# Long-term measurements of the column-averaged mixing ratios of tropospheric substances related to the air pollution using ground-based FTIRs at Rikubetsu

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## 1. Introduction

☆Air pollutants originating from carbon compounds such as reactive volatile organic compounds (VOCs) cause a serious degrading of the air quality near their sources. In addition, these are transported to remote areas with chemical composition changes, and affect air quality in urban areas and their surrounding areas, and therefore, are one of major issues in preserving the air quality.

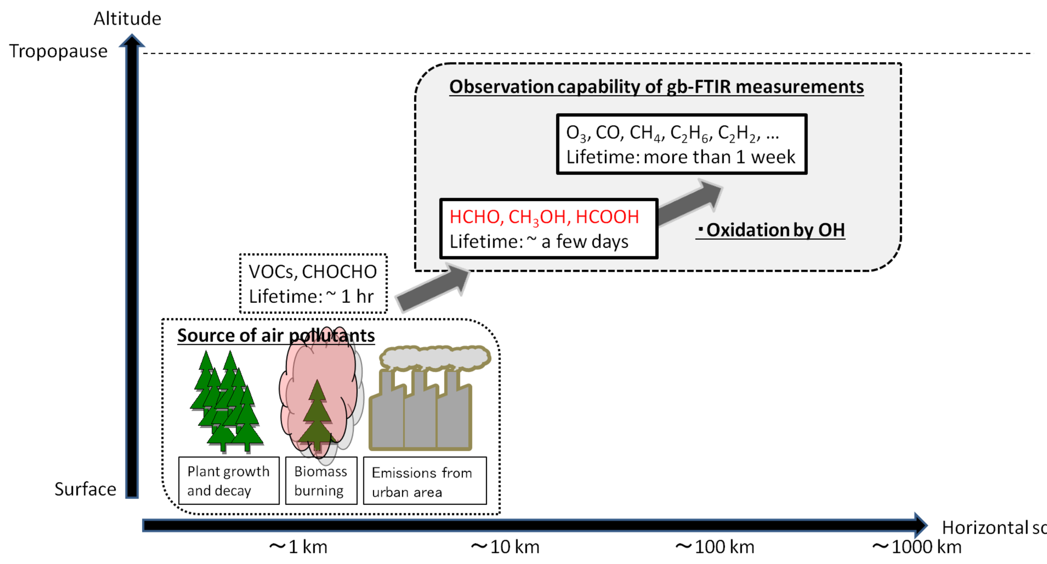


Figure 1) Key organic compounds linked between emission from the surface and pollutants in atmosphere

Figure 2)
Rikubetsu observatory and FTIRs
(middle: Bruker IFS 120M, lower: Bruker IFS 120/5 HR)

## 2. Observation and analysis

<u>☆FTIR Measurements</u>

A solar absorption spectrum using high-resolution FTIRs has been measured at Rikubetsu, Japan (43.5N, 143.8E, 380 m a.s.l.).

- Instrument: 1995.5～2010.5 measured with STEL-Bruker 120M
  2014.1～2016.5 measured with NIES-Bruker 120/5HR
- Spectral resolution: 0.0035 $cm^{-1}$ (both)
- As of 2018, more than 5100 spectra are obtained.

<u>☆Retrievals of vertical distribution</u>

By using SFIT4 (v0.944) with P-T profiles, a priori profiles, line parameters, microwindows and etc, which are listed in the document of "NDACC/IRWG Uniform Retrieval Parameter Summary" for NDACC standard 10 species and in Vigouroux et al (2012, 2018) for other species, the vertical distributions of $O_3$, $CH_4$, $C_2H_6$, CO, HCN, HCHO and $C_2H_2$ are retrieved.

