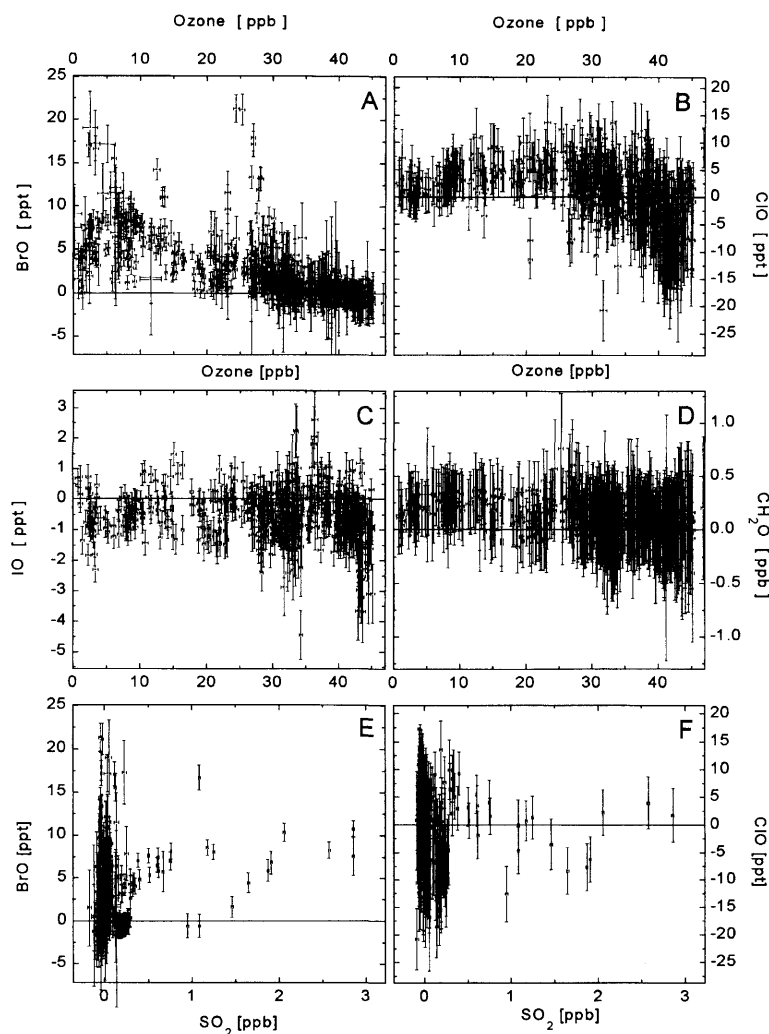


Fig. 9. Correlation-plots of 1996, which show in particular correlation of halogen oxides with ozone (A-C) and formaldehyde (D) and correlation of BrO and ClO with sulfur dioxide (E/F). Note that in the main branch there is a maximum of BrO and ClO concentrations at intermediate ozone concentrations. Furthermore there appears to be a weak dependency of BrO and ClO on SO₂ at very high SO₂ levels.

spectra. Thus, when only the error of an individual measurement is considered, an upper limit for ClO of the order of 20 ppt would be derived in most cases. But the observed values (Fig. 7) are fairly well normal-distributed, which warrants an interpretation of average values. As is also evident from Fig. 7 the average mixing ratios for the low ozone event (19–25 April 1995) and the following “normal ozone” period (after 25 April 1995) are clearly different. During the low ozone period an

average of 21 ± 1.4 ppt (1.4 ppt standard deviation of the mean, 15 ppt variance, see Table 3) is derived, while in the remaining period a much lower average of 1.6 ± 0.5 ppt, is seen.

In principle, also spectral interference by other species could have a systematic influence on the observed levels. In the spectral range of ClO there are also absorption structures of O₃ and SO₂ (Table 2). Therefore we investigated the correlation of ClO with these species (Fig. 10). In the

Table 3. DOAS measurements of halogen oxides in Ny-Ålesund: Detection limits, observed peak levels, and average values during the LOE and the following 'normal ozone' period

Species	STD of individual measurement (ppt)		Peak levels during low O ₃ events (LOE) (ppt)		Average levels during the LOE ($\pm$ error of the mean) (ppt)		Average levels at normal ozone ($\pm$ error of the mean) (ppt)	
	1995	1996	1995	1996	1995	1996	1995	1996
ClO	18	4.5	40	15	21 ± 1.4	3.3 ± 0.2	1.6 ± 0.5	1.3 ± 0.3
BrO	1.5	1.5	30	22	15 ± 0.7	3.5 ± 0.2	0.5 ± 0.04	0.8 ± 0.1
IO	2	0.5	<2.5	<1	<2.5		<1.5	<0.7

