# Evaluation and measurement of tropospheric glyoxal retrieved from MAX-DOAS in Shenzhen, China

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## Introduction

The Pearl River Delta in China experiences frequent ozone ($O_3$) pollution events. Tropospheric oxynitride ($NO_X$) and VOCs play an important role in the production of tropospheric ozone. Glyoxal (CHOCHO) is the smallest α-dicarbonyl compound and a telemetered volatile organic matter (VOC) component. The CHOCHO/HCHO ratio (RGF) can also be used as a tracer of changes in atmospheric VOCs. And the accurate measurement of glyoxal is also essential for calculating the global budget of atmospheric secondary organic aerosols. The multi-axis differential absorption spectroscopy(MAX-DOAS) instrument is a ground-based spectral telemetry technique and it has been widely used in the measurement of trace gases in the atmosphere. However, CHOCHO has very low optical density—one order of magnitude lower than that of $NO_2$, which is an absorbing gas in the same band; thus, the weak absorption of glyoxal is occasionally obscured by noise. The ground-based MAX-DOAS observation of CHOCHO is still limited, and a long-term reliable ground-based observation dataset is still lacking. In this study, an optimal configuration for CHOCHO DOAS fitting, which could minimize influence from interfering species and improve the quality of MAX-DOAS CHOCHO data, was obtained through sensitivity analysis of spectra simulated by SCIATRAN and the actual observed spectra. The derived configuration was applied to the Yangmeikeng(YMK) site in Shenzhen and the CHOCHO observation results were analyzed.

## Experiment and methods

### Measurement Site

The MAX-DOAS equipment was installed on the roof of YMK Station of Shenzhen Ecological Monitoring Center (114.57° E, 22.53° N, 50 m A.S.L.). The site is located near the sea and surrounded by ecological parks, with high vegetation coverage. It is far away from urban areas and surrounded by a national geological park, with a high vegetation coverage and less anthropogenic emissions(Fig. 1).

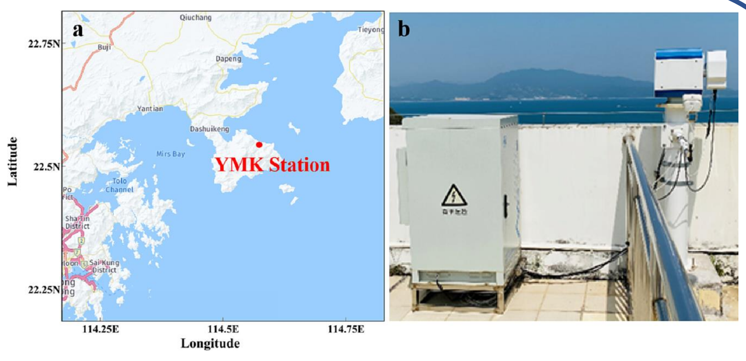


Fig. 1 Location of YMK Site

### Synthetic spectra and inter-comparisons

In general, the exact concentration of CHOCHO in the atmosphere cannot be determined during the field measurement. Therefore, it is difficult to directly estimate the deviation of the MAX-DOAS measurement from the actual situation. In order to analyze DOAS fitting configurations for MAX-DOAS measurements in more detail and to assess the bias under different configurations, we used the forward simulation module of SCIATRAN to simulate the spectrum and skew column concentration as real measurements. SCIATRAN v4.5.7 was used to simulate a set of spectra under observation geometry and solar geometry similar to the actual observation. The prior profile is of exponential type and the vertical column concentration VCD is 6.48 × $10^{14}$ molecules/$cm^2$.

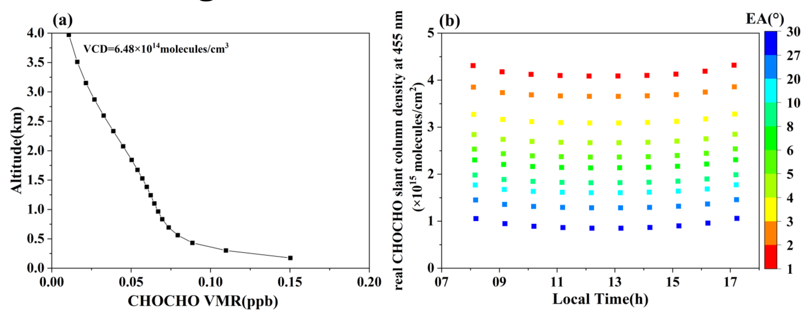


Fig. 2 CHOCHO prior profile and the real CHOCHO delta slant columns at 455

## Results and discussions

We evaluated the influence of wavelength range, polynomial order, intensity shift, and reference spectrum on CHOCHO DOAS fitting through sensitivity analysis. The fitting results under different configurations were compared with the actual values of the simulated spectra. The fitting accuracy was analyzed in terms of mean deviation and linear regression between the calculated values and simulated actual values. In addition, three days on July 22, July 24, and July 31, when the pollution degree increased successively, were selected to compare the dSCD, dSCD error, and root mean square error (RMS) of the actual spectra processed under different fitting configurations.

