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 ($CHCl_3$) was 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 S1 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 15 of the accompanying article. Likewise the profile for trichloromethane is found in figure S2.

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].

Aliphatic hydrocarbons

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

- ethane (CH_3CH_3):
  lifetime = ∼2 months (figure S3),
- ethyne ($CH \equiv CH$):
  lifetime = ∼2–4 weeks (figure S4),
- propane ($CH_3CH_2CH_2CH_3$):
  lifetime = ∼2 weeks (figure S5),
- methylpropane ($CH_3CH(CH_3)_2$):
  lifetime = ∼1 week (figure S6),
- butane ($CH_3CH_2CH_2CH_3$):
  lifetime = ∼5 days (figure S7),
- 2-methylbutane ($CH_3CH_2CH(CH_3)_2$):
  lifetime = 4 days (figure S8),
- pentane ($CH_3CH_2CH_2CH_2CH_3$):
  lifetime = ∼3 days (figure S9)
- isoprene ($CH_2 = C(CH_3)CH = CH_2$):
  lifetime = ∼minutes–hours (figure S10)

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.

Haloaliphatic compounds

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

CFCs

- CFC-12 (CCl_2F_2):
  [dichlorodifluoromethane]
  lifetime = ∼100 years (figure S11)
- CFC-11 (CCl_3F):
  [trichlorofluoromethane]
  lifetime = ∼50 years (figure S12)
- CFC-112 (CCl_2FCCl_2F):
  [tetrachloro-1,2-difluoroethane]
  lifetime = ∼60 years (figure S13)
- CFC-112a (CCl_3CClF_2):
  [tetrachloro-1,1-difluoroethane]
  lifetime = ∼50 years (figure S14)
- CFC-113 (CCl_2FCClF_2)
  [1,1,2-trichloro-1,2,2-trifluoroethane]
  lifetime = ∼90 years (figure S15)
- CFC-114 ($CClF_2CClF_2$)
  [1,2-dichlorotetrafluoroethane]
  lifetime = ∼190 years (figure S16)

HCFCs

- HCFC-22 ($CHClF_2$)
  [chlorodifluoromethane]
  lifetime = ∼12 years (figure S17)
- HCFC-141b (CH_3CCl_2F)
  [1,1-dichloro-1-fluoroethane]
  lifetime = ∼10 years (figure S18)
- HCFC-142b (CH_3CClF_2)
  [1-chloro-1,1-difluoroethane]
  lifetime = ∼18 years (figure S19)

HFCs

- HFC-134a (CH_2FCF_3)
  [1,1,1,2-tetrafluoroethane]
  lifetime = ∼14 years (figure S20)
- HFC-365mfc ($CH_3CF_2CH_2CF_3$)
  [1,1,1,3,3-pentafluorobutane]
  lifetime = ∼9 years (figure S21)

Halons

- Halon-1211 ($CBrClF_2$)
  [bromochlorodifluoromethane]
  lifetime = ∼16 years (figure S22),
- Halon-2402 ($CBrF_2CBrF_2$)
  [1,2-dibromotetrafluoroethane]
  lifetime = ∼30 years (figure S23)

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.

Others

- chloromethane (CH_3Cl)
  lifetime = ∼12 months (figure S24),
- bromomethane (CH_3Br)
  lifetime = ∼9 months (figure S25),
- 1,1,1-trichloroethane (CH_3CCl_3)
  lifetime = ∼6 years (figure S26),
- tetrachloromethane (CCl_4)
  lifetime = ∼26 years (figure S27),
- 1,2-dichloroethane (CH_2ClCH_2Cl)
  lifetime = ∼3 months (figure S28),
- trichloroethene ($CHCl{=}CCl_2$)
  lifetime = ∼5 days (figure S29),
- tetrachloroethene ($CCl_2{=}CCl_2$)
  lifetime = ∼5 months (figure S30)

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.

Aromatic compounds

- benzene (C_6H_6)
  lifetime = ∼months (figure S31)
- chlorobenzene (C_6H_5Cl)
  lifetime = ∼2 weeks (figure S32)

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.

