Atmospheric reactive chlorine and bromine at the Great Salt Lake, Utah

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[1]   The presence of chlorine radical species in the lower troposphere has been postulated, but only indirect evidence of its existence has been reported. We present the first direct spectroscopic observations of up to 15 ± 2 pmoles/mole-air chlorine oxide (ClO) in the mid-latitude boundary layer and confirm a previous discovery of the existence of bromine oxide (up to 6 ± 0.4 pmoles/mole-air BrO). Our observations from October 2000 suggest that reactive halogens are mobilized from salt on the flats around the Great Salt Lake, Utah. The results imply levels of 10^5 Cl atoms per cm^3, which doubles the atmospheric oxidation capacity. Ozone concentrations are anti-correlated with the halogen oxide levels, particularly BrO, indicating that ozone depletion by catalytic reaction cycles may have occurred. If the mobilization of halogens from salt flats that was observed here is widespread, there are important implications for atmospheric chemistry and the biogeochemical cycling of mercury.   *INDEX TERMS:* 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0330 Atmospheric Composition and Structure: Geochemical cycles; 0322 Atmospheric Composition and Structure: Constituent sources and sinks

1.   Introduction

[2]   Reactive halogens can severely impact tropospheric chemistry. The destruction of boundary layer ozone by catalytic reaction cycles involving bromine and chlorine has been observed in polar regions [*Foster et al.*, 2001; *Tuckermann et al.*, 1997] and at the Dead Sea [*Hebestreit et al.*, 1999]. Furthermore, chlorine, and to a certain extent bromine, are strong oxidants. Reactive halogens can also provide a fast pathway to convert elemental gaseous mercury into shorter-lived oxidative states of mercury [*Lu et al.*, 2001]. Observations of reactive halogens in the lower troposphere are sparse. In the Arctic, Br_2, BrCl, and BrO reach levels of 30 pmoles/mole-air [*Foster et al.*, 2001; *Tuckermann et al.*, 1997]. *Tuckermann et al.* [1997] estimated average ClO mixing ratios of 3–20 pmoles/mole-air, but a direct identification was unsuccessful. Indirect estimates of chlorine atom concentrations are in the range of 10^4–10^5 Cl atoms cm^{-3} in the Arctic, and below 10^3 Cl atoms cm^{-3} on a global scale [*Rudolph et al.*, 1997]. At mid-latitudes, BrO has only been observed at the Dead Sea [*Hebestreit et al.*, 1999], with levels up to 180 pmoles/mole-air. Attempts to identify BrO in the extra-polar marine environment have not been successful [*Platt*, 2000]. Reactive chlorine precursors of up to 150 pmoles/mole-air have been observed in a marine environment [*Spicer et al.*, 1998]. Reactive halogens can

be formed by the photolysis of organo-halogens emitted by algae in the ocean. Chlorine and bromine can also be released into the gas-phase by heterogeneous reactions on salt covered surfaces or salt aerosol [*Fickert et al.*, 1999; *Knipping et al.*, 2000].

[3]   Knowledge of the budget of reactive halogens in the global troposphere has considerable gaps [*Keene et al.*, 1999]. The presence of chlorine as a strong oxidant has been proposed but, thus far not directly confirmed. It is unknown whether reactive chlorine chemistry impacts urban environments. Here we intend to answer some of these questions based on our observations during the Vertical Transport and Mixing Experiment 2000 study (VTMX) in the Salt Lake City region.

2.   Experimental

[4]   Our instrument was set up 10 km west of Salt Lake City (Figure 1) and 5 km east southeast of the shore of the Great Salt Lake (40.77 N, 112.06 E, height above sea level 1290 m). The measurements were made by differential optical absorption spectroscopy (DOAS) over a path of length 3.3 ± 0.02 km [*Stutz and Platt*, 1997]. DOAS is a method that identifies and quantifies trace gases by their unique UV-visible narrow band absorption structures in the open atmosphere.