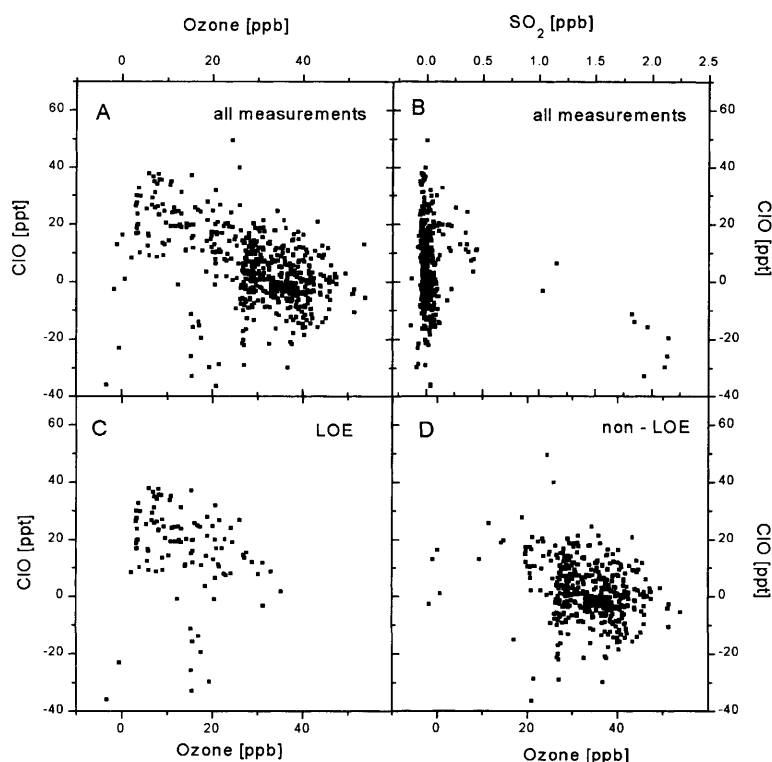


Fig. 10. ClO — O₃ correlation 1995, (A) of all measurements, and (C) during the low ozone event (LOE). ClO — SO₂ correlation, (B) of all measurements, and (D) all measurements except the low ozone event (LOE). The apparently negative ClO concentrations are due to a spectroscopic interference between SO₂ and ClO.

case of ozone there is a negative correlation during the LOE (Fig. 10C), but not for the post-LOE period (Fig. 10D). While the former anticorrelation very likely is due to the ozone depletion chemistry the absence of an anticorrelation during the remaining period makes a spectral interference

unlikely. In the case of SO₂ (Fig. 10B) there is some anticorrelation for high levels of SO₂. Since detectable levels of SO₂ only occurred rarely, the ClO data during those events were disregarded. In summary we conclude that ClO levels comparable to those of BrO were detected during the

LOE. Due to the noise level in the DOAS data we can only give average values for time intervals of several hours during the LOE period from 20 to 24 April but since the average level of ClO is very similar to that of BrO, peak levels are probably also comparable. Inspecting Fig. 7 it appears that the ClO levels during the LOE show less variation than that of BrO.

3.4. ClO-data 1996

Like in 1995 ClO was not detectable in most of the individual spectra in 1996, though the average detection-limit was reduced to 9 ppt. All data from the short light path (3418 m) were omitted in the further analysis, since their individual error is 3–4 times higher than that of the data from the long light path. For the period from 14 to 24 April 1996 the fit-errors increased because the reduced light level due to higher O₃ forced us to narrow the fitting-region. These data were also excluded from the correlation- and statistical analysis.

There are several individual spikes in the ClO concentration, e.g., on 7/8 April 1996, clearly coinciding with high BrO-levels. From statistical analysis (frequency-plots, Fig. 8) mean ClO levels of 1.3 ± 0.3 ppt for the non-LOE-period and 3.3 ± 0.2 ppt for the LOE — period can be derived, both showing fairly normal distribution. The correlation-plot of ClO and O₃ (Fig. 9) suggests maximum ClO-concentrations at about 22 ppb O₃.