Sulfides

- carbonyl sulfide (OCS)
  lifetime = ∼35 years (figure S33)

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

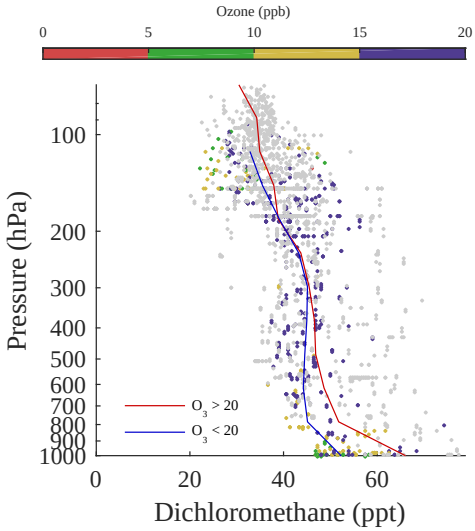

Figure S1: Dichloromethane

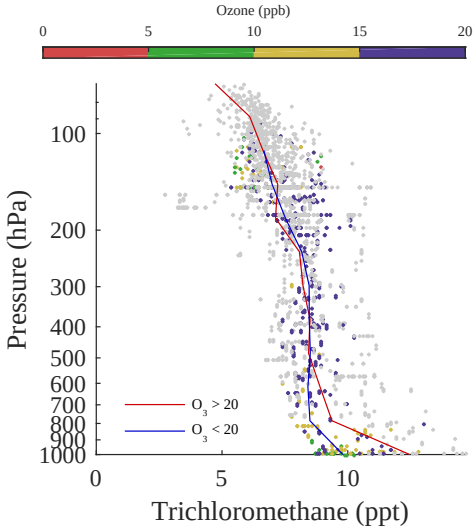

Figure S2: Trichloromethane

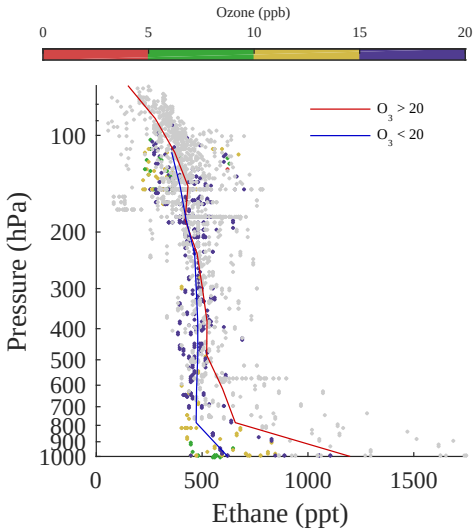

Figure S3: Ethane

