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Revisiting Acetonitrile as Tracer of Biomass Burning in Anthropogenic-Influenced Environments

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Key Points:

- Several ppbv of CH_3CN can be measured in anthropogenic-influenced environments with minor biomass burning impact
- Good correlation between high CH_3CN and CO were revealed showing their shared sources in anthropogenic-influenced environments
- Biomass burning can be distinguished from other CH_3CN sources using the enhancement ratios of CH_3CN and CO

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract Acetonitrile (CH_3CN) has been widely employed as biomass burning tracer. However, the current application of CH_3CN absolute mixing ratio as the thresholds may misidentify biomass burning due to the interference from other CH_3CN sources in anthropogenic-influenced environments. High levels of CH_3CN were observed with minor biomass burning impact but still followed a similar correlation with carbon monoxide (CO), suggesting their shared source, most likely, vehicular emission. By analyzing the available literature including more than 30 worldwide field measurements, the enhancement ratios (EnRs) of CH_3CN to CO for biomass burning were found as 2.01 ± 0.16 ppbv/ppmv, well distinguished from the EnRs obtained in urban measurement (0.26 ± 0.04 ppbv/ppmv). An example is given and the application of EnR to identify biomass burning is discussed. The results suggest that the correlation between CH_3CN and CO and their EnRs can be used as more specific indicators for biomass burning.

Plain Language Summary Biomass burning can contribute significantly to local and regional pollutions. A proper tracer can help us track and quantify biomass burning emissions. In the past few decades, the acetonitrile (CH_3CN) level has been applied as a preferred tracer but the existence of CH_3CN sources other than biomass burning may lead to an overestimation of the burning emissions. Here in this paper, by analyzing our field campaign data and the information from the previous publication, the correlation between acetonitrile and carbon monoxide and their enhancement ratios are found to be more specific indicators for biomass burning without interference from other significant sources. The results would be helpful to reevaluate the biomass burning impact and increase the accuracy of air quality forecasting in future research.

1. Introduction

On a global scale, biomass burning has been recognized as the primary source of fine carbonaceous particles and the second-largest source for total trace gases (Akagi et al., 2011; Stockwell et al., 2015; Yokelson et al., 2013). Pollutants emitted during the burning process can contribute significantly to local and regional air pollution (Chen et al., 2017; Crilley et al., 2015; Languille et al., 2020). The reactive species emitted participate in the reactions in the atmosphere producing secondary pollutants, such as secondary organic aerosols and ozone (O_3), which can amplify the impact of primary pollutants (Alvarado et al., 2015; Gilman et al., 2015; Yokelson et al., 2013). Recognizing and quantifying the amount of biomass burning emissions can help to understand the local source attribution and greatly enhance the accuracy of air quality forecasting in the downwind areas (Alvarado et al., 2015; Heilman et al., 2014; Yokelson et al., 2013).

The tracer method has been widely used to identify certain emission sources. For biomass burning, acetonitrile (de Gouw et al., 2003; G. Wang, et al., 2016; Yuan et al., 2010), hydrogen cyanide (Lobert et al., 1990; Hornbrook et al., 2011), methyl chloride (de Gouw et al., 2004; Singh et al., 2004), furans (Coggon et al., 2016; Gilman et al., 2015), levoglucosan (Bhattarai et al., 2019; Puxbaum et al., 2007; Stone et al., 2008), potassium (K^+) (Chantara et al., 2019; Fourtziou et al., 2017), and chloride (Cl^-) in particles (Chantara et al., 2019), etc.

have been reported as tracers. However, it requires a thorough understanding of the characteristics of local pollution sources before a tracer is selected, especially for compounds that have more than one significant source in the local area. Previous studies showed that methyl chloride and K^+ may not be appropriate tracers for biomass burning in urban areas due to the contribution from industrial emissions (Aiken et al., 2010; Li et al., 2014; Maudlin et al., 2015; Wang et al., 2007), whereas levoglucosan also suffers from short atmospheric lift-time (Hennigan et al., 2010; Hoffmann et al., 2010) and the interference of coal-burning (Fabbri et al., 2009; Yan et al., 2018).

Acetonitrile (CH_3CN) has been employed as the preferred tracer for biomass burning in more than 170 publications given its low background level and relatively long lifetime. However, studies have shown that besides biomass burning, industrial emission (Guan et al., 2020), vehicle emission (Inomata et al., 2013; Jobson et al., 2010; Valach et al., 2014), and coal-burning (Cai et al., 2019) can also contribute to CH_3CN levels in the atmosphere. These sources may not contribute significantly to the global budget of CH_3CN (de Gouw et al., 2003; Holzinger et al., 2001), but their contributions to local CH_3CN can bring large uncertainty when using mixing ratio threshold to evaluate the influences of biomass burning. Besides the mixing ratio approach, the enhancement ratio (EnR) of CH_3CN to carbon monoxide (CO) has also been applied as biomass burning indicator in several field campaigns (Bian et al., 2013; de Gouw et al., 2009; Wisthaler et al., 2002).

In this paper, we assess the current application of the absolute mixing ratio of CH_3CN for tracking biomass burning by analyzing the data obtained in the laboratory experiments and field campaigns conducted all over the world. The enhancement ratio of CH_3CN to CO summarized during the analysis is recommended as a more exclusive approach to identify the biomass burning cases. The feasibility and limitations of using this enhancement ratio are also discussed.

2. Materials and Methods

In this paper, datasets of CH_3CN and CO measured around the world were used to assess the current application of the CH_3CN mixing ratio as a biomass burning tracer. The key information of each field campaign can be seen in Table S1, including campaigns conducted in Mexico City (2006), Los Angeles (2010), Innsbruck (2019), and in the three highly developed megacity clusters in China. The ratios between CH_3CN and CO reported from the literature are summarized. The reviewed literature is organized into three categories: (a) field measurements focusing on the impact of biomass burning emission; (b) laboratory measurements investigating the emission characteristics of biomass burning; (c) field measurements in anthropogenic-influenced areas. The enhancement ratios of CH_3CN and CO measured in traffic tunnels in Shanghai and from chassis dynamometer tests for various vehicles were used to represent the characteristic ratio of vehicular emission. Detailed information of these measurements can be found elsewhere (Wu et al., 2020). CH_3CN measured by PTR-QMS at nominal m/z 42 may suffer from interference signals (Bruns et al., 2017; Dunne et al., 2012). According to the spectrum analysis of our PTR-TOF-MS measurements (see Section S1 in the Supporting Information), we found that the interference signal contributed less than 30% of the nominal signal at m/z 42 based on two field campaigns in China and showed no significant impact on the ratio between CH_3CN and CO.