3.5. IO-data 1995 and 1996

In the case of IO the situation is less clear. In 1995 conservative upper limits for a single measurement are of the order of 2.5 ppt (Table 3). As in the case of ClO a statistical analysis shows a nearly normal distribution of the results (Figs. 7E, F), however an average IO level around –1 ppt is derived by the fitting procedure. Clearly the average concentration cannot be negative, thus there must be some systematic offset of our instrument of unknown origin, for instance caused by spectrometer-generated spectral structures.

Although the average detection-limit for an individual measurement was improved to 0.9 ppt in 1996 we also cannot conclude that IO levels were significantly different from zero. There is no IO detectable in individual spectra, but statistical

analysis yields mean IO mixing ratios of about –0.5 ppt (see frequency-plots, Fig. 8).

For OCIO it was only possible to give an upper limit of the order of the mean detection limit of 1.3 ppt. In the 1996-campaign (and to some extent in 1995) there appears to be some pattern in the behaviour of SO₂ in that SO₂-peak-levels appear to follow maximum BrO concentrations and minimum O₃-concentrations with a delay of about one day. However, during the extended ozone depletion event (4 to 10 May 1996, Fig. 6) high SO₂-concentrations are found on 5 and 6 May only.

About the nature of a possible causal connection between the observed SO₂ peaks and ozone destruction can only be speculated. The SO₂ peaks are probably not caused by local pollution, there is only one appreciable source, the Ny-Ålesund power station, which emits SO₂ as well as NO₂. However there is no correlation between the SO₂- and NO₂ peaks. It is possible that the SO₂ spikes are due to long range transport of anthropogenic pollution, like in Arctic Haze events. It is unlikely, however, that Arctic Haze is a necessary condition for the occurrence of LOEs, since there are indications for boundary layer ozone destruction also in Antarctica (Wessel, 1996; Kreher, 1996), where no anthropogenic pollution like “Antarctic Haze” is present. Therefore it is more likely that the coincidence of SO₂ spikes and LOEs is not a cause effect chain, but rather caused by large scale circulation processes in the Arctic, transporting plumes of Arctic Haze over Ny-Ålesund, in which the SO₂-sulphat conversion has not yet been completed. This observation is in line with the aerosol measurements, which show high concentrations in the nucleation-mode, i.e. of aerosol particles just being formed (Staebler, 1996; private communication).

Ozone-data 1995 and 1996. We assume that most of the observed ozone decay and all of the ozone recovery is caused by advection of air masses with low- or normal ozone contents, respectively. On the other hand, the observed O₃ rate of change ($d[O_3]/dt$, around 1–2 ppb/hour on average, with peaks up to 7 ppb/hour) is comparable to the calculated rate of chemical destruction (1–2 ppb/hour, see eq. (1), above). Thus it could be expected, that the observed ozone decay (caused by advection plus destruction) is faster than the

subsequent recovery (caused by advection only). Therefore, from the ozone data taken by the DOAS-system and additional by a HORIBA-ozone-monitor at the measuring site, the rates of decay and recovery were evaluated.

In 1995, ozone decay rates ranged from 2 ppb/h up to 7 ppb/h, as described by Platt (1997). Over the entire measuring period these authors derived a mean loss rate of $d[\text{O}_3]/dt \approx -2.6$ ppb/h and a mean O_3 recovery rate of +1.3 ppb/h. So the (temporal) decay-recovery-ratio was 2, indeed much larger than unity. The slower recovery could be also be found when comparing the spatial decreasing and increasing slopes $d[\text{O}_3]/dx = (1/v) d[\text{O}_3]/dt$ (where v = mean local wind speed during ozone depletion or recovery). The average spatial decay-recovery-ratio was ≈ 1.5 .

In the 1996 ozone loss- and recovery rates ($d[\text{O}_3]/dt \approx -1.2$ ppb/h and +0.8 ppb/h, respectively) were half as fast than in 1995 (see Table 4, Fig. 11). The decay-recovery-ratio is similar to 1995 as well in time (1.8), and in space (1.4). It can be concluded, that, on average, the rate of ozone decay is indeed faster than the recovery, although there are large variations in both figures. In addition, the spatial ozone gradients give some chemical information in that they indicate the

“age” of the ozone depleted airmass. When we assume that the initial gradient between high-ozone and low-ozone airmasses is infinitely steep it will become diffuse with time. This allows to estimate an upper limit for the time required to destroy the ozone of the order of a few days at most (Hausmann and Platt, 1994).

