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Supplement of

Observations of ozone-poor air in the tropical tropopause layer

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1 Principal WAS chemicals split by aircraft

The following three plots show panels of the six chemicals shown in figure 21 of the accompanying article, split into the three individual aircraft. Figure S1 shows the same panel as figure 21 for just the ATTREX data only, figure S2 shows the panel for just the CONTRAST data only, and figure S3 shows the panel for the CAST aircraft data only. In each figure, the average profile for the high-ozone case (>20 ppbv) is shown in red and for the low-ozone case (<20 ppbv) is shown in blue; the solid lines show the averages for just that aircraft, while the dashed lines show the averages for all the aircraft combined. The amount of CAST aircraft data is small in comparison to CONTRAST and ATTREX and so the effect on the overall averages in figure 21 is negligible. There is some overlap between ATTREX and CONTRAST: the highest altitude that the CONTRAST WAS samples were taken at was ∼150 hPa, and the lowest altitude that the ATTREX WAS samples were taken at was ∼180 hPa.

The ozone measurements taken on board the Gulfstream V aircraft in the CONTRAST campaign were of higher confidence than those taken on board the Global Hawk aircraft in the ATTREX campaign (see section 4.2 of the accompanying article for details on the uncertainties associated with the UCATS ozone measurements from the Global Hawk). However, the differences between the low-ozone cases and the high-ozone cases exist in both the CONTRAST and ATTREX data.

2 More WAS sample chemicals

The following plots are of chemical species measured by the whole air samplers (WAS) that were not plotted in the accompanying article. Firstly, dichloromethane (CH_2Cl_2) and trichloromethane ($CHCl_3$) were measured by all three aircraft, but unlike the other six chemical species measured by all three aircraft, they both have a strong anthropogenic industrial source with relatively long lifetimes of around five months and six months respectively [Montzka et al., 2010; Carpenter et al., 2014; Khalil and Rasmussen, 1999]. Figure S4 shows the vertical profile of dichloromethane coloured by ozone concentration, with average profiles for WAS samples with ozone concentrations greater than 20 ppbv as a red line, and for WAS samples with ozone concentrations less than 20 ppbv as a blue line, in the same way as the panel plot in figure 21 of the accompanying article. Likewise the profile for trichloromethane is found in figure S5.

The remaining plots show chemical species that were not measured by the FAAM BAe 146 of CAST, but were measured by the CONTRAST and ATTREX aircraft, and categorized by their characteristics. Atmospheric lifetime information comes from González Abad et al. [2011]; Rosado-Reyes and Francisco [2007]; Rudolph [2003]; Pike and Young [2009]; Carpenter et al. [2014]; Prinn et al. [1987]; Wallington et al. [1996]; Olaguer [2002]; Rasmussen and Khalil [1983]; Atkinson et al. [1985]; and Brühl et al. [2012].

2.1 Aliphatic hydrocarbons

The aliphatic hydrocarbons measured by the CONTRAST and ATTREX WAS were as follows:

- ethane (CH_3CH_3):
  lifetime = ∼2 months (figure S6),
- ethyne ($CH \equiv CH$):
  lifetime = ∼2–4 weeks (figure S7),
- propane ($CH_3CH_2CH_2CH_3$):
  lifetime = ∼2 weeks (figure S8),
- methylpropane ($CH_3CH(CH_3)_2$):
  lifetime = ∼1 week (figure S9),
- butane ($CH_3CH_2CH_2CH_3$):
  lifetime = ∼5 days (figure S10),
- 2-methylbutane ($CH_3CH_2CH(CH_3)_2$):
  lifetime = 4 days (figure S11),
- pentane ($CH_3CH_2CH_2CH_2CH_3$):
  lifetime = ∼3 days (figure S12)
- isoprene ($CH_2=C(CH_3)CH=CH_2$):
  lifetime = ∼minutes–hours (figure S13)

All the hydrocarbons, with the exception of isoprene, follow a similar pattern with enhanced levels of each in the boundary layer when ozone concentrations were high. The difference diminishes with altitude, and at high altitudes, the difference between the low-ozone régime and the high-ozone régime becomes negligible.

Isoprene, however is a naturally occurring chemical emitted in large quantities by vegetation rather than as a result of the petroleum industry, which accounts for the difference between the other hydrocarbons and isoprene.

2.2 Haloaliphatic compounds

The haloaliphatic compounds, including chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs) and halons, measured by the CONTRAST and ATTREX WAS were as follows:

2.2.1 CFCs

- CFC-12 (CCl_2F_2):
  [dichlorodifluoromethane]
  lifetime = ∼100 years (figure S14)
- CFC-11 (CCl_3F):
  [trichlorofluoromethane]
  lifetime = ∼50 years (figure S15)
- CFC-112 (CCl_2FCCl_2F):
  [tetrachloro-1,2-difluoroethane]
  lifetime = ∼60 years (figure S16)
- CFC-112a (CCl_3CClF_2):
  [tetrachloro-1,1-difluoroethane]
  lifetime = ∼50 years (figure S17)

- CFC-113 (CCl_2FCClF_2)
  [1,1,2-trichloro-1,2,2-trifluoroethane]
  lifetime = $\sim$90 years (figure S18)

- CFC-114 ($CClF_2CClF_2$)
  [1,2-dichlorotetrafluoroethane]
  lifetime = $\sim$190 years (figure S19)

2.2.2 HCFCs

- HCFC-22 ($CHClF_2$)
  [chlorodifluoromethane]
  lifetime = $\sim$12 years (figure S20)

- HCFC-141b (CH_3CCl_2F)
  [1,1-dichloro-1-fluoroethane]
  lifetime = $\sim$10 years (figure S21)

- HCFC-142b (CH_3CClF_2)
  [1-chloro-1,1-difluoroethane]
  lifetime = $\sim$18 years (figure S22)

2.2.3 HFCs

- HFC-134a (CH_2FCF_3)
  [1,1,1,2-tetrafluoroethane]
  lifetime = $\sim$14 years (figure S23)

- HFC-365mfc ($CH_3CF_2CH_2CF_3$)
  [1,1,1,3,3-pentafluorobutane]
  lifetime = $\sim$9 years (figure S24)

2.2.4 Halons

- Halon-1211 ($CBrClF_2$)
  [bromochlorodifluoromethane]
  lifetime = $\sim$16 years (figure S25),

- Halon-2402 ($CBrF_2CBrF_2$)
  [1,2-dibromotetrafluoroethane]
  lifetime = $\sim$30 years (figure S26)

In all of the cases of CFCs, HCFCs, HFCs and halons, very little variation can be seen, and there is no difference between the low-ozone régime and the high-ozone régime. The background values of the majority of them are non-zero, with little variation from the background values observed. All the CFCs, HCFCs, HFCs and halons are industrial chemicals with often extremely long atmospheric lifetimes. It is likely that these chemicals have reached homogeneity in the atmosphere such that there is little difference between the clean low-ozone régime and the polluted high-ozone régime.