### Sensitivity analysis for synthetic spectra and observation spectra

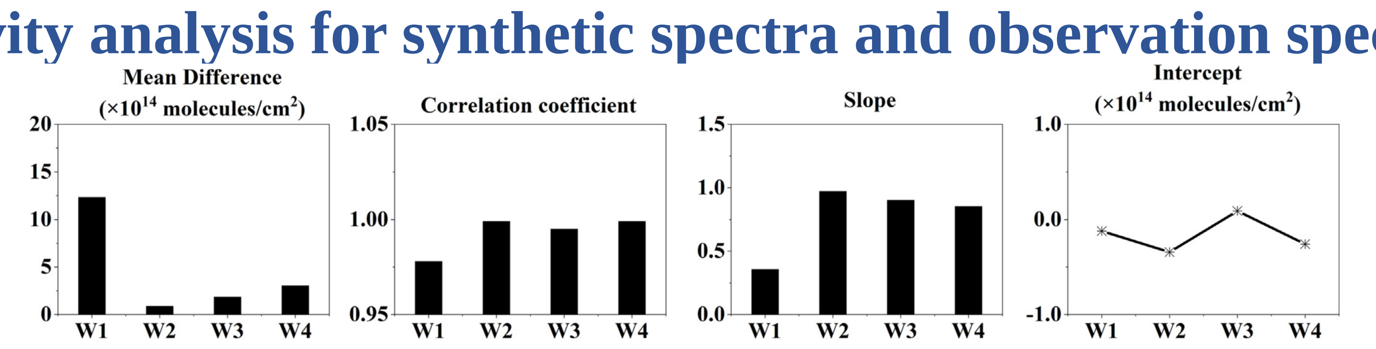


Fig. 3. Mean difference, slope, intercept, and correlation coefficient of the linear regressions between the results derived from synthesized spectra with different wavelength ranges and the actual values.