> P-T: NCEP Reanalysis-1
> A priori of gas: WACCM V6 (40-yrs run)
> $H_2O$ vertical profile: daily average from pre-fitting results
> Vertical grid: 48 layers (0.38-120.0 km)
> line parameters: HITRAN2012 + ATM16 (for $H_2O$ and its isotopes)

<u>Table 1: Retrieval parameters, DOFs and total error of 7 species</u>

| Species | # of MWs | MicroWindow ($cm^{-1}$) | Species to be fitted simultaneously | DOFs | Total error (%) (~2010, 2014~) |
|---|---|---|---|---|---|
| $O_3$ | 1 | 1000.00-1005.00 | $H_2O$, $CO_2$, $C_2H_4$, $OO^{18}O$, $O^{18}OO$ | 5.7 | 0.4%, 1.6% |
| CO | 3 | 2057.70-2058.00<br>2069.56-2069.76<br>2157.50-2159.15 | $O_3$, $CO_2$, OCS, $N_2O$, $H_2O$ | 2.6 | 3%, 2% |
| $CH_4$ | 5 | 2613.70-2615.40<br>2650.60-2651.30<br>2835.50-2835.80<br>2903.60-2904.03<br>2921.00-2921.60 | HDO, $CO_2$, $NO_2$, $H_2O$ | 1.7 | 6%, 6% |
| HCN | 3 | 3268.04-3268.40<br>3287.10-3287.35<br>3299.40-3299.60 | $H_2O$, $C_2H_2$, $CO_2$, $H_2{}^{18}O$ | 2.9 | 18%, 17% |
| $C_2H_6$ | 3 | 2976.66-2976.95<br>2983.20-2983.55<br>2986.45-2986.85 | $H_2O$, $O_3$, $CH_4$ | 1.7 | 7%, 6% |
| $C_2H_2$ | 1 | 3250.25-3252.11 | $H_2O$, $H_2{}^{18}O$ | 1.1 | 25%, 25% |
| HCHO | 4 | 2763.42-2764.17<br>2765.65-2766.01<br>2778.15-2779.10<br>2780.65-2782.00 | HDO, $H_2O$, $O_3$, $CH_4$, $N_2O$ | 1.2 | 30%, 20% |

