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Increase of ambient formaldehyde in Beijing and its implication for VOC reactivity

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Abstract

Influencing atmospheric OH radical budget and tropospheric ozone production, ambient formaldehyde (HCHO) is one of the key oxygenated volatile organic compounds (OVOCs). We present the variations on formaldehyde column densities in summertime in Beijing retrieved from ozone monitoring instrument (OMI) between 2005 and 2011. Satellite columns of HCHO correlated well with available ground-based measurements despite some noticeable differences. The orthogonal distance regression (ODR) method was used to estimate the ratio between satellite columns and ground-level concentrations, whereas ordinary least squares (OLS) method was used to fit the trend of ambient formaldehyde. The formaldehyde concentrations derived from HCHO columns were in the range of 7–12 ppbv and steadily increased at an approximate rate of 0.64 ppbv/yr (7.8% at 2005 level) with an uncertainty of 51%. VOC reactivity quantified by means of OH loss rates showed increasing contribution from formaldehyde and acetaldehyde, rising from 35% in 2005 to 40% in 2010, and decreasing contribution from anthropogenic VOCs, dropping from 49% in 2005 to 40% in 2010. More attention should be paid to understanding the net feedback of increasing formaldehyde to ozone formation potential.

Keywords: Formaldehyde; Satellite observations; Temporal variations; VOC reactivity

Formaldehyde (HCHO) is one of the most abundant oxygenated volatile organic compounds (OVOCs) in the atmosphere, which is an intermediate oxidation product of plenty of volatile organic compound (VOC) species including methane and more reactive VOCs, for example, isoprene can be a major source of HCHO in the forest [1–3]. Photolysis and OH photo-oxidation reactions make the lifetime of HCHO in summer only a few hours participating the cycling between hydroxyl and hydroperoxyl radicals [3]. In addition, HCHO is known as a toxic and carcinogenic threat to human health [2].

Formaldehyde is of increasing concern in China. *In situ* measurements have been conducted in some mega-cities, such as Beijing, Shanghai, and Hong Kong, finding HCHO levels higher than 10 ppbv occasionally [4–6]. Satellite observations showed hotspots and positive trend in the northeastern China [7]. In this work, the synergistic use of

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ground-base and satellite measurements gives us more reliable understanding on the trend of formaldehyde. The contribution of formaldehyde and acetaldehyde to VOC reactivity is also discussed.

To study the temporal variations of formaldehyde in Beijing, we used the total columns of formaldehyde retrieved from Ozone Monitoring Instrument (OMI) aboard on the NASA Aura satellite between 2005 and 2011 (http://disc.sci.gsfc.nasa.gov/Aura/data-holdings/OMI/). The overpass time across China is about 1:45 pm local time. The domain we chose is urban and suburban areas in Beijing (39.7°N−40.3°N, 116.1°E−116.7°E) within the 6th Ring Road approximately. To limit uncertainties, the data was excluded when cloud fraction on the specific day was above 30% [7]. To compare with long-term ground-base measurements at Peking University (PKU) site, only data in August of each year was captured and reprocessed. The ground-based measurements of HCHO were conducted by using an on-line formaldehyde monitor developed based on fluorometric Hantzsch reaction involving cyclization of 2,4-pentanedione and formaldehyde in an ammonium acetate buffer [2,8] while VOCs were measured by online GC/MS or GC/FID [5]. Acetaldehyde (CH_3CHO) concentrations were estimated by multiplying the formaldehyde concentrations by a factor of 0.4, a local ratio derived from *in situ* measurements [6]. VOC reactivity was quantified by means of OH loss rate (L_{OH}), which was calculated by the product of the VOC mixing ratio and its OH reaction rate coefficient [9,10].

To explore the approach of deriving ambient HCHO concentrations from satellite observations, the field ground measurements in Beijing and Jiangmen (in Guangdong) were used to perform regression analysis. The HCHO column densities correlated well with ground-based measurements in both Beijing and Jiangmen (Fig. 1(a) and (b)). The daily variations between the two datasets showed consistent pattern and significant correlation ($p < 0.01$), with Pearson correlation coefficients (r) of 0.51 in Beijing and 0.63 in Jiangmen, respectively. The consistent pattern between the two datasets further confirmed that total formaldehyde concentrations were mainly focused in the lower troposphere [1]. However, there were also some marked differences, which may be partially due to the increasing errors of retrievals and across-track striping problem from OMI [1,11]. These unusual days accounted for about 20% of total observation days. With the assistant from ground-based data, it was practical to detect them by the inter-comparison method, otherwise, larger uncertainties may exist in retrievals of HCHO from satellite.

Based on reasonable correlation between these two sequences of observations, the ratio between satellite columns and ground-based measurements was calculated by using orthogonal distance regression (ODR) method (Fig. 1(c) and (d)). Satellite data and ground-based data were both weighted with measurement errors. ODR method

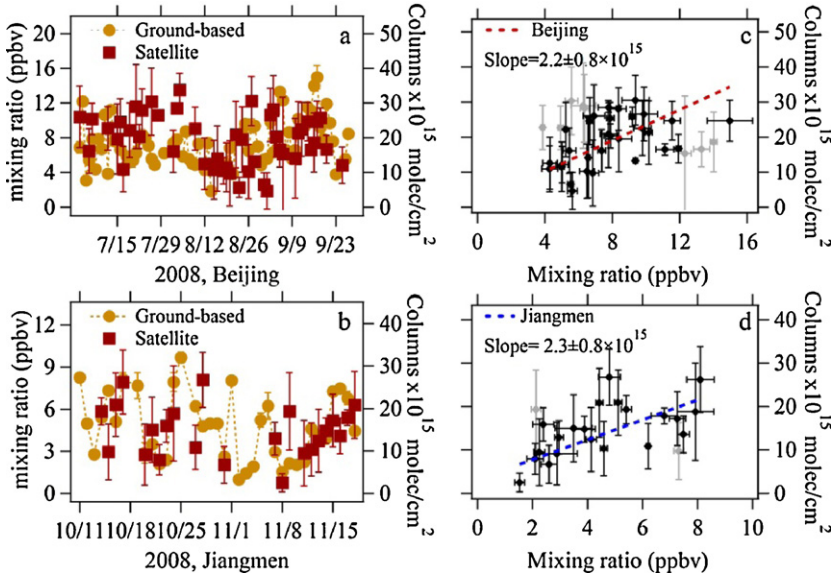

Fig. 1. Comparison of time series between ground-based measurements and satellite columns of formaldehyde in (a) Beijing and (b) Jiangmen. Orthogonal distance regression between satellite columns and ground-based measurements of formaldehyde in (c) Beijing and (d) Jiangmen. The grey dots are marked data excluding the regression. The confidence intervals of the slope are at 95% significance level, and the error bars represent one standard derivation.