2.2.5 Others

- chloromethane (CH_3Cl)
  lifetime = $\sim$12 months (figure S27),

- bromomethane (CH_3Br)
  lifetime = $\sim$9 months (figure S28),

- 1,1,1-trichloroethane (CH_3CCl_3)
  lifetime = $\sim$6 years (figure S29),

- tetrachloromethane (CCl_4)
  lifetime = $\sim$26 years (figure S30),

- 1,2-dichloroethane (CH_2ClCH_2Cl)
  lifetime = $\sim$3 months (figure S31),

- trichloroethene ($CHCl{=}CCl_2$)
  lifetime = $\sim$5 days (figure S32),

- tetrachloroethene ($CCl_2{=}CCl_2$)
  lifetime = $\sim$5 months (figure S33)

All of these chemicals are produced industrially. Chloromethane, bromomethane and 1,2-dichloroethane have the expected profiles for anthropogenic chemicals—the polluted, high-ozone régime is enhanced compared to the clean, low-ozone régime. However, 1,1,1-trichloroethane and tetrachloromethane are the opposite way round; their lifetimes are particularly long, similar to the lifetimes of the CFC, HFC, HCFC and halon groups. Both trichloromethane and tetrachloroethene show large enhancements in the high-ozone régime in the boundary layer, but in the mid-troposphere there is an unexpected enhancement of each in the low-ozone régime.

2.3 Aromatic compounds

- benzene (C_6H_6)
  lifetime = $\sim$months (figure S34)

- chlorobenzene (C_6H_5Cl)
  lifetime = $\sim$2 weeks (figure S35)

Benzene and chlorobenzene are industrial solvents, and both show enhancements in the high ozone régime compared to the low ozone régime, which is what is expected. However, in the mid-troposphere, chlorobenzene shows the opposite.

2.4 Sulfides

- carbonyl sulfide (OCS)
  lifetime = $\sim$35 years (figure S36)

Like dimethyl sulfide, shown in figure 15 of the accompanying article, carbonyl sulfide, shows a slight enhancement in the low-ozone, clean régime.

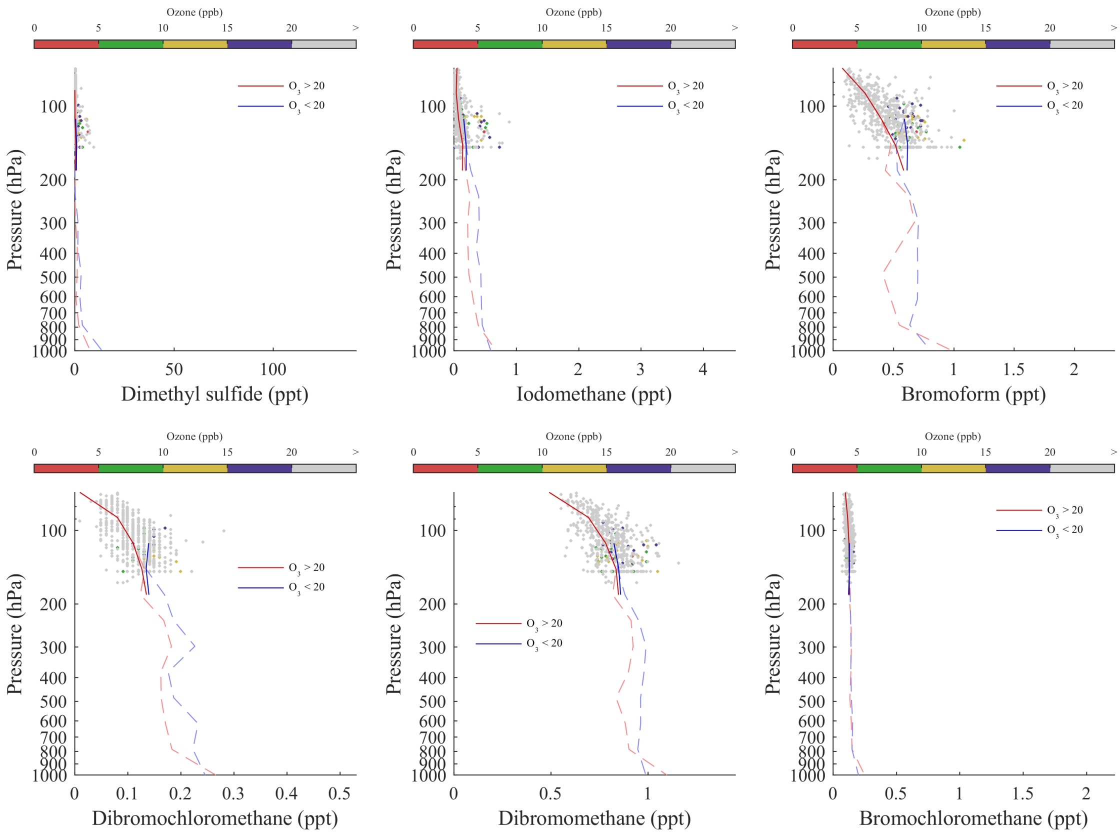

Figure S1: Panel of the six principal WAS chemicals using the ATTREX WAS sample data only.