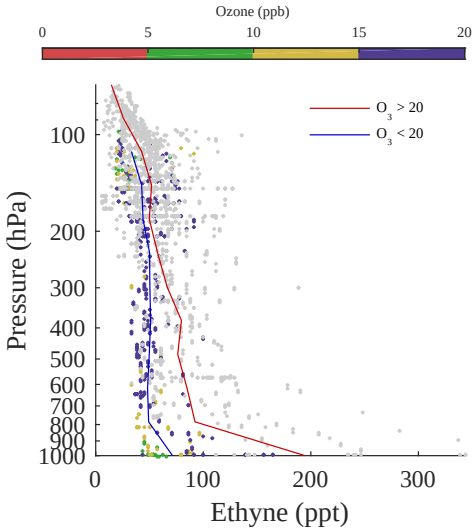

Figure S4: Ethyne

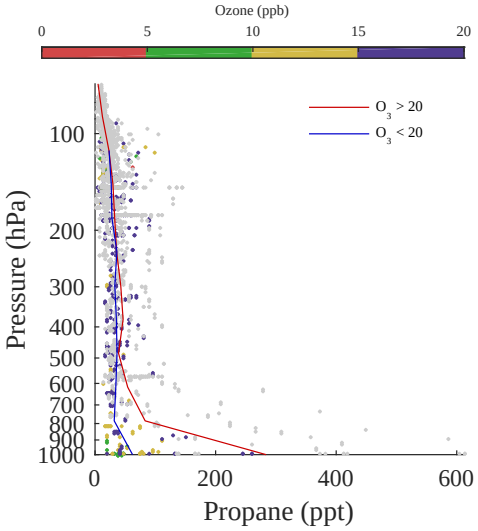

Figure S5: Propane

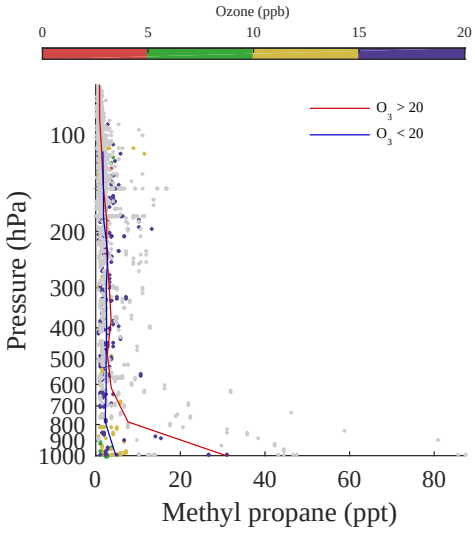

Figure S6: Methylpropane

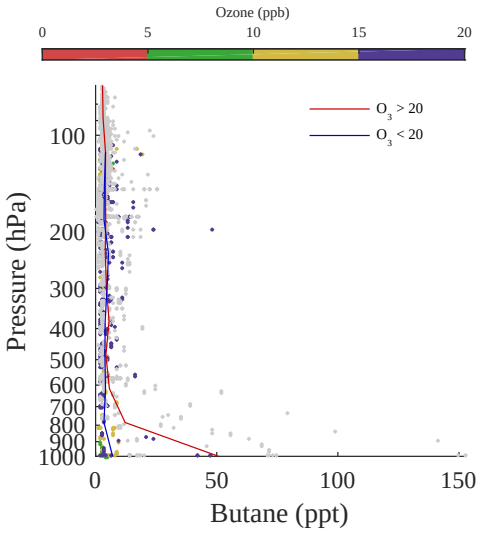

Figure S7: Butane

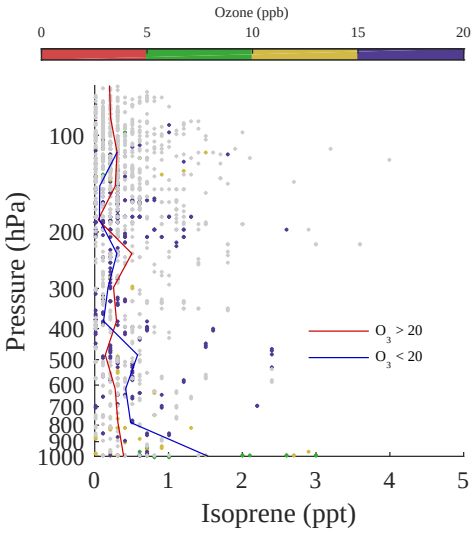

Figure S10: Isoprene

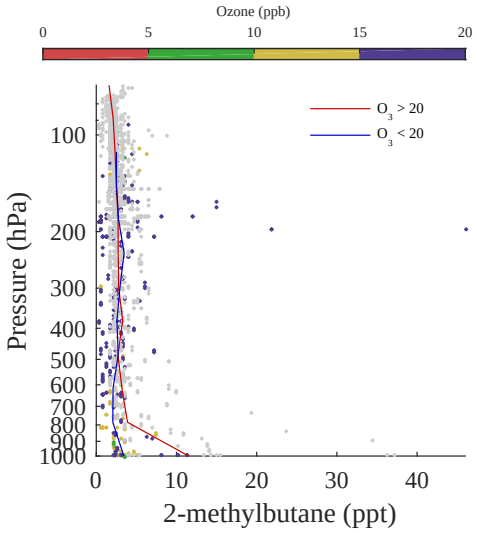