3. Results

3.1. The Application of CH_3CN Mixing Ratio as Biomass Burning Tracer

CH_3CN widely exists in the atmosphere, with background levels of 100–150 pptv measured on the Atlantic Ocean (Hamm & Warneck, 1990) and West Africa (Murphy et al., 2010), 149 $\pm$ 56 pptv in the Pacific troposphere (Singh et al., 2003), and 190 pptv in the megacity cluster in the PRD region, China (Yuan et al., 2010). CH_3CN was determined as biomass burning products in the field soon after the first measurements were made in the lower troposphere by Becker and Ionescu (Becker & Ionescu, 1982). Lobert et al. (Lobert et al., 1990) found the high amounts of nitriles emitted during biomass burning and then proposed CH_3CN as tracer to biomass burning emission. Later studies confirmed the dominant input of biomass burning to the global budget of CH_3CN (de Gouw et al., 2003; Holzinger et al., 1999, 2001), which encouraged the application of CH_3CN as a tracer thereafter. In the last few decades, the mixing ratio of CH_3CN

has been employed as a tracer in more than 170 publications that focused on biomass burning (as shown in Table S2). However, only a small fraction of studies declared the exact mixing ratio thresholds used in their analysis. We summarized the available thresholds of CH_3CN reported and listed them in Table S3. The CH_3CN thresholds varied from 100 pptv to more than 600 pptv across different regions. These thresholds were determined based on the local CH_3CN observations and apparently, CH_3CN exists in the world unevenly distributed.

Ambient measurements in Asian, the US, and European areas observed quite a large range of CH_3CN (Figure 1), varying from 0.047 to 1.08 ppbv on average. During the two wintertime campaigns in the North China Plain at both urban (Beijing) and rural sites (Gucheng) where usually coal burning and vehicular emission dominate the sources (Shi et al., 2020; G. Wang, et al., 2016), the 90th percentiles of CH_3CN mixing ratio were observed as 1.2 and 1.3 ppbv, respectively. The maximum levels of 5 mins average of CH_3CN during the two campaigns can reach 5.0 and 4.5 ppbv, respectively, which are more than 20 times of the reported background (~200 pptv). With such high CH_3CN levels observed from the measurements, the biomass burning emissions would be assumed as the dominated sources if applying the CH_3CN absolute mixing ratio threshold reported from previous literature.

Based on the previous studies (Bian et al., 2013; de Gouw et al., 2009; Lobert et al., 1990; Wisthaler et al., 2002), we performed correlation analysis between CH_3CN and CO mixing ratios based on the available datasets (Figure 2). Positive correlations between CH_3CN and CO from measurements in anthropogenic-influenced areas are revealed even with CH_3CN levels as high as 3 ppbv. The observations indicate that though CH_3CN levels can vary by three orders of magnitude, the ratios between CH_3CN and CO stayed relatively constant. Moreover, the slopes are comparable among different areas (0.26 ± 0.04 ppbv/ppmv) (Figure 3), indicating that CH_3CN and CO came from a similar source. As shown in Figure 2, the observed slopes of CH_3CN and CO are also comparable with the emission ratios of CH_3CN to CO measured from gasoline cars and diesel trucks from chassis dynamometer tests and a tunnel study, suggesting that vehicular emissions may account for the enhancement of CH_3CN in anthropogenic-influenced areas around the world. The correlation analysis between CH_3CN and acetylene, a well-known tracer for vehicular emission (Warneke et al., 2007), also provides supportive evidence (See Figure S5 in Supporting Information). As the result, we conclude that applying the absolute mixing ratio of CH_3CN as biomass burning tracer may lead to misidentification of biomass burning contribution when CH_3CN is significantly enhanced in anthropogenic-influenced areas from non-biomass burning sources (most likely, vehicular emission).

3.2. Enhancement Ratio of CH_3CN to CO

The analysis in the previous section revealed good correlations between CH_3CN and CO based on ambient measurement (Figure 2), indicating that both compounds shared similar sources. Both CH_3CN and CO have relatively long lifetime in the atmosphere (Bian et al., 2013; de Gouw et al., 2009) so their observed enhancement ratio can well represent the source signature while the air mass is transported away from the source. Here, by summarizing our field observations conducted in China and the reported value from the field campaigns conducted in other areas of the world, the enhancement ratios of CH_3CN to CO from biomass burning emissions and anthropogenic-influenced airmasses are further determined. A list of reviewed literature can be found in Table S4 and all the data points were plotted in the upper section of Figure 3. As shown in Figure 3, the enhancement ratios of CH_3CN to CO reported from field measurements of biomass burning (black solid circles), specifically outdoor biomass burning including wildfire and agricultural residue burning, varied from 1.1 to 7.98 ppbv/ppmv with a log-normal peak at 2.01 ppbv/ppmv, which are one order of magnitude larger than the ones measured in anthropogenic-influenced areas (0.26 ± 0.04 ppbv/ppmv). According to the log-normal distribution histogram, the biomass burning distribution is well separated from the distribution of measurements in anthropogenic-influenced areas. The arithmetic means with one standard deviation based on the Gaussian distribution are 3.0 ± 1.7 ppbv/ppmv and 0.26 ± 0.07 ppbv/ppmv for field biomass burning measurement and the measurement in the anthropogenic-influenced environment, respectively. The distribution of emission ratios determined from the laboratory burning tests lies between the field and urban enhancement ratios. Previous publications (Coggon et al., 2016; Lacaux et al., 1996; Lobert et al., 1991; Stockwell et al., 2015) have confirmed the dependency of nitrogen-containing compounds, CH_3CN for example, on the fuel nitrogen content. Much broader nitrogen content of the fuel used