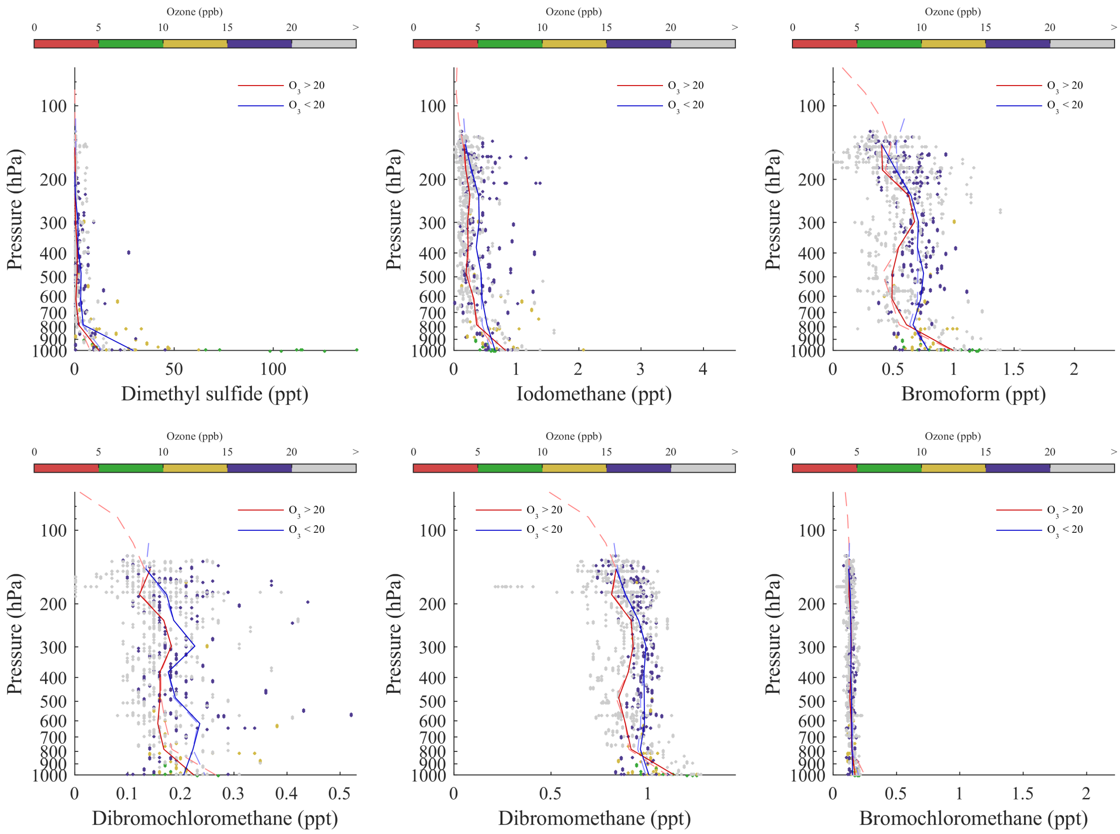

Figure S2: Panel of the six principal WAS chemicals using the CONTRAST WAS sample data only.

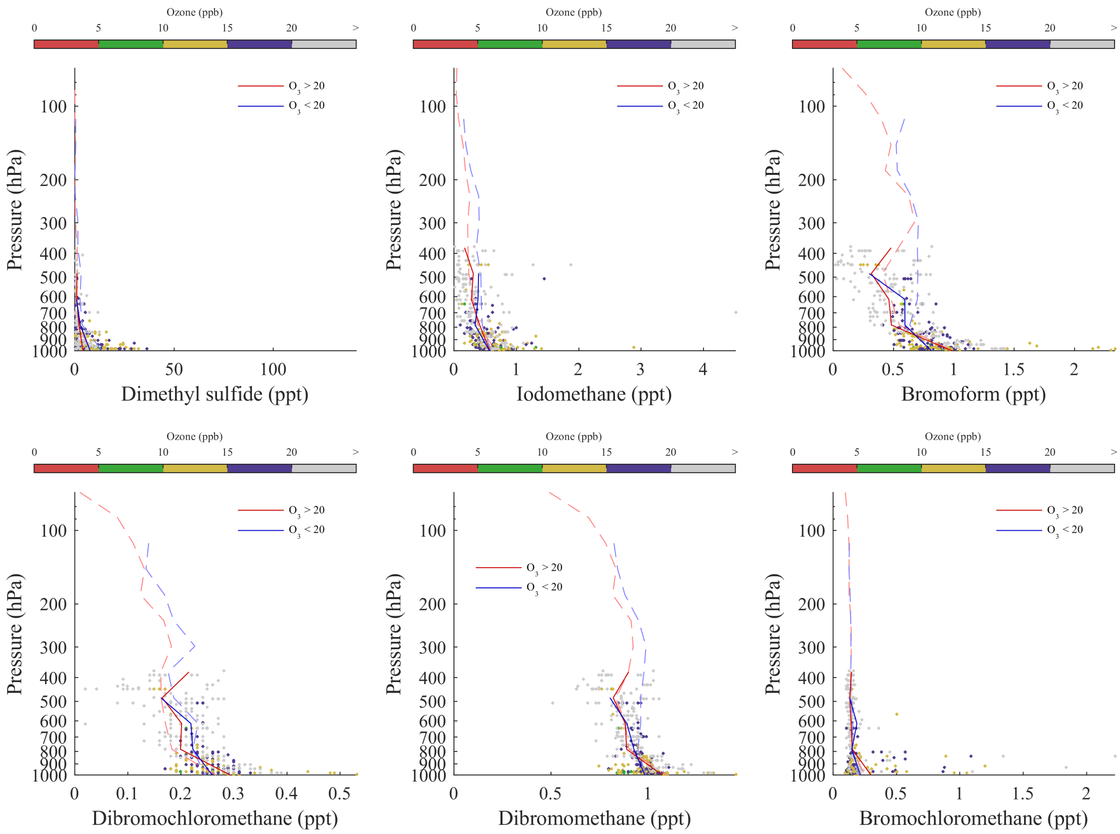

Figure S3: Panel of the six principal WAS chemicals using the CAST aircraft WAS sample data only.