Figure S8: 2-Methylbutane

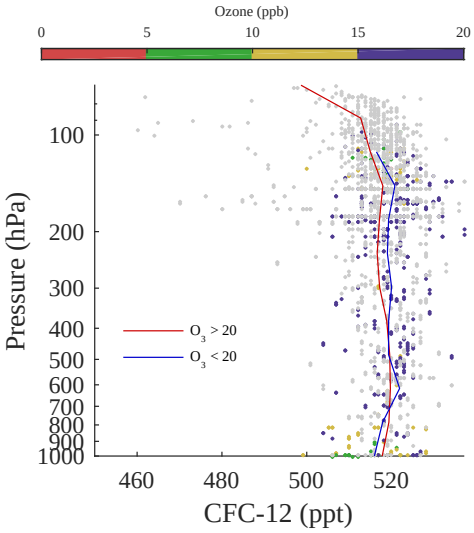

Figure S11: CFC-12

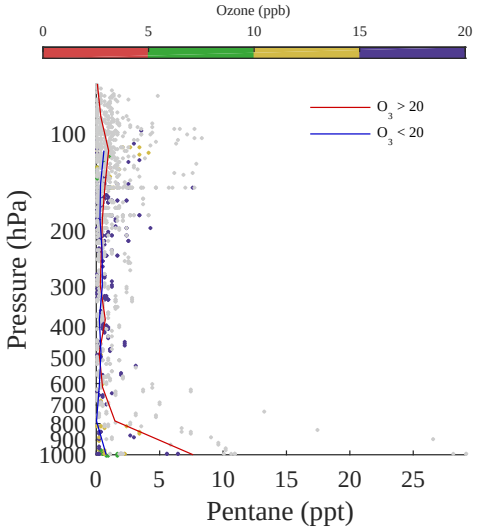

Figure S9: Pentane

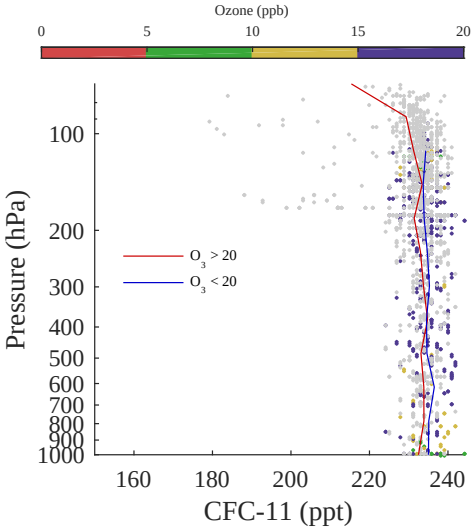

Figure S12: CFC-11

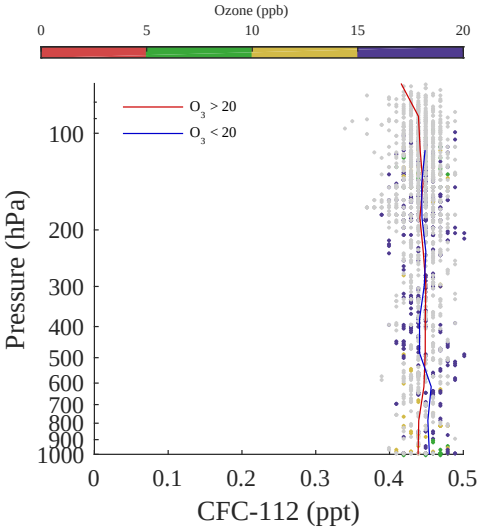

Figure S13: CFC-112

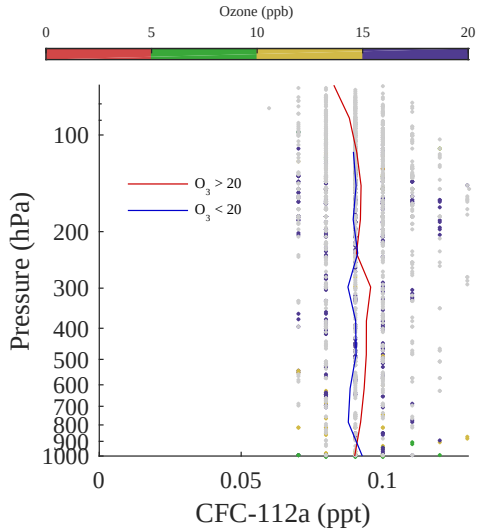

Figure S14: CFC-112a