4. Discussion

It is tempting to compare the rates of halogen radical catalysed ozone destruction calculated from our halogen oxide measurements with measured changes in ozone. Assuming a combined BrO–ClO-mechanism for ozone destruction (LeBras and Platt, 1995) the purely chemical ozone destruction rate can be derived from eq. (1) once the corresponding BrO- and ClO- concentrations are known (assuming the BrO self- and BrO + ClO reactions to be rate limiting). It is clear, however that this can only be an order of magnitude comparison, because the measured XO concentrations give the instantaneous ozone destruction rate, while the ozone level seen is a consequence of the ozone destruction during the last few days.

Table 4. Ozone decay and recovery rates observed during the ARCTOC-campaign in 1996

Date	$d[\text{O}_3]/dt$ (ppb/h)	Decay-recovery- ration in time	v_{wind} (m/s)	$d[\text{O}_3]/dx$ (ppb/km)	Decay-recovery- ratio in space
30.3. 96	−0.61		2.5	−0.07	
31.3. 96	−4.66	3.1	12	−0.11	0.8
1.4. 96	+1.51		3.0	+0.14	
6.4. 96	−0.97	1.9	2.5	−0.11	3.7
7.4. 96	+0.50		4.0	+0.03	
8.4. 96	−0.79	2.2	4.5	−0.05	1.7
9/10.4. 96	+0.36		3.5	+0.03	
12/13.4. 96	−0.43	1.0	3.0	−0.04	0.5
13./14.4. 96	+0.43		1.5	+0.08	
23. – 25.4. 96	−0.24		2.0	−0.03	
1. – 5.5. 96	−0.39	1.1	4.0	−0.03	0.4
6./7.5. 96	+0.36		1.5	+0.07	
8.5. 96	−0.68	0.5	3.0	−0.06	0.5
9.5. 96	+1.25		3.0	+0.11	
12.5. 96	−2.22	2.5	8.0	−0.08	2.0
13./14.5. 96	+0.90		6.0	+0.04	
mean		1.8			1.4
decay	-1.22 ± 1.30			-0.064 ± 0.027	
recovery	0.76 ± 0.18			0.072 ± 0.043	

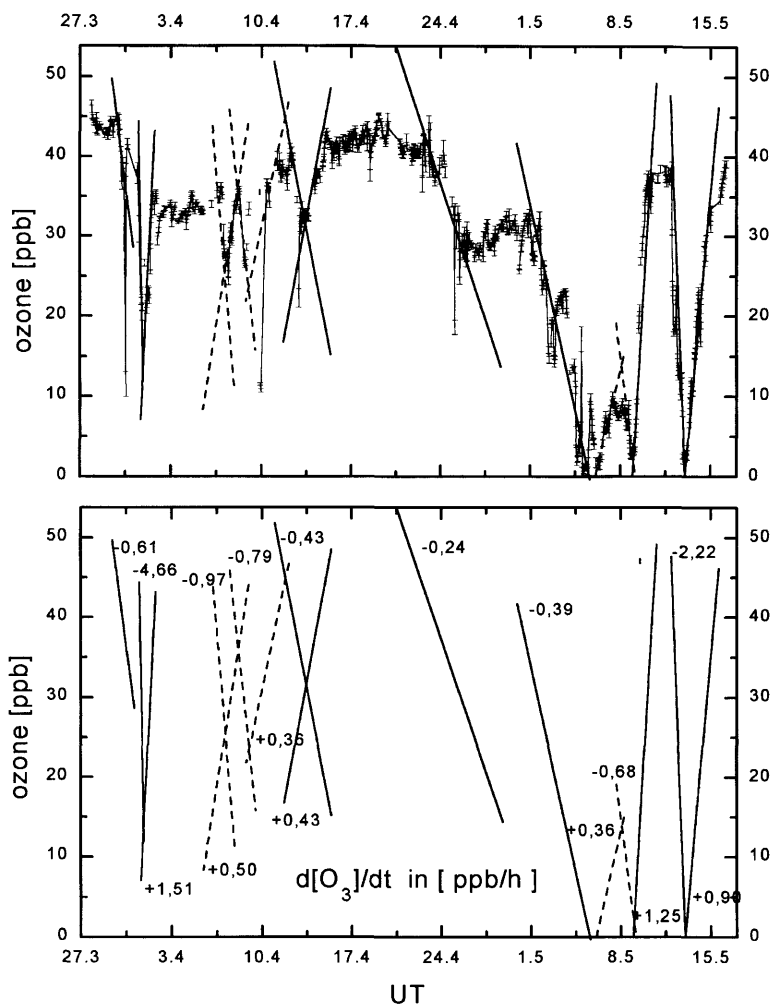


Fig. 11. Time series of DOAS ozone data for 1996, decay and recovery rates are marked by lines (numerical values of rates of ozone change are given in Table 4).