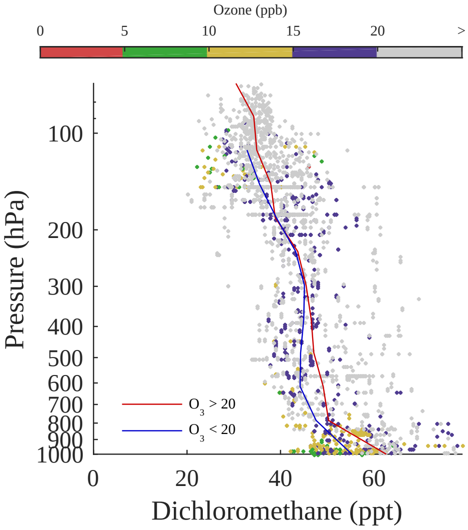

Figure S4: Dichloromethane

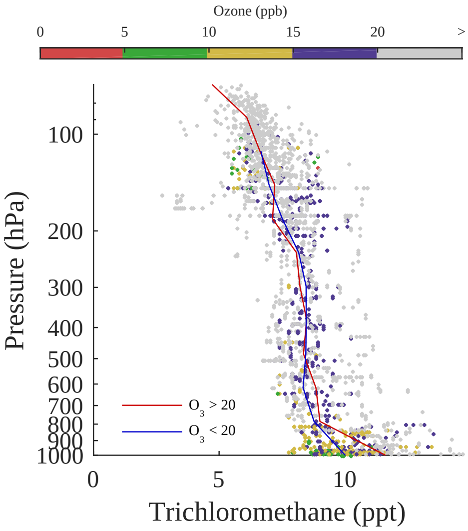

Figure S5: Trichloromethane

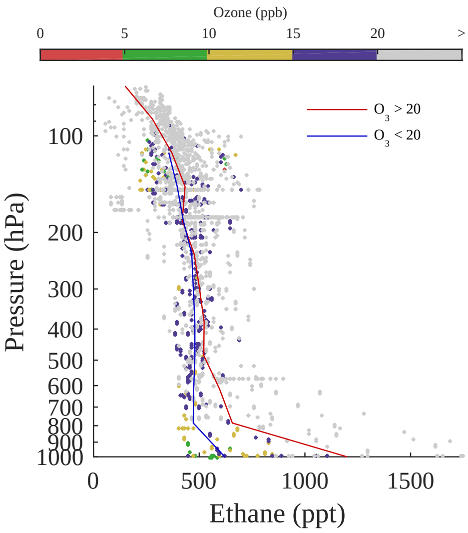

Figure S6: Ethane

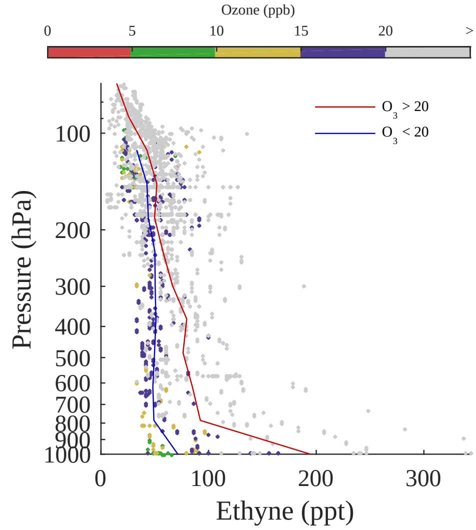

Figure S7: Ethyne

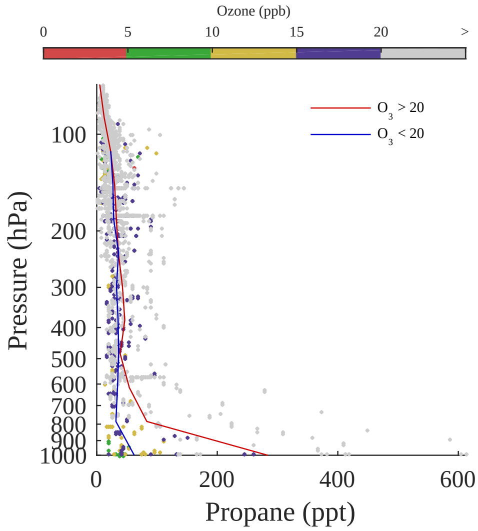

Figure S8: Propane

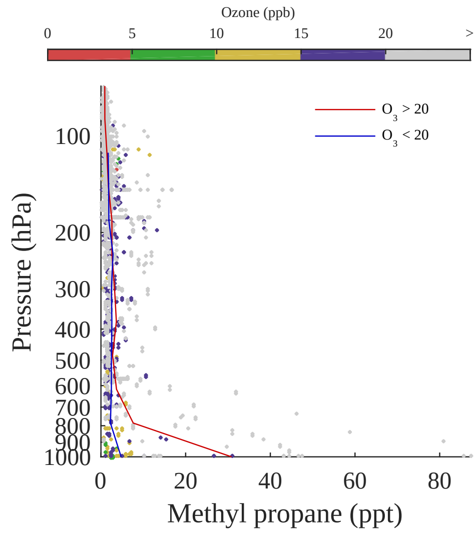

Figure S9: Methylpropane

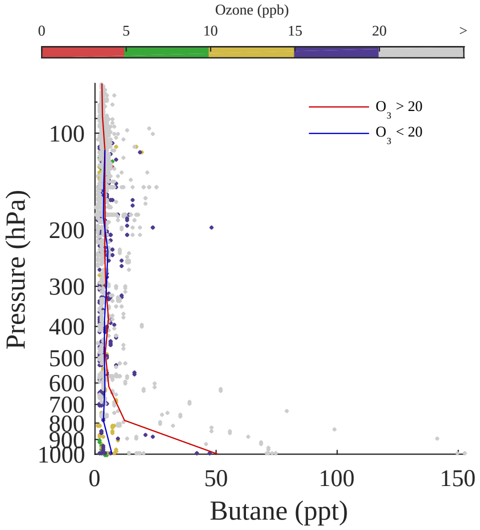

Figure S10: Butane

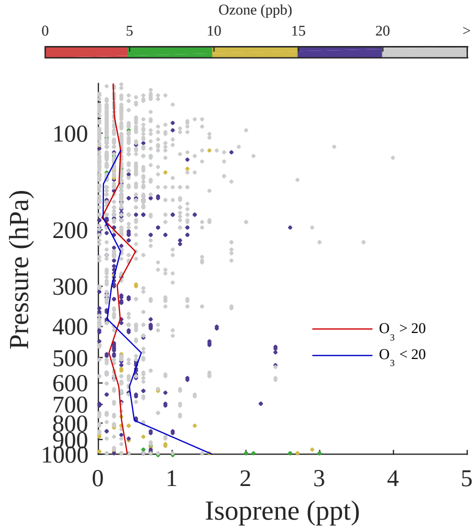

Figure S13: Isoprene

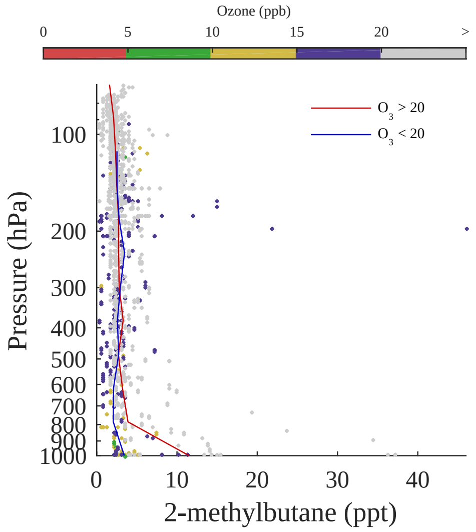

Figure S11: 2-Methylbutane

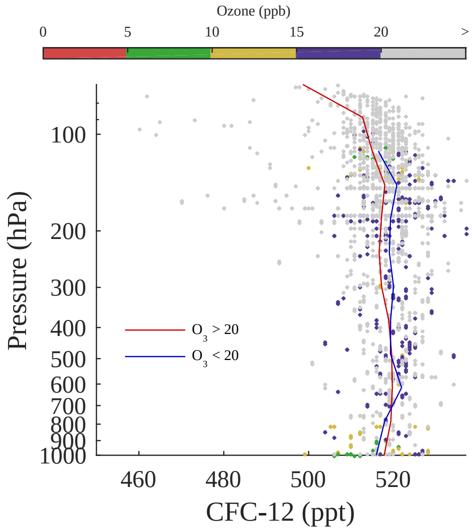

Figure S14: CFC-12

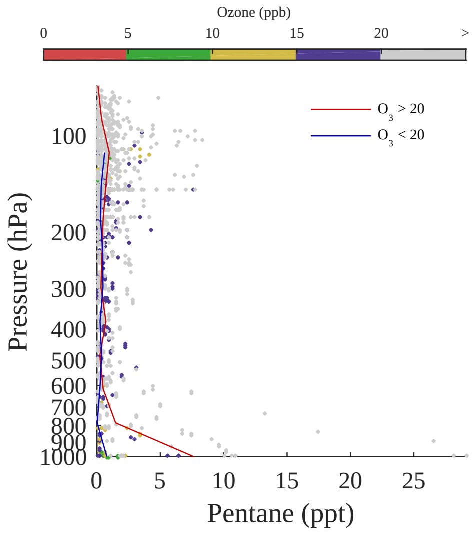

Figure S12: Pentane

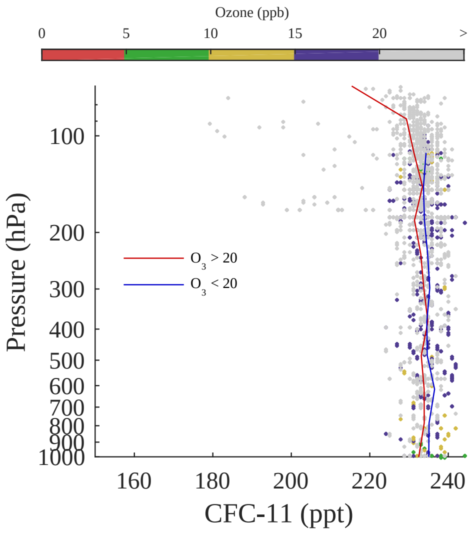

Figure S15: CFC-11

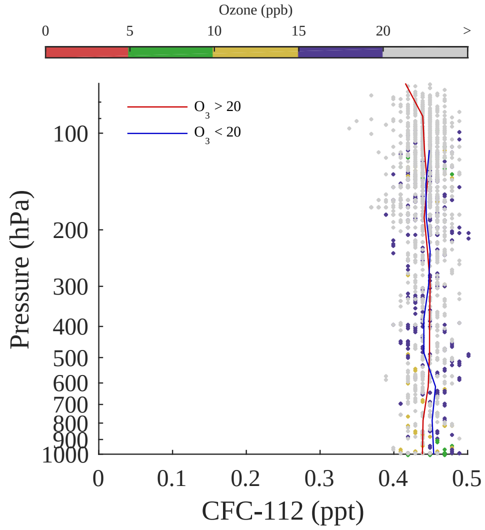

Figure S16: CFC-112

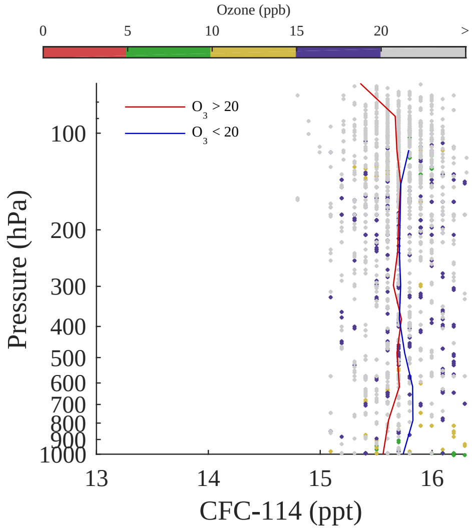

Figure S19: CFC-114

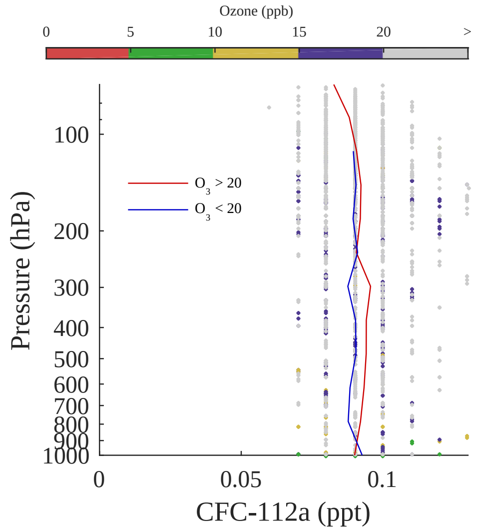

Figure S17: CFC-112a

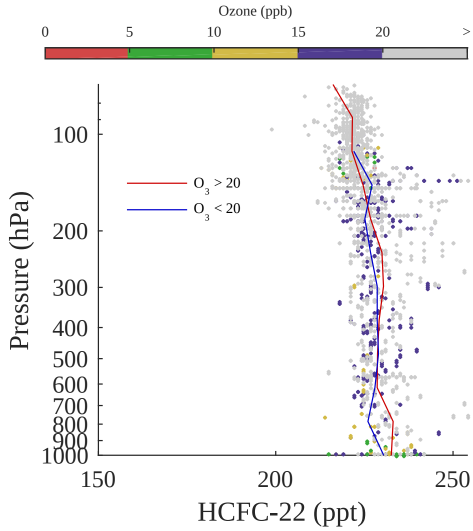

Figure S20: HCFC-22

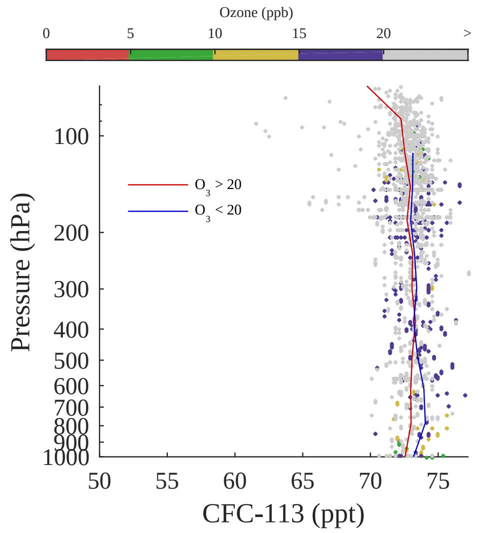

Figure S18: CFC-113