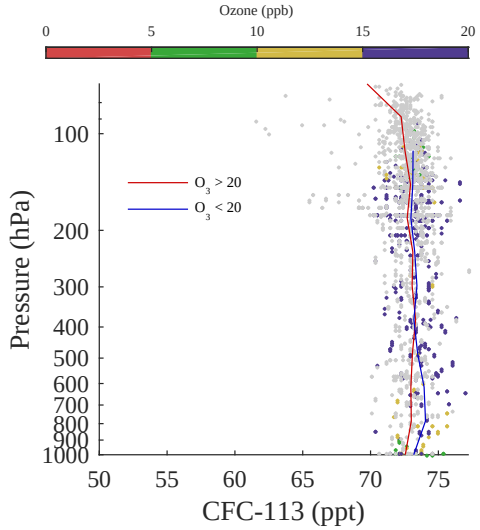

Figure S15: CFC-113

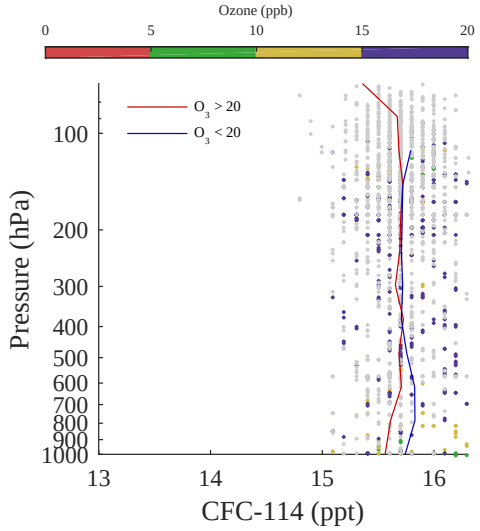

Figure S16: CFC-114

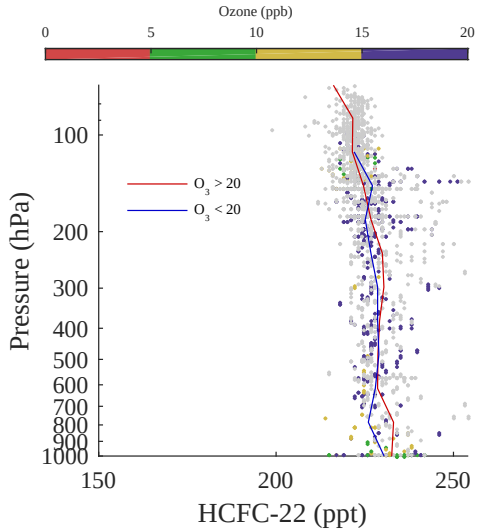

Figure S17: HCFC-22

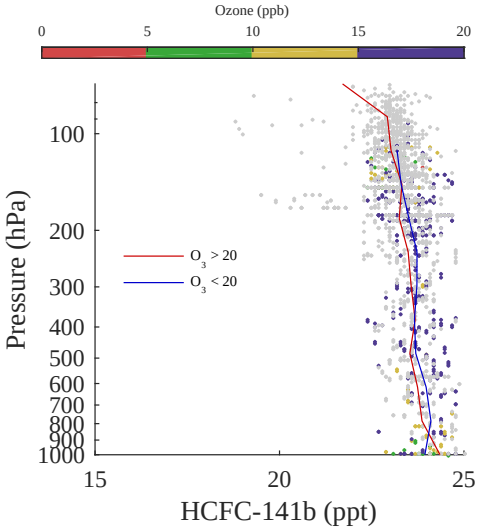

Figure S18: HCFC-141b

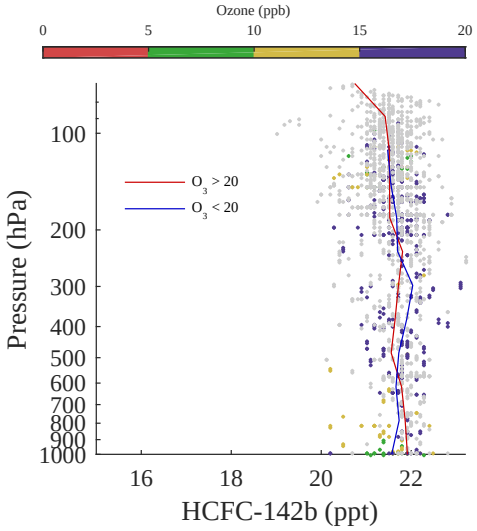

Figure S19: HCFC-142b