In some cases calculated chemical ozone destruction rates appear to match the observed rates of O_3 decay, frequently the ozone decay is faster than can be accounted for by chemical destruction. Clearly the rapid recovery of the ozone concentration cannot be explained by in-situ chemistry. Therefore advection of an air-mass, in which ozone destruction has already taken place before, is the most likely explanation of the phenomenon. Of course, rates of ozone depletion much larger than calculated for purely chemical in-situ destruction can occur by advection.

A rough estimate of purely chemical ozone

destruction rates can be obtained by taking the maximum measured BrO -mixing ratios and a mean of a data ensemble around elevated ClO -levels. This leads to ozone destruction rates of 1.3–2.4 ppb/h ($[BrO] = 30$ ppt, $[ClO] = 15$ to 35 ppt) for 1995, and to 0.4–0.5 ppb/h for 1996 ($[BrO] = 18$ ppt, $[ClO] = 6$ to 11 ppt), respectively.

It is also interesting to compare the levels of reactive halogen species reported here with data obtained by other methods. These are mainly derived by indirect determination of halogen atom concentrations from the observation of hydrocarbon ratios in airmasses of known chemical age

(the “hydrocarbon clock” method) (Jobson et al., 1994; Solberg et al., 1994; Ramacher et al., 1997). While there is criticism of this method, the results nevertheless provide indications for the presence of halogen atoms in the troposphere. In addition some indirect evidence for the presence of reactive Cl-species is due to observation of tropospheric HCl (Vierkorn-Rudolph et al., 1984).

Table 5 summarises some estimates and measurements of XO and X-atom concentrations. In order to compare the results of the different measurement techniques $[XO]/[X]$ ratios were taken from model calculations by Borken, (1996), based on considerations similar to those leading to eq. (2) (Platt and Janssen, 1996). It is worth to remember that the $[XO]/[X]$ ratio is strongly dependent on the O_3 concentration. In particular it drops significantly by about an order of magnitude at very low (<5 ppb) ozone levels. As ozone mixing ratios are fairly rarely below 5 ppb, even during LOEs, one may have a closer look at the intercomparison levels derived from the higher end of $[XO]/[X]$ ratios. Given the large uncertainties in the determination of the X-atom con-

centration from hydrocarbon clock observations as well as the uncertainty of the estimation of the $[XO]/[X]$ ratios, the data are in fair agreement. In the case of Cl-atoms the 1995-DOAS-derived data $((19-480) \cdot 10^4 \text{ cm}^{-3})$ are about 5 to 60 times higher than the hydrocarbon clock results $((1-8) \cdot 10^4 \text{ cm}^{-3})$. In 1996, the DOAS Cl-data $((3.7-92) \cdot 10^4 \text{ cm}^{-3})$ range from the levels found by the hydrocarbon clock methods to about 10 times higher values. The DOAS derived Br-atom levels $((0.9-8) \cdot 10^7 \text{ cm}^{-3}$ for 1995 and $(0.2-2) \cdot 10^7 \text{ cm}^{-3}$ for 1996) are comparable to the hydrocarbon clock data $(1-10 \cdot 10^7 \text{ cm}^{-3})$.

Furthermore, in the correlation-plots for the 1996 results (Fig. 9) between halogen oxides (BrO and ClO) and ozone, there appears to be a maximum in the ClO- and BrO concentration for intermediate levels in O_3 . This can be understood as follows: On the one hand from reaction (R1) it is clear that at higher XO levels more ozone will be destroyed and therefore the highest ozone levels should only be found at low or moderate XO concentrations. On the other hand at low ozone levels the loss of halogen atoms by (R5) and (R9)

Table 5. Direct and indirect determinations of X-atom and XO concentrations for Arctic regions, in molec./cm³ (X = Cl, Br, I)