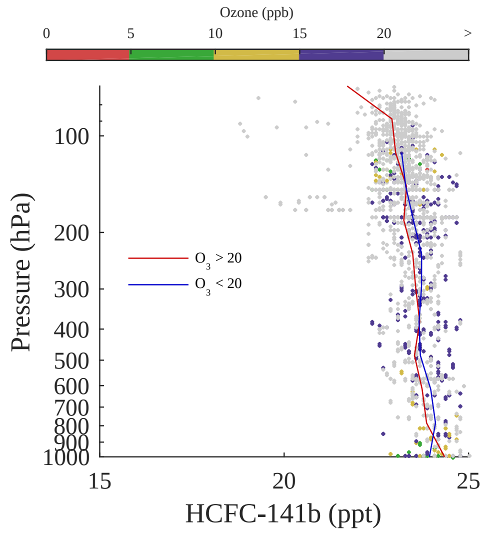

Figure S21: HCFC-141b

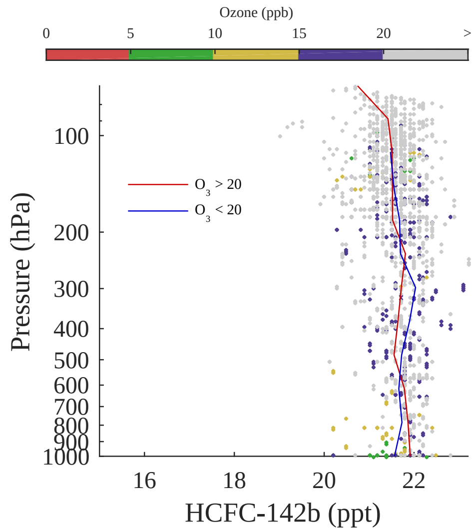

Figure S22: HCFC-142b

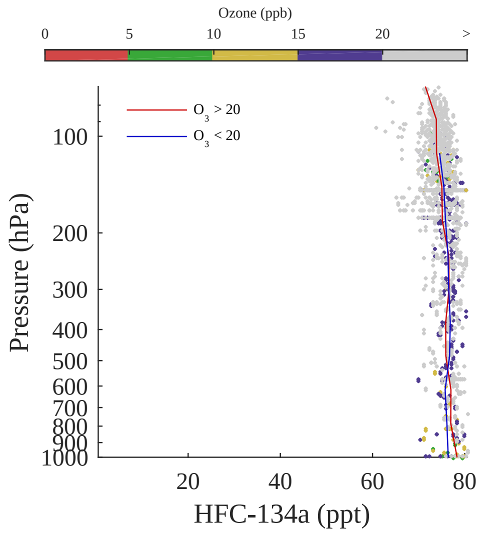

Figure S23: HFC-134a

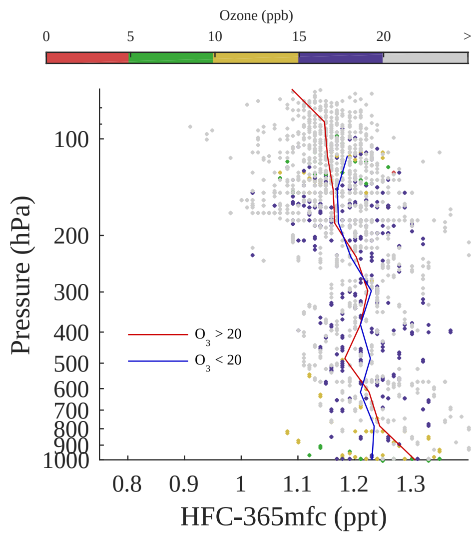

Figure S24: HFC-365mfc

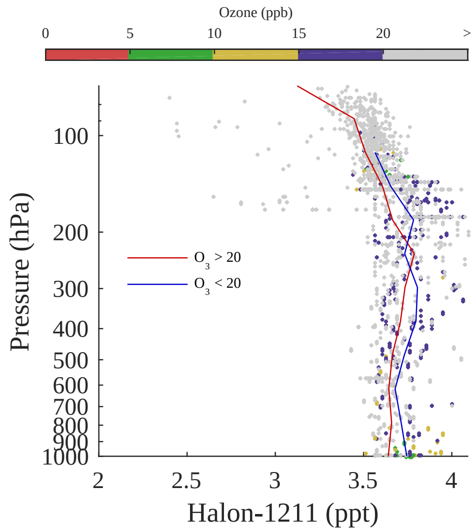

Figure S25: Halon 1211

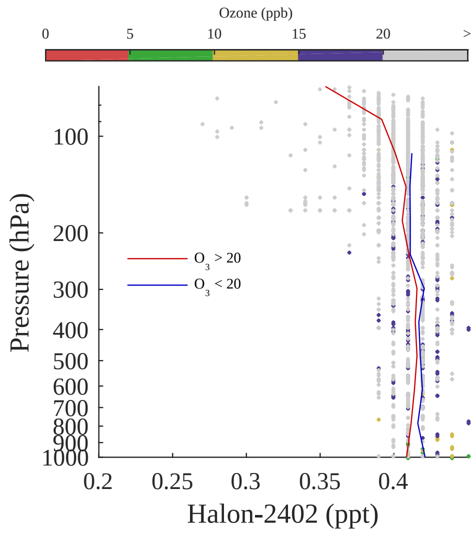

Figure S26: Halon 2402

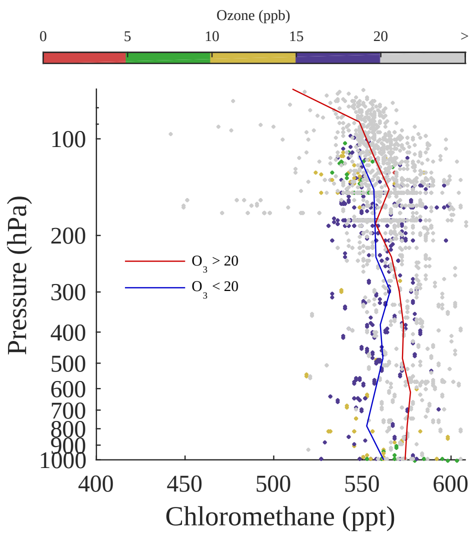

Figure S27: Chloromethane

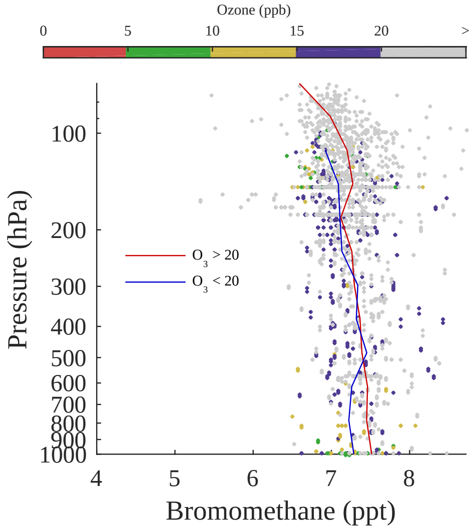

Figure S28: Bromomethane

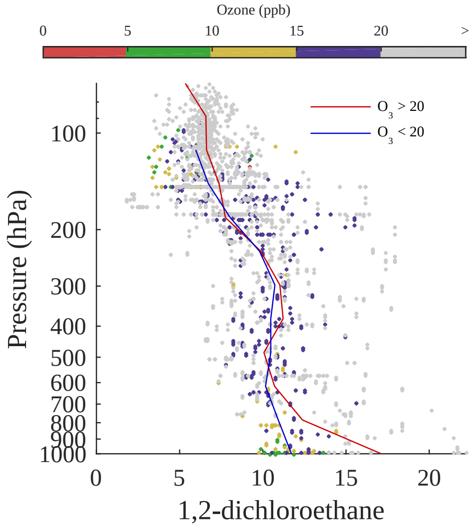

Figure S31: 1,2-dichloroethane

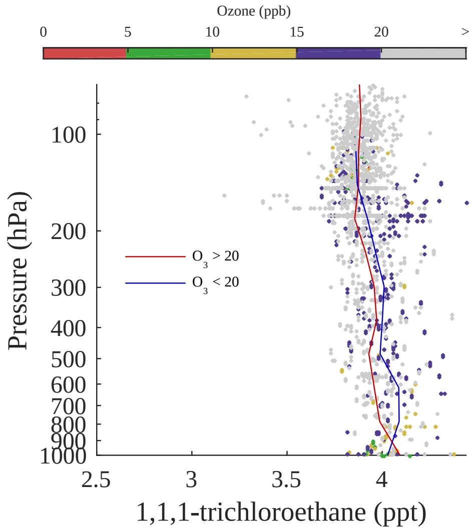

Figure S29: 1,1,1-trichloroethane

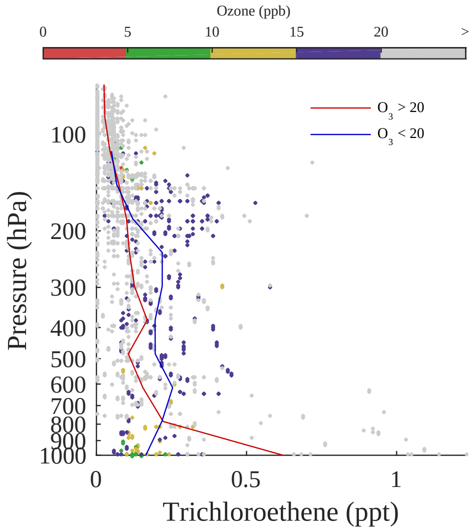

Figure S32: Trichloroethene

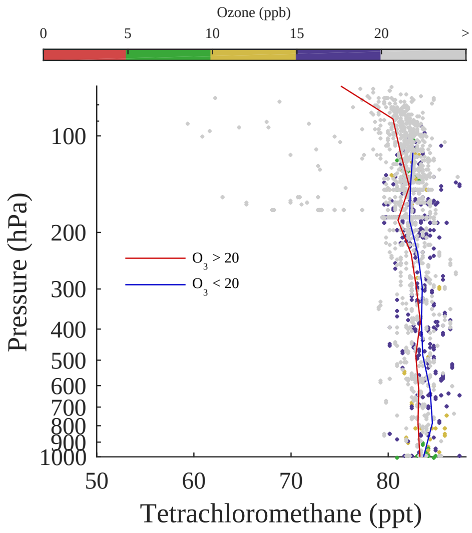

Figure S30: Tetrachloromethane

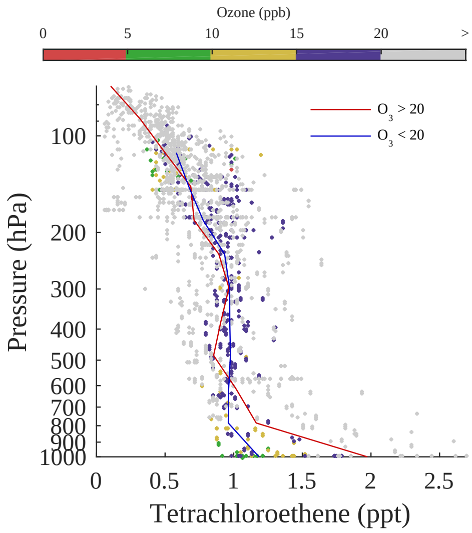

Figure S33: Tetrachloroethene

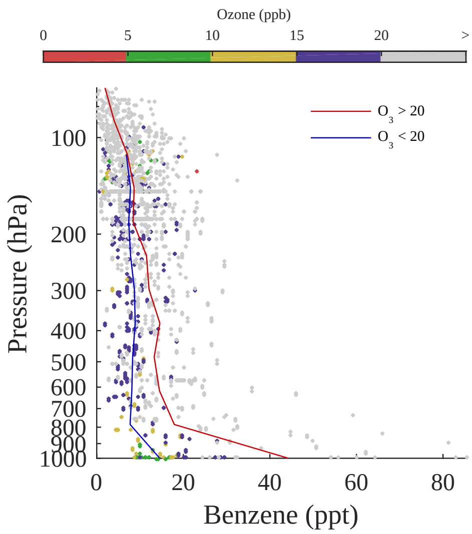

Figure S34: Benzene

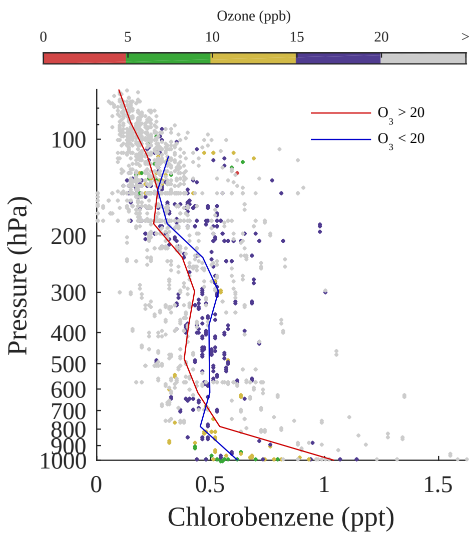

Figure S35: Chlorobenzene

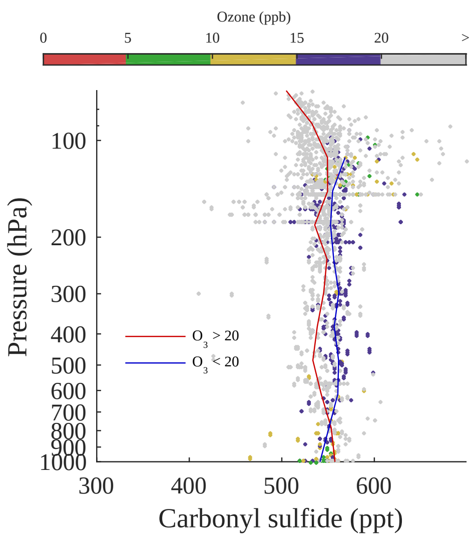

Figure S36: Carbonyl sulfide