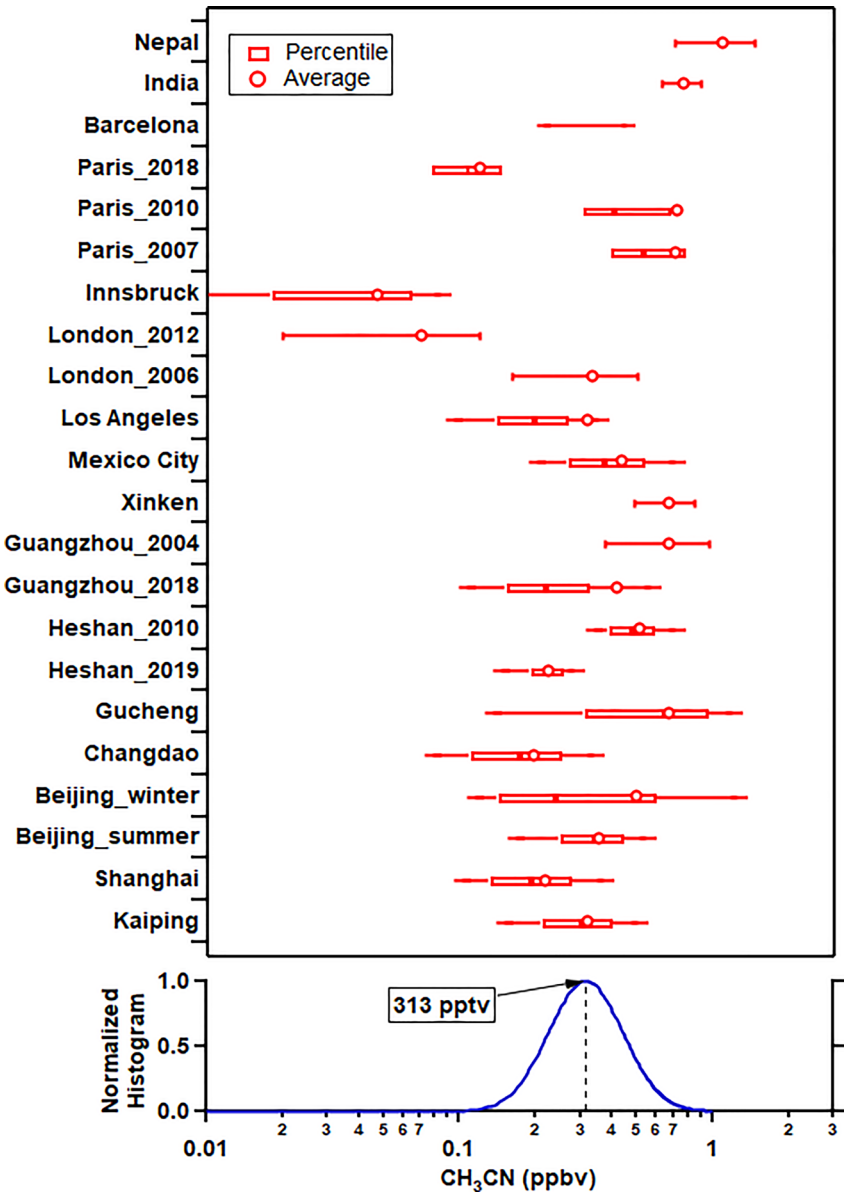

Figure 1. CH_3CN (ppbv) measured in multiple field campaigns in India, Nepal, and China representing the Asia region, US cities representing the North America region, and three European cities including Innsbruck, London, Paris, and Barcelona. In the top panel, box plots show the 10^{th}, 25th, 50th, 75th, and 90th percentiles with average levels in solid circles. For some field campaigns, only the average levels and standard deviation were available. The Barcelona campaign only reported the range of CH_3CN levels. The lower panel has the log-normalized histogram showing the distribution of the average levels of CH_3CN measured from the above field campaigns. A level of 313 pptv was found to have the highest probability. (a) Barcelona measurement data in 2009 can be found in Seco et al. (2013). (b) Paris measurement data can be found in Gros et al. (2011) for 2007, Baudic et al. (2016) for 2010, and Languille et al. (2020) for 2018. (c) London measurement data can be found in Langford et al. (2010) for 2006 and Valach et al. (2014) for 2012. (d) Data measured in India and Nepal can be found in Sahu et al. (2016) and Sarkar et al. (2016), respectively.

in the laboratory explained the wide range of emission ratios, as detailed discussed in Coggon et al (2016). The burning of excelsior, millet, wiregrass, etc. is associated with lower emission ratios that are comparable with anthropogenic emissions. These fuels are apparently associated with lower nitrogen contents. About half of the biomass burning field campaigns shown in Figure 3 were from forest fires. It is probably that the leaves and branches with the highest nitrogen content (Coggon et al., 2016) accounted for a larger portion of the biomass burnt in forest fire, leading to higher enhancement ratios compared with the laboratory

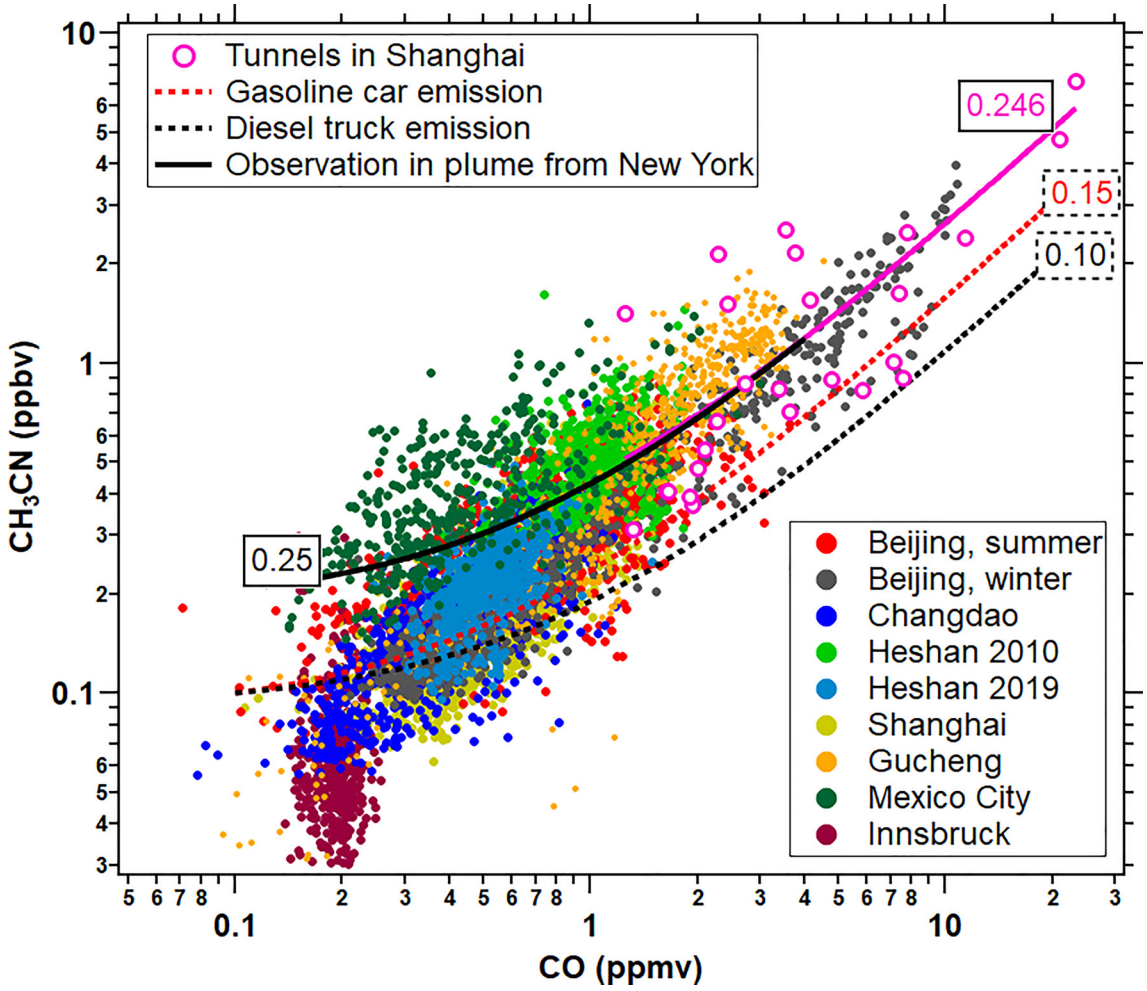

Figure 2. Scatter plot of CH_3CN (ppbv) and CO (ppmv) from multiple field campaigns conducted in anthropogenic-influenced areas shown in solid circles. All the online measurement data were averaged over 1 h. Data with higher time resolution can be seen in Figure S1. Canister tunnel measurements by GC-MS were plotted in open circles with a fitted slope of 0.246. Samples were taken in the main tunnels in Shanghai and the detailed analysis method can be seen in Wang et al. (2010). The averaged EnRs directly measured from gasoline car and diesel truck emissions by PTR-ToF-MS were added as dashed line in red and black, respectively, by assuming the backgrounds of CH_3CN (0.1 ppbv) and CO (0.1 ppmv). The operation condition of PTR-ToF-MS in vehicle emission test was described in Wu et al. (2020). The $\Delta CH_3CN/\Delta CO$ ratio observed in a plume from New York was appended as well with a solid line (reported by de Gouw et al., 2009).