[5]   The mixing ratio of ClO was derived from its absorptions in the wavelength window from 284–302 nm by a least squares fit [*Stutz and Platt*, 1996]. We included absorption reference spectra of ozone, ClO, NO_2, SO_2, HCHO, the spectral structure of the lamp, and an additive 5th degree polynomial in our analysis [*Burrows et al.*, 1998; *Burrows et al.*, 1999; *Sander and Friedl*, 1989]. To reduce unwanted spectral structures caused by slow changes of the instrument, we also included an atmospheric spectrum measured at 11:16 local time (LT) as a reference in our analysis. From the results at 10:00 LT, when high NO_2 would have converted a large fraction of any ClO present to $ClONO_2$, we estimated the ClO mixing ratio of the atmospheric reference spectrum to be below 3–4 pmoles/mole-air. The ClO mixing ratios reported here are therefore relative to the much lower mixing ratios of the 11:16 reference spectrum. Figure 2a shows that the ClO absorptions agree well with those determined in the laboratory [*Sander and Friedl*, 1989]. The average error of the ClO mixing ratios over the period shown here is 1.8 pmoles/mole-air, and the average detection limit is 3 to 4 pmoles/mole-air.

[6]   The absorptions of BrO were analyzed at two different spectrometer-grating positions in the wavelength windows 312.9 to 341.5 nm and 309.3 to 352.7 nm. We included reference spectra of ozone, BrO, O_3, NO_2, HCHO, SO_2, [*Burrows et al.*, 1998; *Burrows et al.*, 1999; *Orphal et al.*, in press] a spectrum of the lamp, an additive polynomial, and an atmospheric reference spectrum in the analysis. The BrO mixing ratio of the atmospheric reference spectrum was estimated to be below the detection limit of around 0.5 pmoles/mole-air. An absolute analysis of the spectra without the atmospheric reference spectra gave similar results, but

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[1]Now at Automotive Lighting, Reutlingen, Germany.
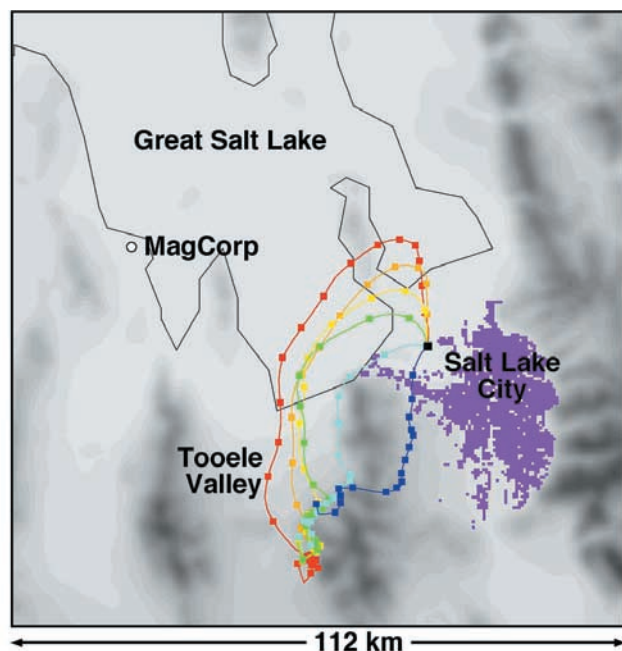
Figure 1. Three dimensional air parcel backtrajectories for air arriving at the DOAS site (black square) at different times of October 14. The colors indicate the local time at which air arrived at the site: (blue 11:00, cyan 12:00, green 13:25, yellow 14, orange 21:15, and red 17:00). The squares on the trajectories indicate 1 hour intervals. The open circle shows the location of the MagCorp chlorine plant.

the errors were higher. Figure 2b shows that the BrO absorption bands were clearly identified. The average BrO detection limit for the period shown here was 0.4 pmoles/mole-air. Ozone mixing ratios were determined from the absolute BrO fit with a detection limit of 1.5 nmoles/mole-air. Nitrogen dioxide was analyzed in the wavelength window from 424.1 to 447.3 nm with an average detection limit of 120 pmoles/mole-air.

[7] In the VTMX study a dense network of meteorological observations was operated in the Great Salt Lake Basin [*Doran et al.*, 2002]. Back trajectories were calculated to ascertain the path of air parcels transported over the DOAS site (Figure 1). The trajectories employed wind speed and direction from hourly meteorological analyses based on the assimilation of the observed winds in the region with a mesoscale model using a 1-km horizontal grid spacing. The wind fields were then interpolated linearly in time and the trajectory positions were calculated at 15-min intervals.