References

Atkinson, R., Aschmann, S. M., Winer, A. M., and Pitts, J. N. (1985). Atmospheric Gas Phase Loss Processes for Chlorobenzene, Benzotrifluoride, and 4-Chlorobenzotrifluoride, and Generalization of Predictive Techniques for Atmospheric Lifetimes of Aromatic Compounds. *Archives of Environmental Contamination and Toxicology*, 14(4):417–425.

Brühl, C., Lelieveld, J., Crutzen, P. J., and Tost, H. (2012). The role of carbonyl sulphide as a source of stratospheric sulphate aerosol and its impact on climate. *Atmospheric Chemistry and Physics*, 12(3):1239–1253.

Carpenter, L. J., Reimann, S., Burkholder, J. B., Clerbaux, C., Hall, B. D., Hossaini, R., Laube, J. C., and Yvon-Lewis, S. A. (2014). Update on Ozone-Depleting Substances (ODSs) and Other Gases of Interest to the Montreal Protocol. In *Scientific Assessment of Ozone Depletion: 2014*. World Meteorological Association/United Nations Environment Programme.

González Abad, G., Allen, N. D. C., Bernath, P. F., Boone, C. D., McLeod, S. D., Manney, G. L., Toon, G. C., Carouge, C., Wang, Y., Wu, S., Barkley, M. P., Palmer, P. I., Xiao, Y., and