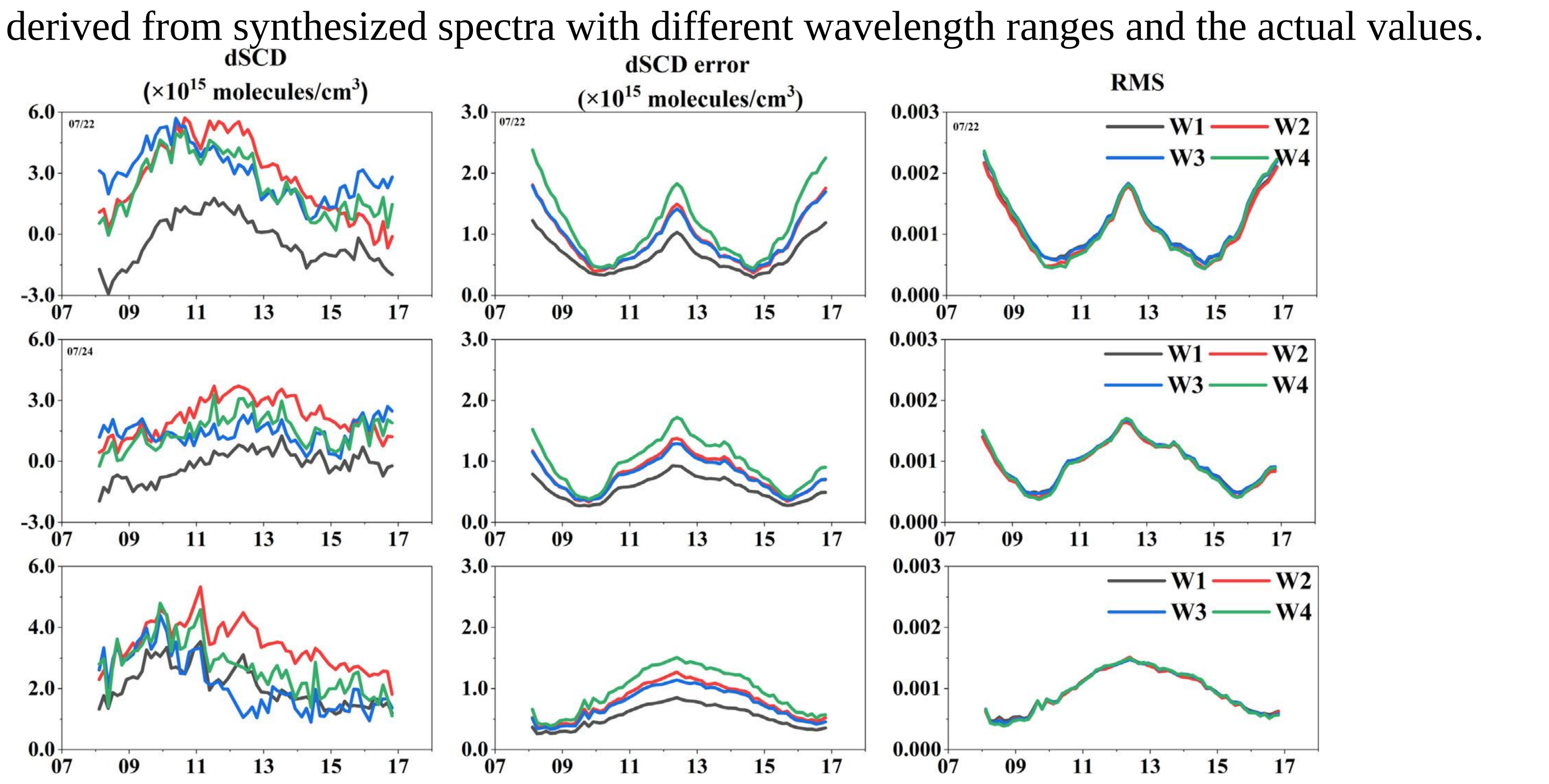


Fig. 4. dSCD, dSCD error, and RMS derived from the 3° spectrum on July 22, 24, and 31 with different wavelength ranges.

According to the results of the sensitivity analysis, the wavelength range is a sensitive factor influencing the accuracy of the CHOCHO fitting results. In this study, the wavelength range of 420–459 nm was applied (excluding 442–450 nm). The fourth order polynomial was selected to reduce the influence of slow spectral change, and the sequential reference spectrum was selected in this study.