measurements. Based on the above discussion, we conclude that the data measured in biomass burning can clearly be separated from typical measurements in anthropogenic-influenced areas using the enhancement ratio of CH_3CN to CO, showing its potential as a more specific indicator to track biomass burning plumes in anthropogenic-influenced environments.

An example of the application of the correlation between CH_3CN and CO and their enhancement ratio as indicator to identify biomass burning from measurements in Changdao and Beijing is shown in Figure 4. The enhancement ratio calculations can be seen in Supporting Information Section 3. For Changdao measurements between April 5th 23:00 and April 6th 3:00, elevated mixing ratios of CH_3CN up to 1.6 ppb were observed and CH_3CN levels correlated well with CO ($R = 0.82$). The enhancement ratios of CH_3CN to CO during this period were also significantly elevated as well, compared to the enhancement ratios for the periods before and after the plume (0.31 ± 0.02 ppbv/ppmv, see Supporting Information Section S2). As the result, this plume was identified as biomass burning emissions. For the case of measurements in wintertime of Beijing, the CH_3CN levels were also observed to reach >1.5 ppbv above the typical background with an even better correlation with CO ($R = 0.97$). However, a low enhancement ratio (0.24 ± 0.01 ppbv/ppmv) was obtained by including all the data points, suggesting that biomass burning had minimal influence

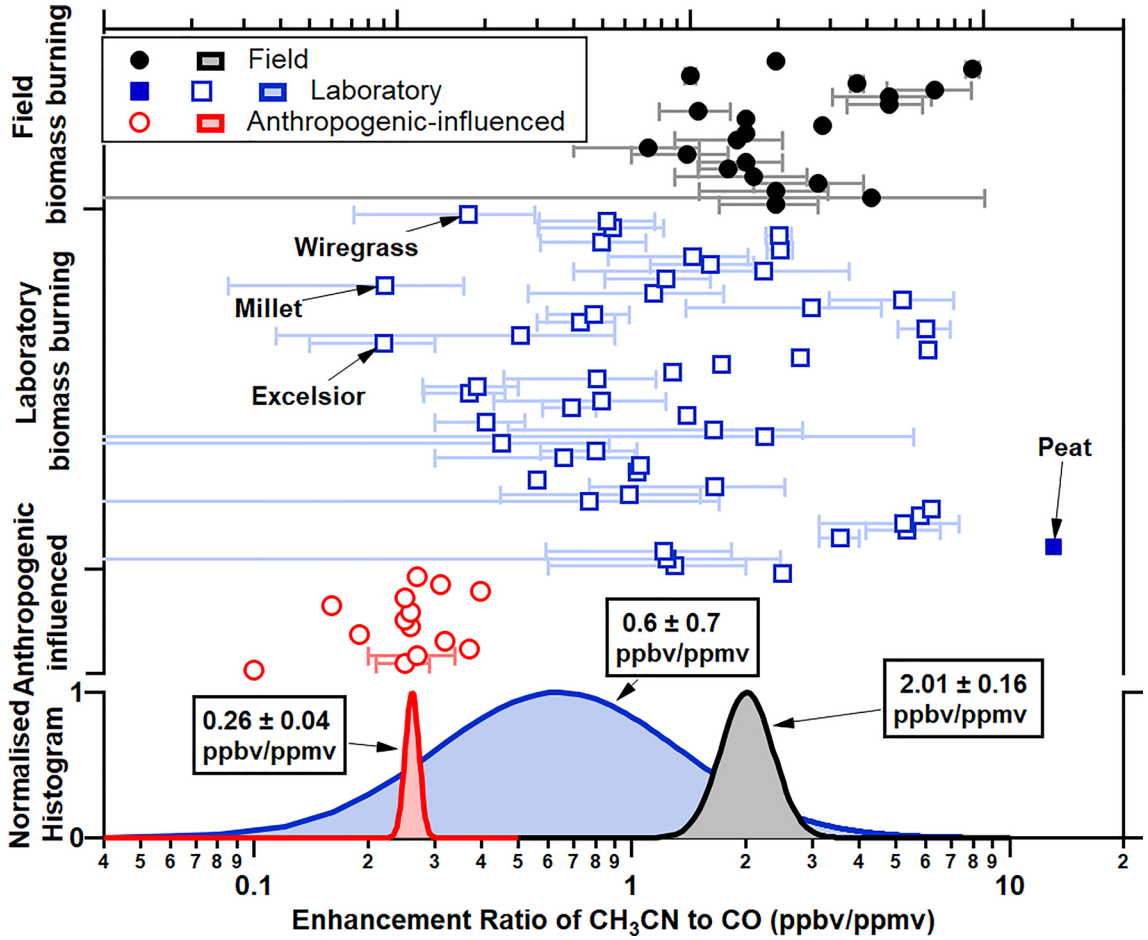

Figure 3. Enhancement ratios of CH_3CN to CO (ppbv/ppmv) measured in previous literature. The references can be seen in Table S4. The top panel has the enhancement ratios of CH_3CN to CO based on previous studies about biomass burning, including both in-situ measurement of local fires (in black) and the burning experiments simulated in the laboratory (in blue). The red open circles are the enhancement ratios reported from measurements in anthropogenic-influenced areas. The log-normalized histogram in the lower panel demonstrates the distinguishable range of EnRs in urban areas and in-situ biomass burning measurements. The separated histograms and the log-normal fits can be found in Figure S6. For the laboratory results, the histogram was made without the 17.3 ppbv/ppmv data point for peat.

during the example period. The two different cases about the measurements in Changdao and Beijing imply that applying the enhancement ratio of CH_3CN to CO as indicator can distinguish biomass burning from typical emissions in anthropogenic-influenced areas and avoid the possible misidentification when high CH_3CN levels are measured from other sources, such as vehicular emission in anthropogenic-influenced environments.