3. Results

[8] Figure 3 shows that after NO_2 drops below the detection limit around noon on October 14, ClO and BrO levels rise significantly above their detection limits and remain elevated until 16:00. ClO and BrO mixing ratios reach maxima of 15 ± 2 pmoles/mole-air and 6 ± 0.4 pmoles/mole-air at 13:00, respectively. A less pronounced maximum of ClO and BrO was observed 2 hours later. The ozone mixing ratios (Figure 3) are around 35 nmoles/mole-air. The short term variations of ozone show a statistically significant correlation with BrO ($r^2 = 0.84$ for N of 50). The correlation with ClO is weaker. We did not observe elevated BrO or ClO mixing ratios during any other period in October. Nevertheless, halogens might have been present in other forms. At the typically higher daytime NO_2 mixing ratios on other days, the halogen oxide steady state with the respective nitrates would have been shifted to the nitrates, lowering the halogen oxide levels.

[9] During the morning of October 14, katabatic down-valley flows resulted in southerly winds in the vicinity of the DOAS site, bringing polluted air from the Salt Lake City area. After 11:00 LT, the wind direction gradually reversed because daytime heating of the land surface produced a lake breeze, and cleaner air was observed. Wind speeds were between $2-3$ m s^{-1} at the DOAS site between 11:00 and 18:00 LT. The daytime temperatures on October 13 and 14 were 8°C and 12°C, with relative humidities of 98% and 60% respectively. Several light rain episodes, with a total of 6 mm precipitation, were reported in the 24 hours before the morning of October 14, followed by partly cloudy skies during daytime. Air parcel back trajectories to the DOAS site show that after 12:00 LT, the air originated from Tooele valley, west of Salt Lake City (Figure 1). After being localized in the Tooele valley during the night the air moved north in the early morning, reaching the lakeshore at 7:00 LT and then circulated clockwise in the following 3 to 7 hours over the lake. In the 1 to 2 hours prior to arriving at the DOAS site, the air moved southward over the lakeshore and salt marshes.

[10] The Great Salt Lake basin has a number of industrial Cl_2 sources, which are mostly co-located with large NO_x sources in the urban areas on the eastern shore of the lake (www.epa.gov/tri/). We can exclude those sources based on our trajectory calculations and the low NO_2 levels on October 14. No larger anthropogenic halogen sources are located in the sparsely populated Tooele valley. The largest industrial source of Cl_2 in the Great Salt Lake
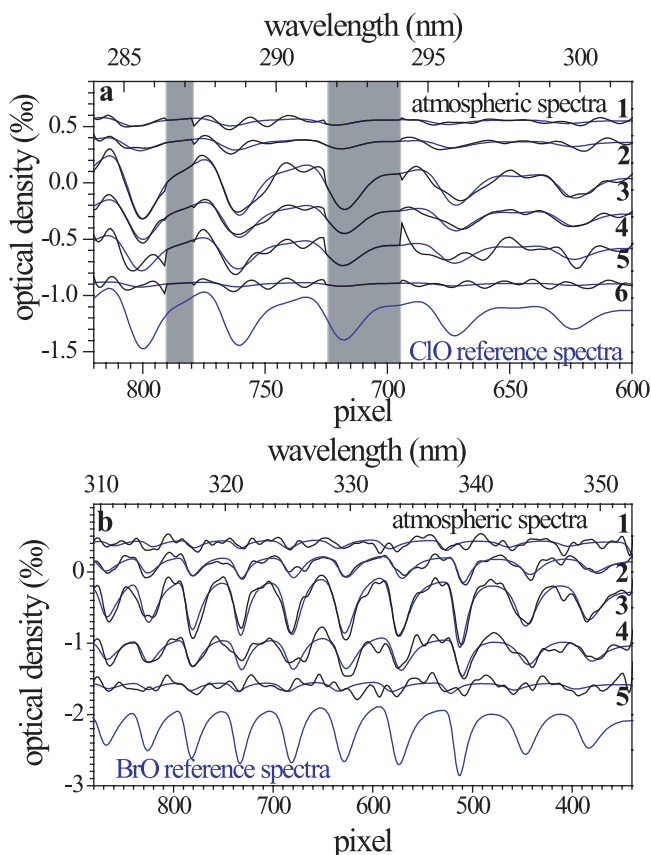
Figure 2. ClO (a) and BrO (b) absorption structures during October 14. The black lines are the atmospheric spectra after removing all absorptions except those by the respective halogen oxides. The blue lines are the respective fitted reference spectra that were calculated from a literature absorption cross section [*Orphal et al.*, in press; *Sander and Friedl*, 1989]. The numbers identify the data points in Figure 3. Spectra are offset to each other to simplify the graph. The gray intervals in (a) mark spectral regions that were excluded from the fit.
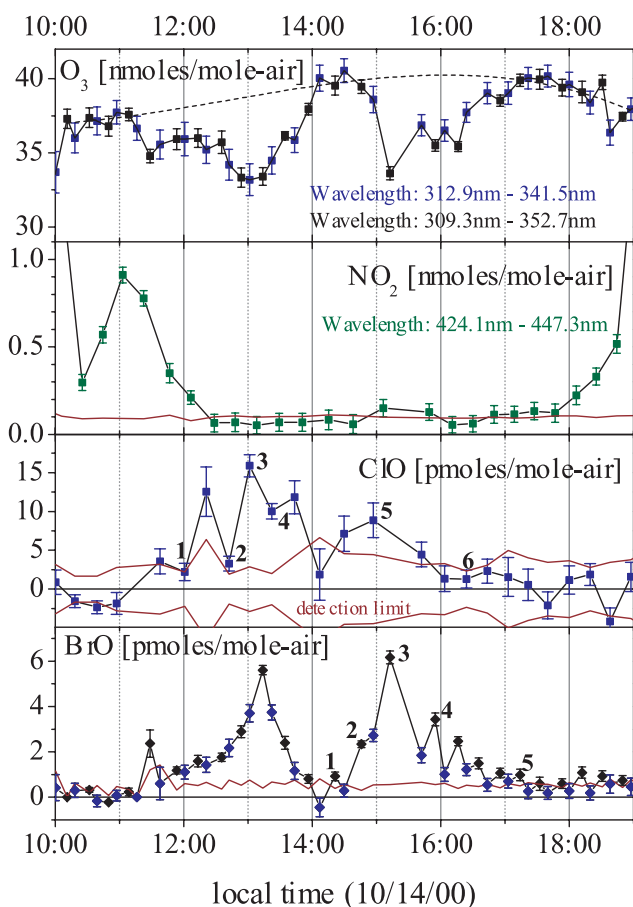
Figure 3. Trace gas mixing ratios on October 14. The different symbols in the ozone and BrO traces indicate the different grating position used in the measurements. The solid brown lines show the detection limit determined for each individual spectrum. The dashed line in the upper graph shows the low frequency behavior of the ozone mixing ratio. All errors are 1σ.