Author	Site	Cl [10 ⁴ cm ⁻³]	O [10 ⁷ cm ⁻³]	Br [10 ⁷ cm ⁻³]	BrO [10 ⁷ cm ⁻³]	I [10 ⁷ cm ⁻³]	IO [10 ⁷ cm ⁻³]
Jobson et al. (1995)	Alert and north >82°N	1-8^{a)}	0.1-20	1-6^{a)}	5-300	—	—
Solberg et al. (1994, 1996)	Ny-Ålesund ≈79°N	3-6^{a)}	0.3-15	3-10^{a)}	15-500	—	—
Ramacher et al. (1997)	Ny-Ålesund ≈79°N	4^{e)}	0.4-10	2^{e)}	10-100	—	—
Hausmann and Platt (1994)	Alert 82°N	—	—	≤(1-10)	≤52 ^{b)}	—	—
this work (1995)	Ny-Ålesund 79°N	19-480	48^{b)}	0.9-8 (≤0.9-18)	44^{b)} (≤90 ^{d)}	<0.3	<1.5 ^{e)}
this work (1996)	Ny-Ålesund 79°N	3.7-92	9.2^{b)}	0.2-2 (≤0.7-13)	9.8^{b)}d) (≤65 ^{d)})	<0.3	<1.4 ^{e)}

Quantities derived from DOAS- or hydrocarbon clock observations, respectively, are shown in **boldface**, remaining data are calculated from assumed $[XO]/[X]$ ratios of $[BrO]/[Br] = 5-50$, $[ClO]/[Cl] = 100-2500$ and $[IO]/[I] < 5$ (Borken, 1996; Platt and Janssen, 1996).

^{a)} Derived from relative rates of hydrocarbon decay (hydrocarbon clock).

^{b)} Direct UV spectroscopic (DOAS) measurement.

^{c)} Upper limits (detection-limit) by DOAS-measurements.

^{d)} Maximum DOAS-measured values.

^{e)} Calculated from reported Cl- and Br- doses assuming constant conditions for 3 days.

becomes dominant compared to the reaction with ozone (R1), thus XO concentrations should also decline.

A further consequence of the presence of elevated levels of ClO simultaneously with BrO is considerable formation of OCIO through channel c of the ClO + BrO — reaction (no. 2 in Table 1) and possibly through the reaction of ClO + IO. At the ClO and BrO levels observed this production combined with a typical OCIO photolytic lifetime of 9 sec ($SZA = 80^\circ$) will lead to a steady-state OCIO mixing ratio of about 0.6 ppt in 1995 and 0.02 ppt in 1996. So at our detection-limit of 1.3 ppt, detection of OCIO was not to be expected.

It should also be noted that the high levels of ClO_x inferred from the measured ClO concentrations (as well as from hydrocarbon clock observations) influence the rate of ozone destruction not only directly through reaction of ClO with BrO (or IO) but also via formation of OH — and HO₂ from Cl-atom reactions with organic species. As a consequence the HO₂ — O₃ destruction cycle might be enhanced, and also the liberation of BrO_x via autocatalytic reaction cycles like (R16).

5. Summary

Our observations can be summarised as follows.

- The levels of BrO found in the European arctic during this study are comparable to those reported for arctic Canada (Alert) (Hausmann and Platt, 1994).
- Chlorine monoxide levels were found to range from a few ppt up to mixing ratios comparable to those of BrO.
- Levels of IO never exceeded the detection limit of a few ppt.
- A general coincidence between periods of depleted ozone levels and high BrO and ClO concentrations was found, while in the case of IO no clear signal is seen.
- Analysis of the data suggests that the bulk of the ozone loss is most likely caused by a combination of BrO_x (= Br + BrO)- and BrO_x + ClO_x-catalysed ozone destruction (with the BrO self reaction and ClO + BrO reaction being the rate limiting steps, respectively).

- Nevertheless a noticeable contribution of the BrO + IO reaction cannot be excluded.

- The observed halogen oxide levels are sufficiently high to destroy between 0.5 (1996) and up to 2.4 (1995) ppb of O₃ per hour, thus to completely eliminate 40 ppb of initial O₃ within 1–3 days.

- Even higher observed rates of O₃ change up to 4.5 ppb/h (1996) to 7 ppb/h (1995) (Platt, 1997) can be attributed to advection of airmasses already depleted in ozone as pointed out previously by several authors (Hausmann and Platt, 1994).

- The Br-atom concentrations deduced from BrO measurements and estimates of BrO/Br ratios are 1995 are consistent with data derived from observations of hydrocarbon depletion (“hydrocarbon clock”) observations in the arctic, while DOAS-observations in 1996 were at least by a factor 4 lower.

- Chlorine atom levels deduced from DOAS — ClO measurements exceed “hydrocarbon clock” determinations (in the arctic) by about a factor of 3 to 7 for 1995 and are consistent with “hydrocarbon clock” data in 1996.

- Ozone destruction patterns were different in 1995 and 1996, in that both, ozone decay rates and concentration levels of halogen oxides, were lower in 1996 than in 1995.

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