### Profile inversion

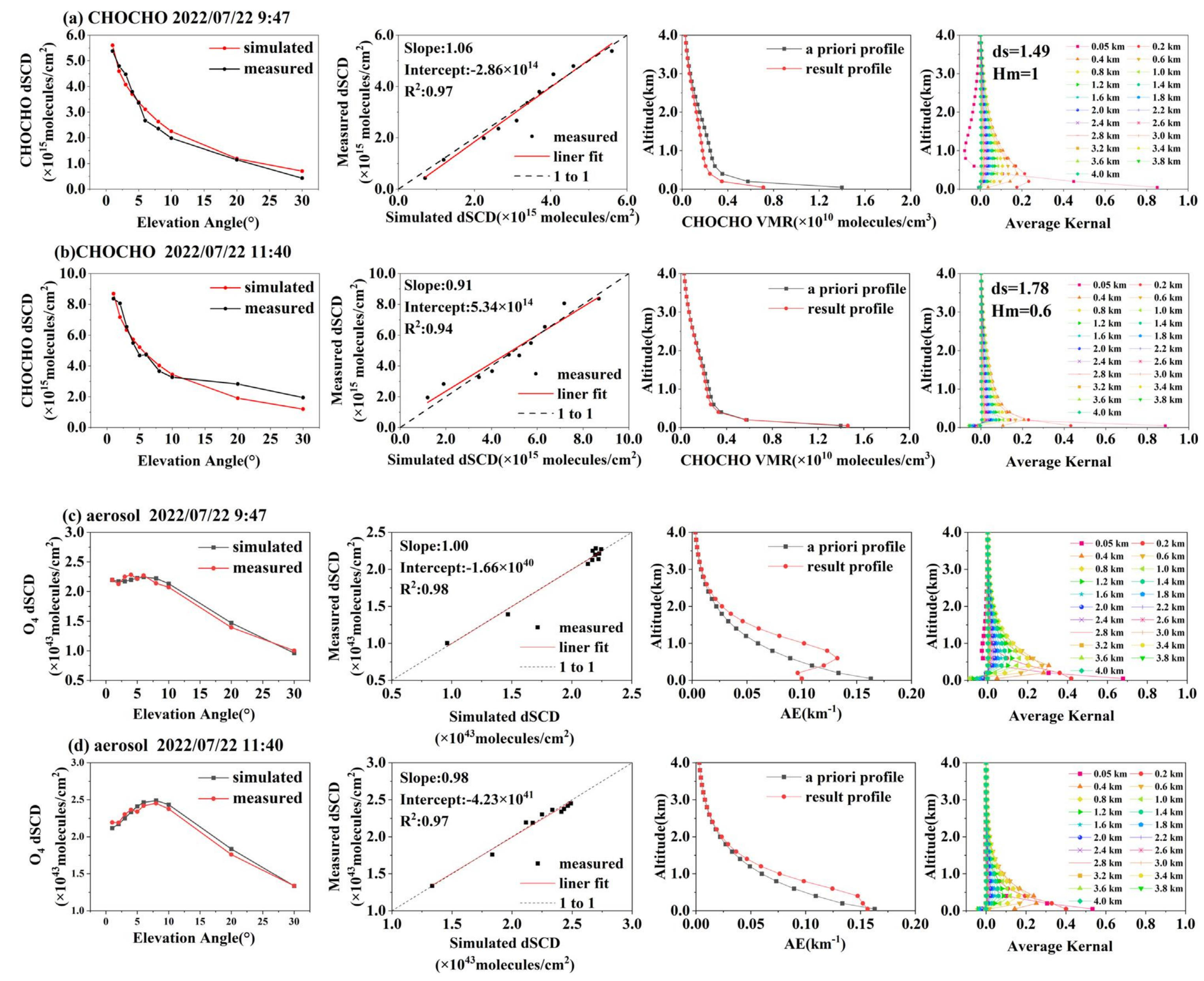
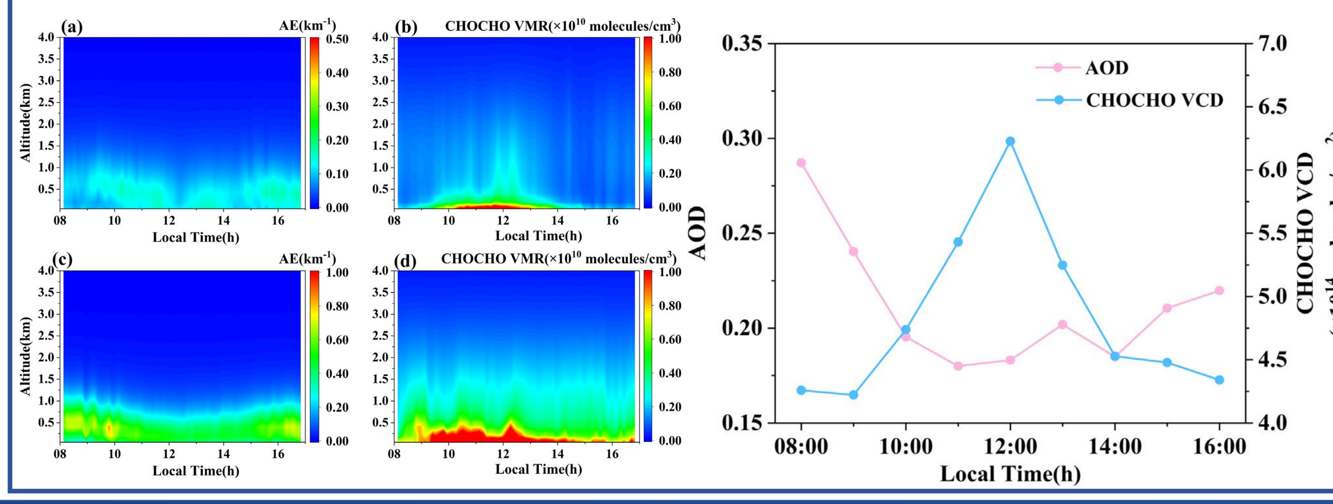


Fig. 5 CHOCHO and aerosol extinction profile retrieval examples with different concentrations.

With the gradual increase of the observed elevation, the gap between the simulated and measured values and increase and the sensitive height decreases. In this study, the average sensitive heights of aerosol and CHOCHO in this experiment were 1.2 km and 1 km, respectively.

### CHOCHO observation results




The observed near-surface CHOCHO concentration ranged from 0.02 to 0.71 ppb during the experiment.

## Conclusion

The main conclusions are as follows:

- The sensitivity analysis of the synthetic and observed spectra showed that the wavelength range is a sensitive factor influencing the accuracy of the CHOCHO fitting results. In this study, the wavelength range of 420–459 nm was applied excluding (442–450 nm), and the difference between the calculated value from the simulated spectra and the actual value was the smallest at only 0.89 × $10^{14}$ molecules/$cm^2$.
- The fourth order polynomial was selected to reduce the influence of slow spectral change, and the sequential reference spectrum was selected because the fixed reference spectrum led to the increase of the difference between the calculated and actual values in the morning and evening.
- The near-surface CHOCHO concentration ranged from 0.02 to 0.71 ppb. The results of profile distribution showed that the concentration of CHOCHO was concentrated below 500 m near the ground, and the concentration and pollution height began to rise around 09:00, reached the maximum at around 12:00, and then gradually decreased.

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