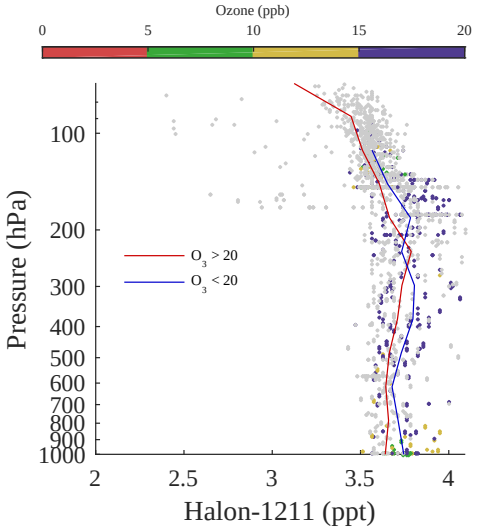

Figure S22: Halon 1211

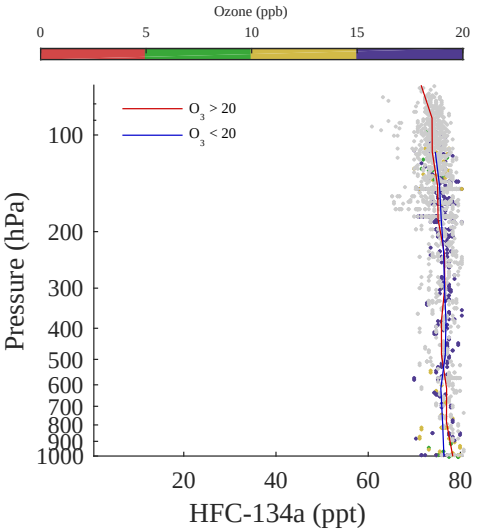

Figure S20: HFC-134a

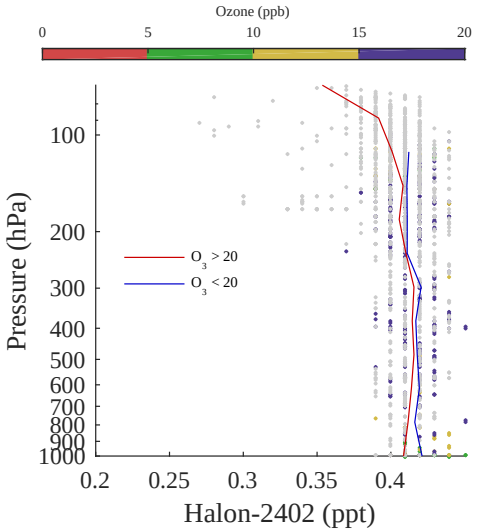

Figure S23: Halon 2402

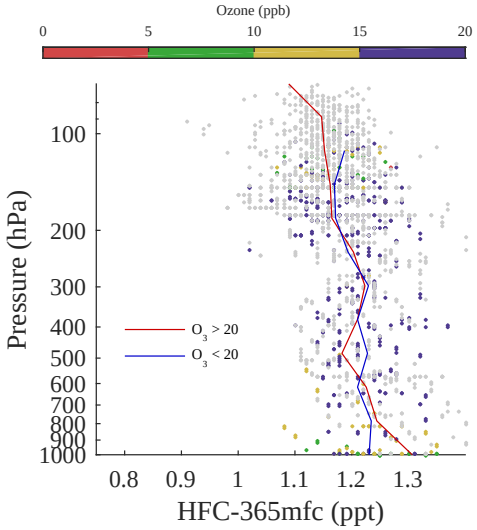

Figure S21: HFC-365mfc

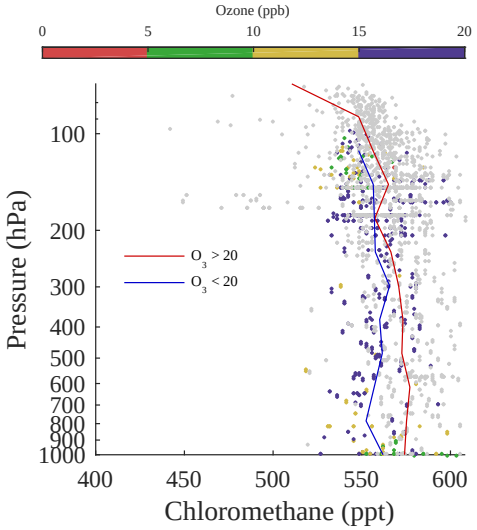

Figure S24: Chloromethane