3.3. Further Consideration of Applying Enhancement Ratio as Indicator: Additional Sources

We have observed that narrow peaks of CH_3CN with quite a short timescale were captured occasionally during some of the urban measurements. Figure S6 shows two examples of measurements in Guangzhou and Los Angeles, respectively. As shown in Figure S6, without any significant change of CO ($R < 0.2$) and oxygenated volatile organic compounds (OVOCs) species that are emitted from biomass burning in large quantity (methanol as an example), the elevated CH_3CN levels were likely due to other sources with concentrated CH_3CN instead of biomass burning. This was also reported previously during ground measurements in Boulder, CO in US (Coggon et al., 2016). We speculate that these CH_3CN plumes were emitted from chemical laboratories nearby the measurement sites, as CH_3CN is used as solvent for several analytical instruments, e.g., liquid chromatograph and mass spectrometer with electrospray ion sources (U.S.EPA., 1996). Other studies also pointed out that solvent use might be a non-negligible source for

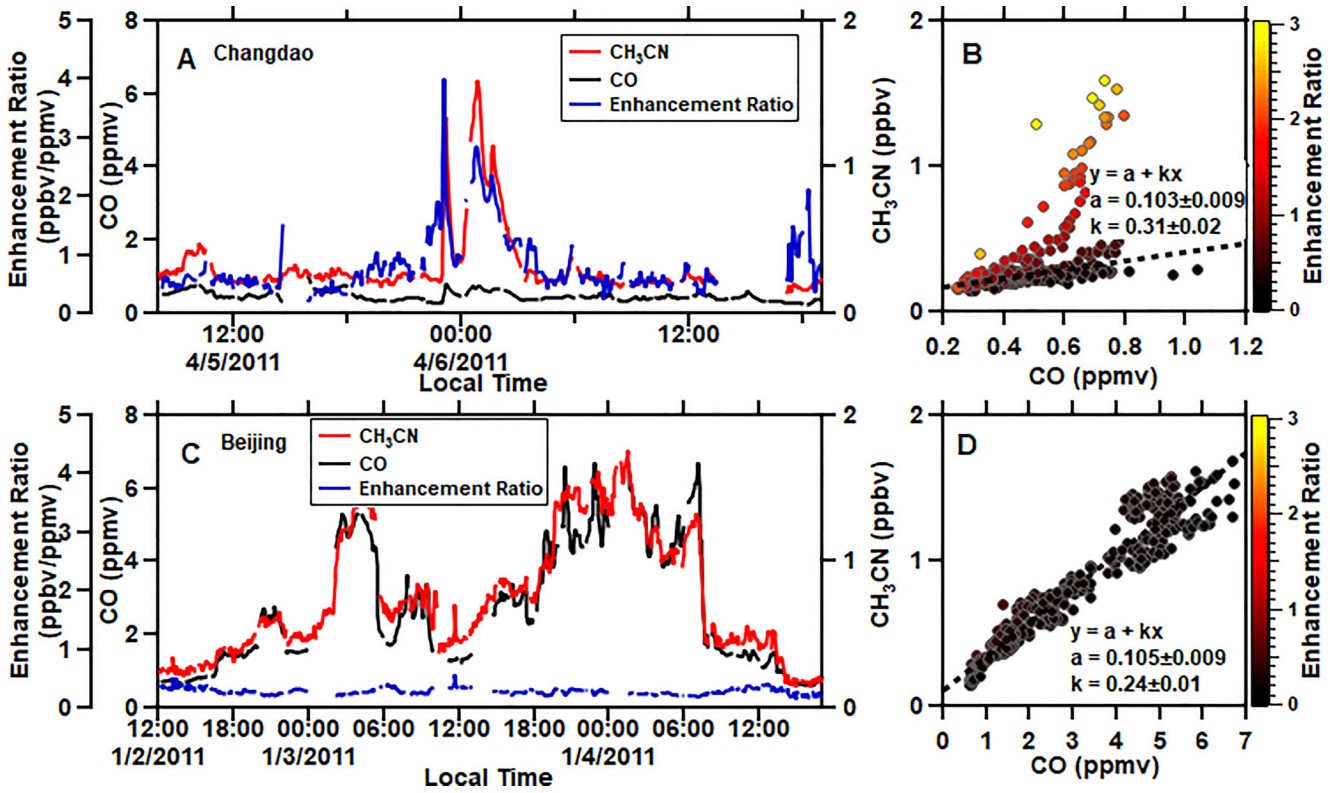

Figure 4. Time series of CO (in black, ppmv) and CH_3CN (in red, ppbv) mixing ratios observed in Changdao measured in 2011 (panel A) and Beijing measured in 2010 (panel C). The enhancement ratios ($\Delta CH_3CN/\Delta CO$) were also included in the time series plots (in blue). The scatter plots on the right panels show the correlation between CH_3CN and CO (panel B and D). The ODR fitted slopes and intercepts for the no-fire data of Changdao and entire example data of Beijing were added with one standard deviated associated. The data points in the scatter plots were all color-coded based on the enhancement ratios. Both scatter plots used the same color range to show the distinguished enhancement ratio.

CH_3CN in anthropogenic-influenced areas (Baudic et al., 2016; Languille et al., 2020; Storer et al., 2015; Yurdakul et al., 2013) and the contribution may be up to 50% in Paris (Languille et al., 2020). Here, we show that using the enhancement ratio of CH_3CN to CO, along with checking the correlation of CH_3CN with CO and/or other VOCs species that are known to be emitted by biomass burning, can effectively avoid misidentification due to these solvent-related emissions of CH_3CN in anthropogenic-influenced regions.

Residential combustion using solid fuel for cooking and heating covered about 2.8 billion people worldwide (Bonjour et al., 2013), in which biomass fuel accounted for a significant portion given its cheaper cost and easier access. Recognizing and tracking residential biomass burning is of importance for analyzing local atmospheric pollution. However, previous publications have shown that the $\Delta CH_3CN/\Delta CO$ of residential biomass burning varied from 0.03 ppbv/ppmv to 0.68 ppbv/ppmv (Bruns et al., 2017; Stockwell et al., 2015), which were much smaller compared with the $\Delta CH_3CN/\Delta CO$ range of field biomass burning summarized in Figure 3. The lower nitrogen content of the fuel used in the residential combustion was likely the reason (Bruns et al., 2017; Coggon et al., 2016). In rural areas, the emission of residential biomass burning can be the dominant source of local and regional pollution (Chafe et al., 2015; Languille et al., 2020; VanderSchelden et al., 2017; Venkataraman et al., 2005). Under such circumstances, other compounds should be included in the source apportionment analysis, such as furans, oxygenated aromatics, etc (Coggon et al., 2019). However, these compounds have relatively short atmospheric lifetimes given their high reactivities, so they can only be used as biomass burning tracers near the sources, which limits their applications. Future studies are needed to find more appropriate tracers for identifying residential biomass burning.