Basin is the Magnesium Corporation of America plant (MagCorp, see Figure 1) on the western side of the basin, which emitted 20000 tons Cl_2 in 1999 (www.epa.gov/tri/). Trajectories (Figure 1) show that the air bearing elevated halogen oxides on the afternoon of October 14 did not pass close to the MagCorp plant in the 18 hours prior to arrival at the DOAS site. The Cl_2 emissions before sunset on October 13 were photolyzed and mostly converted into HCl, which would have been removed by wet deposition during the rain episodes on October 13 and 14. Additional evidence comes from our NO_2 and BrO measurements. MagCorp emits 780 tons of NO_x per year. No Br_2 emissions are reported. Therefore, we estimated an upper limit emission of 14 tons per year, according to the Cl_2 emissions and the Br^-/Cl^- ratio in the lake salt. We estimated the dilution for two cases: A direct plume traveling 2 m/s and reaching a cross section of 1×25 km at our site, and an accumulation of the emissions over 12 hours in a volume of 50 km $\times$ 50 km $\times$ 1 km. In both cases the dilution factors are very similar and we estimate a NO_x and Br_2 mixing ratio of 500 pmol/mol-air and 1.5 pmol/mol-air respectively. Although we have omitted any loss mechanisms for bromine, this upper limit estimate is lower than our observations of up to 6 pmol/mol-air BrO. Therefore, a source different than MagCorp must be responsible for the observed BrO levels. Taking into account the loss of NO_x due to the OH + NO_2 reaction and the photostationary state between NO, NO_2 and $ClONO_2$, we estimate NO_2 mixing ratios of ~200 pmol/mol-air NO_2 for ~5 pmol/mol-air ClO as observed at at 12:40 and 14:20. This

estimate is above the values of <100 pmol/mol-air NO_2 from our measurements.

[11] We conclude that the reactive halogens we observed were most likely released from the natural salt in the Great Salt Lake area. A release of halogens from the lake water, which has a pH of 8.0 [*Lynn et al.*, 1980], seems unlikely, since a pH below 7 [*Fickert et al.*, 1999] and a much higher salinity is needed. Salt aerosol formed by breaking waves are also an unlikely source since there is little chance of acidification in the relatively unpolluted air at that time. Crystallized surface salt deposits on the northern end of Tooele valley and the shore north of our site, on the other hand, provide a large surface area that can be acidified from dry and wet deposition of pollutants from nearby Salt Lake City, and upon which heterogeneous reactions release halogens by mechanisms similar to those observed in the Arctic. It is also possible that salt crystals were lifted into the air by winds with speeds of $5-7$ m s^{-1} during the morning of October 14.