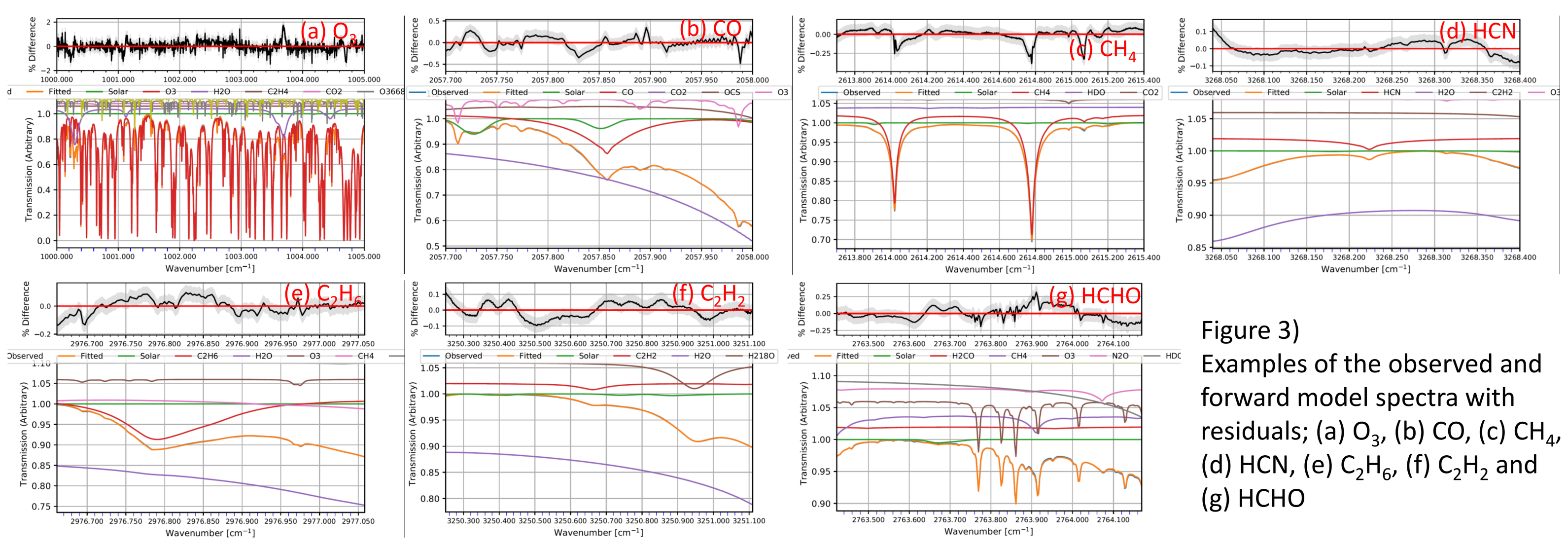


Figure 3)
Examples of the observed and forward model spectra with residuals; (a) $O_3$, (b) CO, (c) $CH_4$, (d) HCN, (e) $C_2H_6$, (f) $C_2H_2$ and (g) HCHO

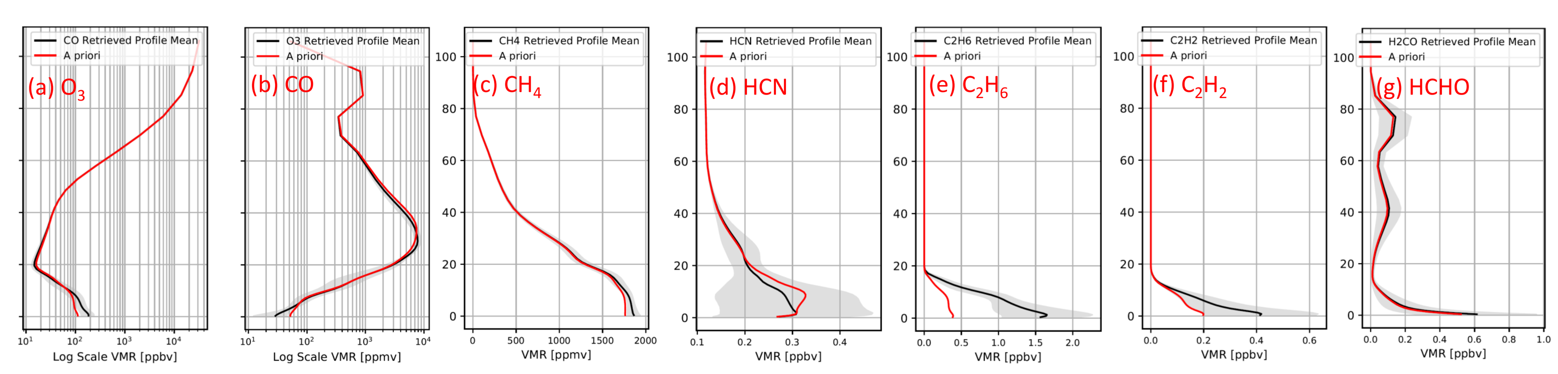


Figure 4) Mean of all the retrieved vertical profile with the a priori; (a) $O_3$, (b) CO, (c) $CH_4$, (d) HCN, (e) $C_2H_6$, (f) $C_2H_2$ and (g) HCHO