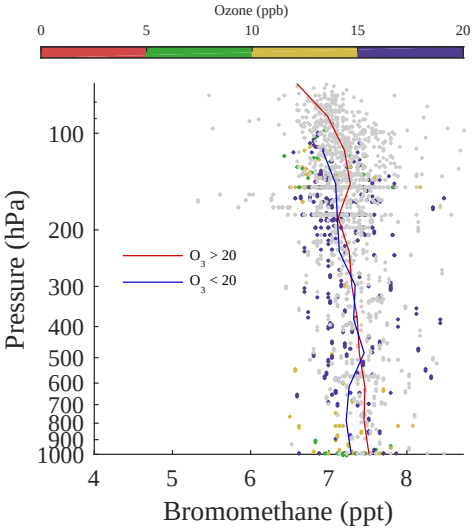

Figure S25: Bromomethane

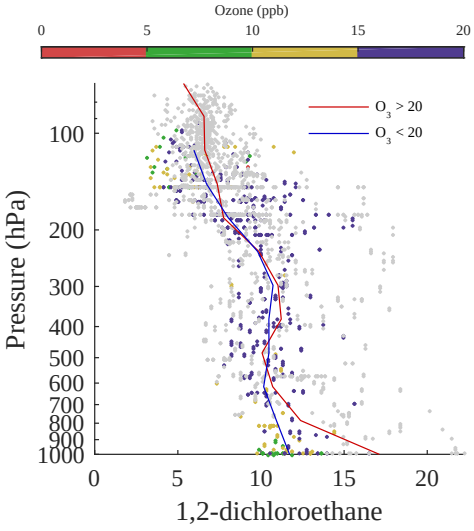

Figure S28: 1,2-dichloroethane

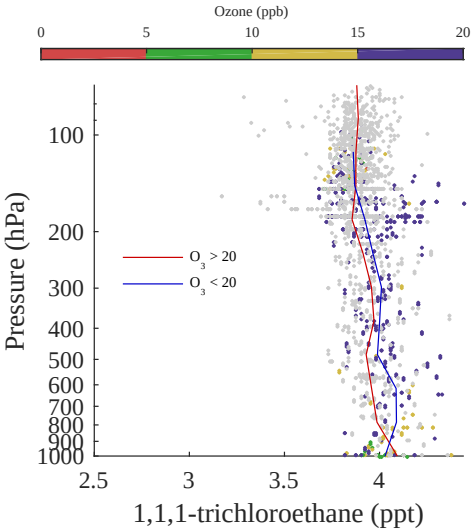

Figure S26: 1,1,1-trichloroethane

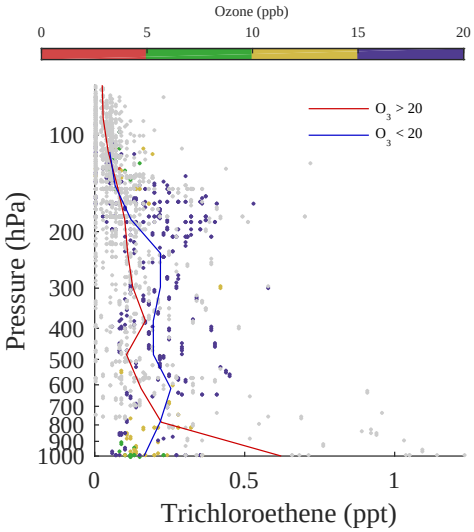

Figure S29: Trichloroethene

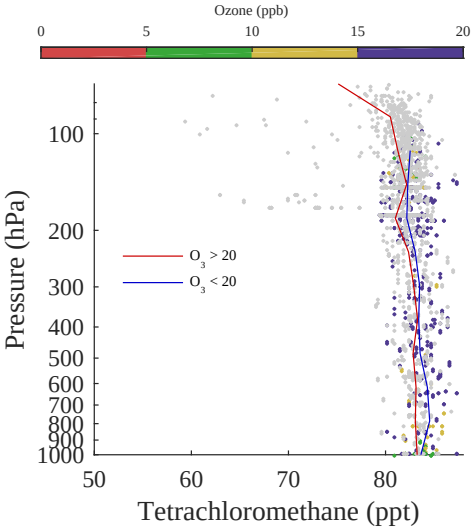

Figure S27: Tetrachloromethane