4. Conclusions

By summarizing the measurement data over China, the U.S., and several European cities, a large variation of CH_3CN in the ambient environment was revealed, ranging from 47 pptv to 660 pptv on average. A significant portion of the CH_3CN data measured in the field was well above the reported background levels, suggesting the widely existence of CH_3CN sources other than biomass burning. Positive correlations between CH_3CN and CO were found in anthropogenic-influenced areas based on the correlation analysis even with CH_3CN levels as high as several ppbv. Observed slopes of CH_3CN and CO suggested the significant impact of vehicle emission in anthropogenic-influenced environments in the world. The enhancement ratios of CH_3CN to CO were found as 2.01 ± 0.16 ppbv/ppmv for biomass burning, which is one order of magnitude larger than the ones obtained in urban measurement (0.26 ± 0.04 ppbv/ppmv). Compared with the CH_3CN absolute mixing ratio as the threshold for tracking biomass burning plume, the correlation with CH_3CN and CO and their enhancement ratio are found to be more specific indicators that can identify biomass burning under the interference from vehicle emission and solvent usage.

Data Availability Statement

Data of Los Angeles used in this paper can be found in the data server of National Oceanic and Atmospheric Administration (https://csl.noaa.gov/groups/csl7/measurements/2010calnex/Ground/DataDownload/). Data measured in Mexico City can be found in the data server of University Corporation for Atmospheric Research (https://data.eol.ucar.edu/master_lists/generated/milagro/). Other data used in this paper can be accessed via doi (https://doi.org/10.7910/DVN/HMWFNM).

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References

Aiken, A. C., De Foy, B., Wiedinmyer, C., Decarlo, P. F., Ulbrich, I. M., Wehrli, M. N., et al. (2010). Mexico city aerosol analysis during MILAGRO using high resolution aerosol mass spectrometry at the urban supersite (T0)-Part 2: Analysis of the biomass burning contribution and the non-fossil carbon fraction. *Atmospheric Chemistry and Physics*, *10*(12), 5315–5341. https://doi.org/10.5194/acp-10-5315-2010

Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T., et al. (2011). Emission factors for open and domestic biomass burning for use in atmospheric models. *Atmospheric Chemistry and Physics*, *11*(9), 4039–4072. https://doi.org/10.5194/acp-11-4039-2011

Alvarado, M. J., Lonsdale, C. R., Yokelson, R. J., Akagi, S. K., Coe, H., Craven, J. S., et al. (2015). Investigating the links between ozone and organic aerosol chemistry in a biomass burning plume from a prescribed fire in California chaparral. *Atmospheric Chemistry and Physics*, *15*(12), 6667–6688. https://doi.org/10.5194/acp-15-6667-2015

Baudic, A., Gros, V., Sauvage, S., Locoge, N., Sanchez, O., Sarda-Estève, R., et al. (2016). Seasonal variability and source apportionment of volatile organic compounds (VOCs) in the Paris megacity (France). *Atmospheric Chemistry and Physics*, *16*(18), 11961–11989. https://doi.org/10.5194/acp-16-11961-2016

Becker, K. H., & Ionescu, A. (1982). Acetonitrile in the lower troposphere. *Geophysical Research Letters*, *9*(12), 1349–1351. https://doi.org/10.1029/GL009i012p01349

Bhattarai, H., Saikawa, E., Wan, X., Zhu, H., Ram, K., Gao, S., et al. (2019). Levoglucosan as a tracer of biomass burning: Recent progress and perspectives. *Atmospheric Research*, *220*(November 2018), 20–33. https://doi.org/10.1016/j.atmosres.2019.01.004

Bian, H., Colarco, P. R., Chin, M., Chen, G., Rodriguez, J. M., Liang, Q., et al. (2013). Source attributions of pollution to the Western Arctic during the NASA ARCTAS field campaign. *Atmospheric Chemistry and Physics*, *13*(9), 4707–4721. https://doi.org/10.5194/acp-13-4707-2013

Bonjour, S., Adair-Rohani, H., Wolf, J., Bruce, N. G., Mehta, S., Prüss-Ustün, A., et al. (2013). Solid fuel use for household cooking: Country and regional estimates for 1980–2010. *Environmental Health Perspectives*, *121*(7), 784–790. https://doi.org/10.1289/ehp.1205987

Bruns, E. A., Slowik, J. G., El Haddad, I., Kilic, D., Klein, F., Dommen, J., et al. (2017). Characterization of gas-phase organics using proton transfer reaction time-of-flight mass spectrometry: Fresh and aged residential wood combustion emissions. *Atmospheric Chemistry and Physics*, *17*(1), 705–720. https://doi.org/10.5194/acp-17-705-2017

Cai, S., Zhu, L., Wang, S., Wisthaler, A., Li, Q., Jiang, J., & Hao, J. (2019). Time-resolved intermediate-volatility and semi volatile organic compound emissions from household coal combustion in Northern China. *Environmental Science and Technology*, *53*(15), 9269–9278. https://doi.org/10.1021/acs.est.9b00734

Chafe, Z. A., Brauer, M., Klimont, Z., Van Dingenen, R., Mehta, S., Rao, S., et al. (2015). Household cooking with solid fuels contributes to ambient PM2.5air pollution and the burden of disease. *Environmental Health Perspectives*, *122*(12), 1314–1320. https://doi.org/10.1289/ehp.1206340

Chantara, S., Thepnuan, D., Wiriya, W., Prawan, S., & Tsai, Y. I. (2019). Emissions of pollutant gases, fine particulate matters and their significant tracers from biomass burning in an open-system combustion chamber. *Chemosphere*, *224*, 407–416. https://doi.org/10.1016/j.chemosphere.2019.02.153

Chen, J., Li, C., Ristovski, Z., Milic, A., Gu, Y., Islam, M. S., et al. (2017). A review of biomass burning: Emissions and impacts on air quality, health and climate in China. *Science of the Total Environment*, *579*(November 2016), 1000–1034. https://doi.org/10.1016/j.scitotenv.2016.11.025

Coggon, M., Lim, C., Koss, A., Sekimoto, K., Yuan, B., Gilman, J., et al. (2019). OH-chemistry of non-methane organic gases (NMOG) emitted from laboratory and ambient biomass burning smoke: Evaluating the influence of furans and oxygenated aromatics on ozone and secondary NMOG formation. *Atmospheric Chemistry and Physics*, *19*(23), 1–42. https://doi.org/10.5194/acp-2019-516

Coggon, M., Warneke, C., Aikin, K. C., Veres, P. R., Yuan, B., Koss, A., et al. (2016). Emissions of nitrogen-containing organic compounds from the burning of herbaceous and arboraceous biomass: Fuel composition dependence and the variability of commonly used nitrile tracers. *Geophysical Research Letters*, *43*(18), 9903–9912. https://doi.org/10.1002/2016GL070562