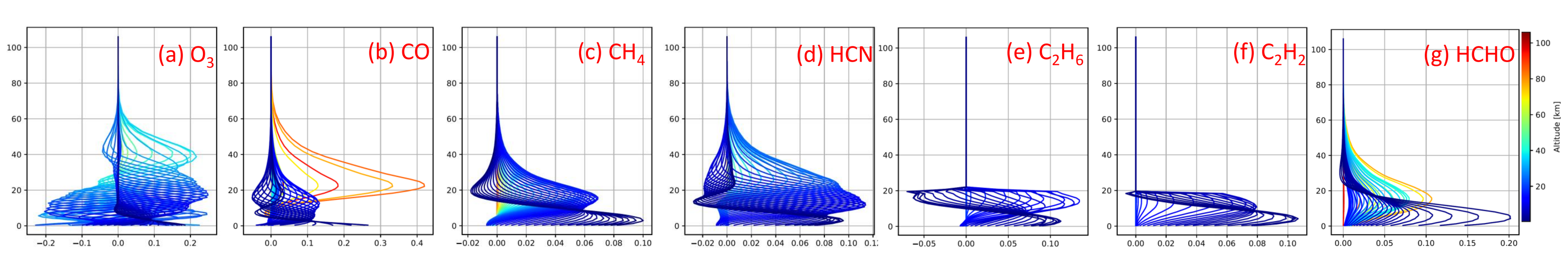


Figure 5) Averaging kernels of (a) $O_3$, (b) CO, (c) $CH_4$, (d) HCN, (e) $C_2H_6$, (f) $C_2H_2$ and (g) HCHO

## 3. Seasonal and long-term variability of the observed species in the troposphere

<u>☆Seasonal variability of the total column amounts</u>

Spring maximum: $O_3$ (Mar), CO (Apr), $C_2H_6$ (Mar), $C_2H_2$ (Feb)
Summer maximum: HCN (May-Aug), HCHO (Jul)
Almost constant: $CH_4$

↓

- These are consistent with the previous results using Hokkaido FTIRs dataset. (Zhao et al. 2002; Y. Nagahama & Suzuki 2007)

- The observed seasonal variability reflects the source and sink processes of the species.

=>a primary sink process of long-lived species is oxidation by OH, and therefore, they show the summer-fall minimum.

=>sink of tropospheric HCN is due to contact with ocean, and therefore, HCN shows the winter minimum because of low sea surface temperature in mid-latitude region.

=>HCHO is an intermediate product from VOCs with a shorter lifetime, and therefore, the summer maximum of HCHO may reflect the amount of VOCs and the distance from them.