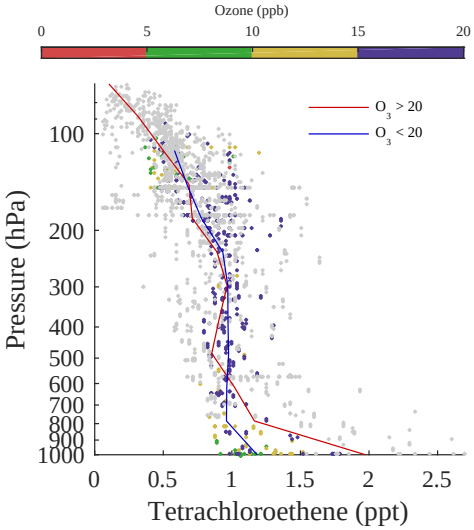

Figure S30: Tetrachloroethene

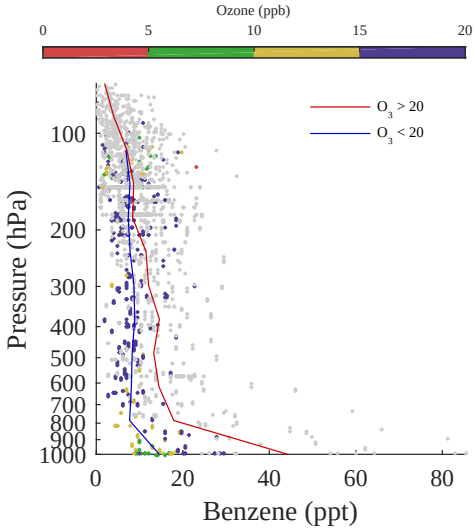

Figure S31: Benzene

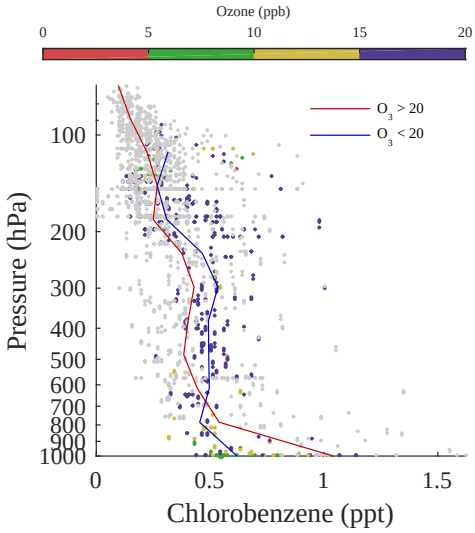

Figure S32: Chlorobenzene

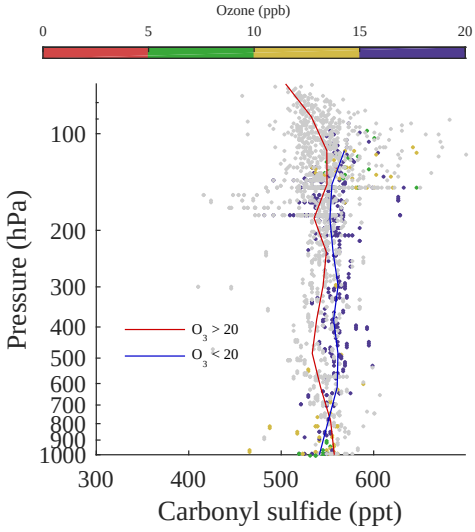

Figure S33: Carbonyl sulfide

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