Crilley, L. R., Bloss, W. J., Yin, J., Beddows, D. C. S., Harrison, R. M., Allan, J. D., et al. (2015). Sources and contributions of wood smoke during winter in London: Assessing local and regional influences. *Atmospheric Chemistry and Physics*, *15*(6), 3149–3171. https://doi.org/10.5194/acp-15-3149-2015

de Gouw, J. A., Cooper, O. R., Warneke, C., Hudson, P. K., Fehsenfeld, F. C., Holloway, J. S., et al. (2004). Chemical composition of air masses transported from Asia to the U.S. West coast during ITCT 2K2: Fossil fuel combustion versus biomass-burning signatures. *Journal of Geophysical Research: Atmospheres*, *109*(23), 1–15. https://doi.org/10.1029/2003JD004202

de Gouw, J. A., Warneke, C., Parrish, D. D., Holloway, J. S., Trainer, M., & Fehsenfeld, F. C. (2003). Emission sources and ocean uptake of acetonitrile (CH3CN) in the atmosphere. *Journal of Geophysical Research: Atmosphere*, *108*(11), 1–8. https://doi.org/10.1029/2002jd002897

de Gouw, J. A., Welsh-Bon, D., Warneke, C., Kuster, W. C., Alexander, L., Baker, A. K., et al. (2009). Emission and chemistry of organic carbon in the gas and aerosol phase at a sub-urban site near Mexico City in March 2006 during the MILAGRO study. *Atmospheric Chemistry and Physics*, *9*(10), 3425–3442. https://doi.org/10.5194/acp-9-3425-2009

Dunne, E., Galbally, I. E., Lawson, S., & Patti, A. (2012). Interference in the PTR-MS measurement of acetonitrile at m/z 42 in polluted urban air - A study using switchable reagent ion PTR-MS. *International Journal of Mass Spectrometry*, *319*(320), 40–47. https://doi.org/10.1016/j.ijms.2012.05.004

Fabbri, D., Torri, C., Simoneit, B. R. T., Marynowski, L., Rushdi, A. I., & Fabiańska, M. J. (2009). Levoglucosan and other cellulose and lignin markers in emissions from burning of Miocene lignites. *Atmospheric Environment*, *43*(14), 2286–2295. https://doi.org/10.1016/j.atmosenv.2009.01.030

Fourtziou, L., Liakakou, E., Stavroulas, I., Theodosi, C., Zarmpas, P., Psiloglou, B., et al. (2017). Multi-tracer approach to characterize domestic wood burning in Athens (Greece) during wintertime. *Atmospheric Environment*, *148*, 89–101. https://doi.org/10.1016/j.atmosenv.2016.10.011

Gilman, J. B., Lerner, B. M., Kuster, W. C., Goldan, P. D., Warneke, C., Veres, P. R., et al. (2015). Biomass burning emissions and potential air quality impacts of volatile organic compounds and other trace gases from temperate fuels common in the United States. *Atmospheric Chemistry and Physics*, *15*(15), 21713–21763. https://doi.org/10.5194/acpd-15-21713-2015

Gros, V., Gaimoz, C., Herrmann, F., Custer, T., Williams, J., Bonsang, B., et al. (2011). Volatile organic compounds sources in Paris in spring 2007. Part I: Qualitative analysis. *Environmental Chemistry*, *8*(1), 74–90. https://doi.org/10.1071/en10068

Guan, H., Wang, X., Han, R., Yuan, L., Meng, S., Wang, S., & Du, Z. (2020). High-resolution and -precision spectra of acetonitrile at the ν5-band for laser remote sensing. *Journal of Quantitative Spectroscopy and Radiative Transfer*, *255*. https://doi.org/10.1016/j.jqsrt.2020.107254

Hamm, S., & Warneck, P. (1990). The interhemispheric distribution and the budget of acetonitrile in the troposphere. *Journal of Geophysical Research*, *95*(D12). https://doi.org/10.1029/jd095id12p20593

Heilman, W. E., Liu, Y., Urbanski, S., Kovalev, V., & Mickler, R. (2014). Wildland fire emissions, carbon, and climate: Plume rise, atmospheric transport, and chemistry processes. *Forest Ecology and Management*, *317*, 70–79. https://doi.org/10.1016/j.foreco.2013.02.001

Hennigan, C. J., Sullivan, A. P., Collett, J. L., & Robinson, A. L. (2010). Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals. *Geophysical Research Letters*, *37*(9), 2–5. https://doi.org/10.1029/2010GL043088

Hoffmann, D., Tilgner, A., Iinuma, Y., & Herrmann, H. (2010). Atmospheric stability of levoglucosan: A detailed laboratory and modeling study. *Environmental Science and Technology*, *44*(2), 694–699. https://doi.org/10.1021/es902476f

Holzinger, R., Jordan, A., Hansel, A., & Lindinger, W. (2001). Automobile emissions of acetonitrile: Assessment of its contribution to the global source. *Journal of Atmospheric Chemistry*, *38*(2), 187–193. https://doi.org/10.1023/A:1006435723375

Holzinger, R., Wameke, C., Hansel, A., Jordan, A., Lindinger, W., Scharffe, D. H., et al. (1999). Biomass burning as a source of formaldehyde, acetaldehyde, methanol, acetone, acetonitrile, and hydrogen cyanide. *Geophysical Research Letters*, *26*(8), 1161–1164. https://doi.org/10.1029/1999GL900156

Hornbrook, R. S., Blake, D. R., Diskin, G. S., Fried, A., Fuelberg, H. E., Meinardi, S., et al. (2011). Observations of nonmethane organic compounds during ARCTAS; Part 1: Biomass burning emissions and plume enhancements, *Atmospheric Chemistry and Physics*, *11*(21), 11103–11130. https://doi.org/10.5194/acp-11-11103-2011

Inomata, S., Tanimoto, H., Fujitani, Y., Sekimoto, K., Sato, K., Fushimi, A., et al. (2013). On-line measurements of gaseous nitro-organic compounds in diesel vehicle exhaust by proton-transfer-reaction mass spectrometry. *Atmospheric Environment*, *73*, 195–203. https://doi.org/10.1016/j.atmosenv.2013.03.035

Jobson, B. T., Volkamer, R. A., Velasco, E., Allwine, G., Westberg, H., Lamb, B. K., et al. (2010). Comparison of aromatic hydrocarbon measurements made by PTR-MS, DOAS and GC-FID during the MCMA 2003 field experiment. *Atmospheric Chemistry and Physics*, *10*(4), 1989–2005. https://doi.org/10.5194/acp-10-1989-2010

Lacaux, J. P., Delmas, R., & Jambert, C. (1996). NOx emissions from African savanna fires. *Journal of Geophysical Research*, *101*, 585–595. https://doi.org/10.1029/96jd01624

Langford, B., Nemitz, E., House, E., Phillips, G. J., Famulari, D., Davison, B., et al. (2010). Fluxes and concentrations of volatile organic compounds above central London, UK. *Atmospheric Chemistry and Physics*, *10*(2), 627–645. https://doi.org/10.5194/acp-10-627-2010

Languille, B., Gros, V., Petit, J. E., Honoré, C., Baudic, A., Perrussel, O., et al. (2020). Wood burning: A major source of volatile organic compounds during wintertime in the Paris region. *Science of the Total Environment*, *711*(November 2019), 135055. https://doi.org/10.1016/j.scitotenv.2019.135055