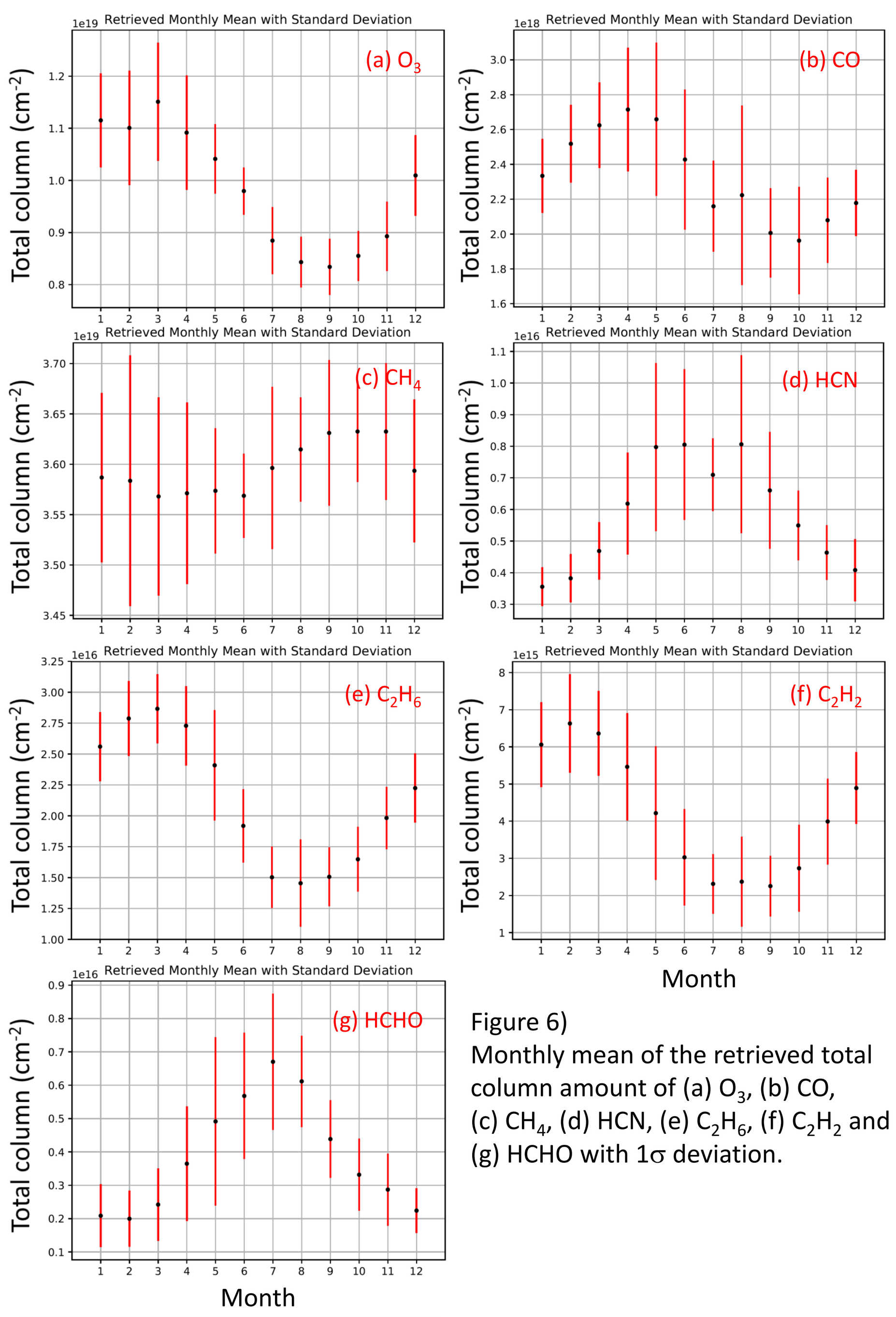


Figure 6)
Monthly mean of the retrieved total column amount of (a) $O_3$, (b) CO, (c) $CH_4$, (d) HCN, (e) $C_2H_6$, (f) $C_2H_2$ and (g) HCHO with 1σ deviation.

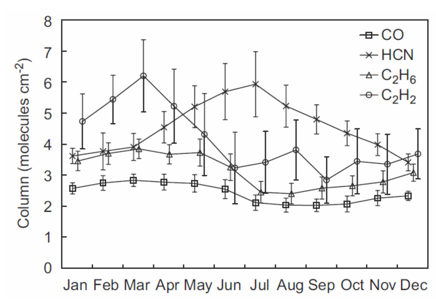


Figure 7)
Monthly mean of the retrieved total column amount of CO, HCN, $C_2H_6$ and $C_2H_2$ with 1σ deviation.
(Y. Nagahama & Suzuki, 2007)