[12] The observed anti-correlation between ozone and BrO is most likely caused by a catalytic destruction of ozone. Dry deposition and non-halogen chemical destruction in unpolluted air has time constants that are typically larger than those found in the short term ozone variations. We calculated a local catalytic destruction rate of 0.3 nmoles/mole-air ozone per hour at the observed levels of 6 pmoles/mole-air BrO. To explain the observed short-term ozone variation, reaction times of several hours or higher reactive halogen concentrations must have persisted in the air mass prior to our observations.

[13] Calculations reveal that a release of the halogens close to our site is unlikely. We therefore favor the northern end of Tooele valley as the halogen source area. On the other hand, it is unclear how high mixing ratios of reactive chlorine can be maintained over $6-7$ hours. We propose two possible explanations: (1) At mixing ratios of 2 nmoles/mole-air HCl, recycling through the OH + HCl reaction can maintain the observed ClO reaction. (2) Halogen recycling on the aerosol, similar to the one proposed in the Arctic, occurs via the uptake of HCl, HBr, HOCl, and HOBr and the release of Br_2 and BrCl. The source of the aerosol is salt suspension by the strong winds in the northern end of Tooele valley.

4. Discussion

[14] The first direct observation of chlorine oxide in the troposphere reported here has important implications for radical chemistry. We investigated the effects of the halogens with a steady state photochemical box model of the clean troposphere including the known gas-phase halogen reactions [*Stutz et al.*, 1999]. The most important change to this system when enough bromine and chlorine are added to reproduce our ClO and BrO observation is the presence of 10^5 chlorine atoms per cm^3. This level of Cl atoms doubles the hydrocarbon oxidation capacity of the atmosphere. As a secondary effect, the OH concentration is increased by 50% through the radical propagation steps following the Cl + CH_4 reaction. Reactive halogens also convert a large fraction of nitrogen oxides into halogen nitrates. For example, 90% of the NO_x can be held in the form of chlorine nitrate ($ClONO_2$) in our case. The trajectory analysis shows that the observed halogens will be transported into Salt Lake City, where they may affect urban air chemistry. Reactive bromine leads to a destruction of ozone. Reactive halogens can also impact the biogeochemical cycle of mercury by transforming Hg^0 a more biologically available form of mercury [*Lu et al.*, 2001]. For populated areas like the Salt Lake City region, the presence of halogens can therefore also enhance the deposition of locally emitted and imported background mercury.

[15] It is surprising that an activation of chlorine and bromine has thus far not been observed in marine environments, while salt lakes such as the Great Salt lake and the Dead Sea [*Hebestreit et al.*, 1999] release a large amount of reactive halogens into the atmosphere. We attribute the presence of reactive halogens to the

presence of concentrated high molality salt solutions or crystalline salt around salt lakes that can host heterogeneous reactions that cannot otherwise occur in more dilute lake or ocean saltwater. The Great Salt Lake is similar to a large number of saline areas around the world. The salinity of the surface water of the southern part of the Great Salt Lake is approximately 3 times higher than that of standard mean ocean water, (60 g Cl^-/liter). In contrast, the salinity of the Dead Sea is about 10 times higher. An important difference between the Great Salt Lake, the ocean, and the Dead Sea is the Br^-/Cl^- ratio, which is 0.07%, 0.34% and 2.5%, respectively [*Sturm*, 1980]. An enrichment of bromide is therefore not a prerequisite for BrO generation. In other words, even at low Br/Cl ratios there is still adequate Br in the surface land salt reservoir to maintain atmospheric levels of BrO through air-surface heterogeneous reactions.

[16] Our observations open the question of whether every salt lake and/or saline soil releases reactive halogens, and what implications this possible source would have. On a global scale, saline soils cover $\sim 3.6 \times 10^6$ km^2 [*Abrol et al.*, 1998] and could contribute significantly to tropospheric halogen levels. This source may influence tropospheric ozone, an important greenhouse gas. On a regional scale, it would change the atmospheric chemistry of tropospheric oxidants, and mercury. In the case of mercury this could then influence ecosystems close to the halogen source areas. Finally, it should be noted that due to expanding salinization of soils in arid and semi-arid regions [*Abrol et al.*, 1998] this halogen source may become more important in the future.