M., F. T. (2011). Ethane, ethyne and carbon monoxide concentrations in the upper troposphere and lower stratosphere from ACE and GEOS-Chem: a comparison study. *Atmospheric Chemistry and Physics*, 11(18):9927–9941.

Khalil, M. A. K. and Rasmussen, R. A. (1999). Atmospheric chloroform. *Atmospheric Environment*, 33(7):1151–1158.

Montzka, S. A., Reimann, S., Engel, A., Kr ́uger, K., O'Doherty, S., and Sturges, W. T. (2010). Ozone-Depleting Substances (ODSs) and Related Chemicals. In *Scientific Assessment of Ozone Depletion: 2010*, chapter 1, pages 1.1–1.108. World Meteorological Association/United Nations Environment Programme.

Olaguer, E. P. (2002). The Distribution of the Chlorinated Solvents Dichloromethane, Perchloroethylene, and Trichloroethylene in the Global Atmosphere. *Environmental science and pollution research international*, 9(3):175–182.

Pike, R. C. and Young, P. J. (2009). How plants can influence tropospheric chemistry: the role of isoprene emissions from the biosphere. *Weather*, 64(12):332–336.

Prinn, R., Cunnold, D., Rasmussen, R., Simmonds, P., Alyea, F., Crawford, A., Fraser, P., and Rosen, R. (1987). Atmospheric Trends in Methylchloroform and the Global Average for the Hydroxyl Radical. *Science*, 238(4829):945–950.

Rasmussen, R. A. and Khalil, M. A. K. (1983). Atmospheric benzene and toluene. *Geophysical Research Letters*, 10(11):1096–1099.

Rosado-Reyes, C. M. and Francisco, J. S. (2007). Atmospheric oxidation pathways of propane and its by-products: Acetone, acetaldehyde, and propionaldehyde. *Journal of Geophysical Research—Atmospheres*, 112(14).

Rudolph, J. (2003). Tropospheric Chemistry and Composition | Aliphatic Hydrocarbons. In *Encyclopedia of Atmospheric Sciences*, pages 2355–2365. Elsevier Science.

Wallington, T. J., Bilde, M., Møgelberg, T. E., Sehested, J., and Nielsen, O. J. (1996). Atmospheric Chemistry of 1,2–Dichloroethane: UV Spectra of $CH_2ClCHCl$ and $CH_2ClCHCl$ and $CH_2ClCHClO_2$ Radicals, Kinetics of the Reactions of $CH_2ClCHCl$ Radicals with O_2 and $CH_2ClCHClO_2$ Radicals with NO and NO_2, and Fate of the Alkoxy Radical $CH_2ClCHClO$. *The Journal of Physical Chemistry A*, 100(14):5751–5760.