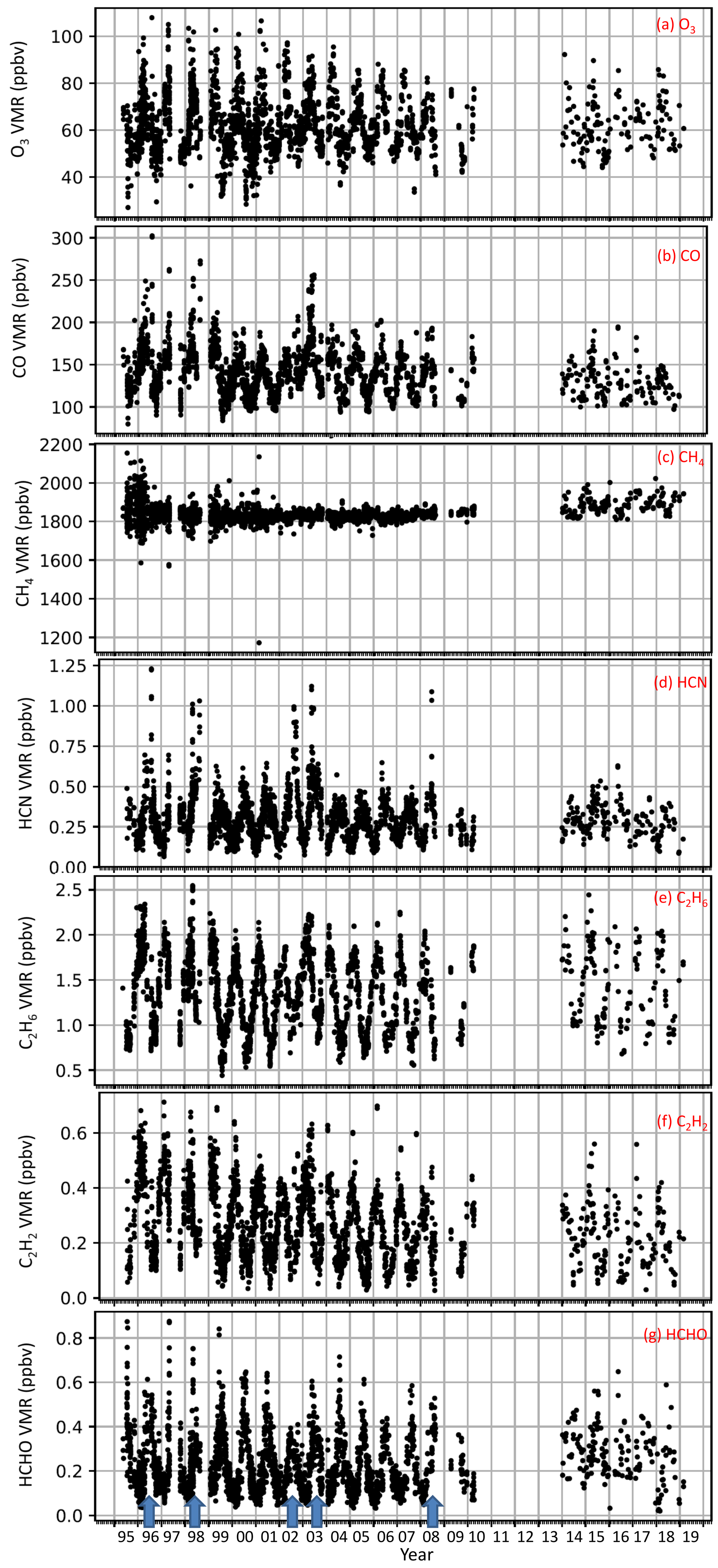


Figure 6) Time-series of the column-averaged mixing ratio of (a) $O_3$, (b) CO, (c) $CH_4$, (d) HCN, (e) $C_2H_6$, (f) $C_2H_2$ and (g) HCHO in the troposphere (surface-8 km). Arrows indicate a period of huge forest fires in Siberia.

<u>☆Long-term variability of the column-averaged mixing ratios in the troposphere (surfece-8 km)</u>

- trends
  no significant trend: $O_3$, CO, HCN, $C_2H_2$, HCHO
  positive trend: $CH_4$, $C_2H_6$

- short-term enhancement caused by biomass burning
  clearly appear in CO, HCN
  moderately appear in $C_2H_6$, $C_2H_2$
  not significant in $O_3$, $CH_4$, HCHO

## 4. Summary

- Vertical distribution of $O_3$, CO, $CH_4$, HCN, $C_2H_6$, $C_2H_2$ and HCHO are retrieved from the solar absorption spectra taken with high-resolution FTIRs in Rikubetsu observatory, Japan since 1995.

- Except for CH4, we find seasonal variability of the total column amounts of 6 species. For $O_3$, CO, $C_2H_6$ and $C_2H_2$, the spring maximum is detected. For HCN and HCHO, the summer maximum of the total column is detected.

- Long-term trends and short-term enhancements of the species are estimated. For $CH_4$ and $C_2H_6$, the positive trend is detected, although no significant trend appears in the other species.

## References

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