References

Abrol, I. P., J. S. P. Yadav, and F. I. Massoud, *Salt-Affected Soils and their Management*, Food and Agriculture Organization of the United Nations, Rome Italy, 1998.

Burrows, J. P., et al., Atmospheric remote-sensing reference data from GOME: Part I. Temperature-dependent absorption cross-sections of NO_2 in the 231–794 nm range, *J. Quant. Spect. Radiat.*, 60, 1025–1031, 1998.

Burrows, J. P., A. Richter, A. Dehn, B. Deters, and S. Himmelmann, Atmospheric remote-sensing reference data from GOME–2. Temperature-dependent absorption cross sections of O_3 in the 231–794 nm range, *J. Quant. Spect. Radiat.*, 61, 509–517, 1999.

Doran, J. C., J. D. Fast, and J. Horel, The VTMX 2000 campaign, *Bull. Am. Met. Soc.*, in press, 2002.

Fickert, S., J. W. Adams, and J. N. Crowley, Activation of Br_2 and BrCl via uptake of HOBr onto aqueous salt solutions, *J. Geophys. Res.*, 104, 23,719–23,727, 1999.

Foster, K. L., et al., The role of Br_2 and BrCl in surface ozone destruction at polar sunrise, *Science*, 291, 471–474, 2001.

Hebestreit, K., et al., DOAS measurements of tropospheric bromine oxide in mid-latitudes, *Science*, 283, 55–57, 1999.

Keene, W. C., et al., Composite global emissions of reactive chlorine from anthropogenic and natural sources: Reactive chlorine emissions inventory, *J. Geophys. Res.*, 104, 8429–8440, 1999.

Knipping, E. M., et al., Experiments and simulations of ion-enhanced interfacial chemistry on aqueous NaCl aerosols, *Science*, 288, 301–306, 2000.

Lu, J. Y., et al., Magnification of atmospheric mercury deposition to polar regions in springtime: The link to tropospheric ozone depletion chemistry, *Geophys. Res. Lett.*, 28, 3219–3222, 2001.

Lynn, P. L., L. A. Hutchinson, and M. K. Muir, Heavy metals in the Great Salt Lake, Utah, in *Great Salt Lake: A scientific, historical and economic overview*, edited by J. W. Gwynn, pp. 195–200, Utah Department of Natural Resources, Bulletin 116, Salt Lake City, 1980.

Orphal, J., et al., Laboratory spectroscopy in support of UV-visible remote-sensing of the atmosphere, in *Recent Research Developments in Physical Chemistry*, edited by S. G. Pandalai, in press.

Platt, U., Reactive halogen species in the mid-latitude troposphere—Recent discoveries, *Wat. Air. Soil. Poll.*, 123(1–4), 229–244, 2000.

Rudolph, J., B. Ramacher, C. PlassDulmer, K. P. Muller, and R. Koppmann, The indirect determination of chlorine atom concentration in the troposphere from changes in the patterns of non-methane hydrocarbons, *Tellus*, B49, 592–601, 1997.

Sander, S. P., and R. R. Friedl, Kinetics and product studies of the reaction ClO + BrO using flash photolysis ultraviolet absorption, *J. Phys. Chem.*, 93, 4764–4771, 1989.

Spicer, C. W., et al., Unexpectedly high concentrations of molecular chlorine in coastal air, *Nature*, 394, 353–356, 1998.

Sturm, P. A., The Great Salt Lake brine system, in *Great Salt Lake: A scientific, historical and economic overview*, edited by J. W. Gwynn, pp. 147–162, Utah Department of Natural Resources, Bulletin 116, Salt Lake City, 1980.

Stutz, J., and U. Platt, Numerical analysis and estimation of the statistical error of differential optical absorption spectroscopy measurements with least-squares methods., *Appl. Opt.*, 35, 6041–6053, 1996.

Stutz, J., and U. Platt, Improving long-path differential optical absorption spectroscopy with a quartz-fiber mode mixer, *Appl. Opt.*, 36, 1105–1115, 1997.

Stutz, J., K. Hebestreit, B. Alicke, and U. Platt, Chemistry of halogen oxides in the troposphere: Comparison of model calculations with recent field data, *J. Atmos. Chem.*, 34, 65–85, 1999.

Tuckermann, M., et al., DOAS-observation of halogen radical-catalysed Arctic boundary layer ozone destruction during the ARCTOC-campaigns 1995 and 1996 in Ny-Ålesund, Spitsbergen, *Tellus*, 49B, 533–555, 1997.

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