Li, M., Shao, M., Li, L. Y., Lu, S. H., Chen, W. T., & Wang, C. (2014). Quantifying the ambient formaldehyde sources utilizing tracers. *Chinese Chemical Letters*, *25*(11), 1489–1491. https://doi.org/10.1016/j.cclet.2014.07.001

Lobert, J., Scharffe, D., Hao, W. M., Kuhlbusch, T. a, Seuwen, R., Warneck, P., & Crutzen, P. J. (1991). Experimental evaluation of biomass burning emissions: Nitrogen and carbon containing compounds. *Global biomass burning. Atmospheric, climatic, and biospheric implications*. Retrieved from http://inis.iaea.org/search/search.aspx?orig_q=RN:23066772

Lobert, J., Scharffe, D. H., Hao, W. M., & Crutzen, P. J. (1990). Importance of biomass burning in the atmospheric budgets of nitrogen-containing gases. *Nature*, *346*(6284), 552–554. https://doi.org/10.1038/346552a0

Maudlin, L. C., Wang, Z., Jonsson, H. H., & Sorooshian, A. (2015). Impact of wildfires on size-resolved aerosol composition at a coastal California site. *Atmospheric Environment*, *119*, 59–68. https://doi.org/10.1016/j.atmosenv.2015.08.039

Murphy, J. G., Oram, D. E., & Reeves, C. E. (2010). Measurements of volatile organic compounds over West Africa. *Atmospheric Chemistry and Physics*, *10*(12), 5281–5294. https://doi.org/10.5194/acp-10-5281-2010

Puxbaum, H., Caseiro, A., Sánchez-Ochoa, A., Kasper-Giebl, A., Claeys, M., Gelencsér, A., et al. (2007). Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background. *Journal of Geophysical Research Atmospheres*, *112*(23), 1–11. https://doi.org/10.1029/2006JD008114

Sahu, L. K., Yadav, R., & Pal, D. (2016). Source identification of VOCs at an urban site of western India: Effect of marathon events and anthropogenic emissions. *Journal of Geophysical Research : Atmosphere*, *121*(5), 2416–2433. https://doi.org/10.1038/175238c010.1002/2015jd024454

Sarkar, C., Sinha, V., Kumar, V., Rupakheti, M., Panday, A., Mahata, K. S., et al. (2016). Overview of VOC emissions and chemistry from PTR-TOF-MS measurements during the SusKat-ABC campaign: high acetaldehyde, isoprene and isocyanic acid in wintertime air of the Kathmandu Valley. *Atmospheric Chemistry and Physics*, *16*(6), 3979–4003. https://doi.org/10.5194/acp-16-3979-2016

Seco, R., Peñuelas, J., Filella, I., Llusia, J., Schallhart, S., Metzger, A., et al. (2013). Volatile organic compounds in the western Mediterranean basin: Urban and rural winter measurements during the DAURE campaign. *Atmospheric Chemistry and Physics*, *13*(8), 4291–4306. https://doi.org/10.5194/acp-13-4291-2013

Shi, Y., Xi, Z., Simayi, M., Li, J., & Xie, S. (2020). Scattered coal is the largest source of ambient volatile organic compounds during the heating season in Beijing. *Atmospheric Chemistry and Physics*, 1–42. https://doi.org/10.5194/acp-2020-168

Singh, H. B., Salas, L., Herlth, D., Kolyer, R., Czech, E., Viezee, W., et al. (2003). In situ measurements of HCN and CH3CN over the Pacific Ocean: Sources, sinks, and budgets. *Journal of Geophysical Research: Atmosphere*, *108*(20). https://doi.org/10.1029/2002jd003006

Singh, H. B., Salas, L. J., Chatfield, R. B., Czech, E., Fried, A., Walega, J., et al. (2004). Analysis of the atmospheric distribution, sources, and sinks of oxygenated volatile organic chemicals based on measurements over the Pacific during TRACE-P. *Journal of Geophysical Research D: Atmospheres*, *109*(15). https://doi.org/10.1029/2003JD003883

Stockwell, C. E., Veres, P. R., Williams, J., & Yokelson, R. J. (2015). Characterization of biomass burning emissions from cooking fires, peat, crop residue, and other fuels with high-resolution proton-transfer-reaction time-of-flight mass spectrometry. *Atmospheric Chemistry and Physics*, *15*(2), 845–865. https://doi.org/10.5194/acp-15-845-2015

Stone, E. A., Snyder, D. C., Sheesley, R. J., Sullivan, A. P., Weber, R. J., & Schauer, J. J. (2008). Source apportionment of fine organic aerosol in Mexico City during the MILAGRO experiment 2006. *Atmospheric Chemistry and Physics*, *8*(5), 1249–1259. https://doi.org/10.5194/acp-8-1249-2008

Storer, M., Curry, K., Squire, M., Kingham, S., & Epton, M. (2015). Breath testing and personal exposure - SIFT-MS detection of breath acetonitrile for exposure monitoring. *Journal of Breath Research*, *9*(3). https://doi.org/10.1088/1752-7155/9/3/036006

U.S.EPA. (1996). *Method 8315A (SW-846). Determination of Carbonyl Compounds by High Performance Liquid Chromatography (HPLC). Revision 1*. Washington, DC. https://doi.org/10.1021/ac60283a030

Valach, A. C., Langford, B., Nemitz, E., MacKenzie, A. R., & Hewitt, C. N. (2014). Concentrations of selected volatile organic compounds at kerbside and background sites in central London. *Atmospheric Environment*, *95*, 456–467. https://doi.org/10.1016/j.atmosenv.2014.06.052

VanderSchelden, G., de Foy, B., Herring, C., Kaspari, S., VanReken, T., & Jobson, B. (2017). Contributions of wood smoke and vehicle emissions to ambient concentrations of volatile organic compounds and particulate matter during the Yakima wintertime nitrate study. *Journal of Geophysical Research*, *122*(3), 1871–1883. https://doi.org/10.1002/2016JD025332

Venkataraman, C., Habib, G., Eiguren-Fernandez, A., Miguel, A. H., & Friedlander, S. K. (2005). Residential biofuels in South Asia: Carbonaceous aerosol emissions and climate impacts. *Science*, *307*(5714), 1454–1456. https://doi.org/10.1126/science.1104359

Wang, B., Shao, M., Lu, S. H., Yuan, B., Zhao, Y., Wang, M., et al. (2010). Variation of ambient non-methane hydrocarbons in Beijing city in summer 2008. *Atmospheric Chemistry and Physics*. https://doi.org/10.5194/acp-10-5911-2010

Wang, G., Cheng, S., Wei, W., Zhou, Y., Yao, S., & Zhang, H. (2016). Characteristics and source apportionment of VOCs in the suburban area of Beijing, China. *Atmospheric Pollution Research*, *7*(4), 711–724. https://doi.org/10.1016/j.apr.2016.03.006

Wang, Q., Shao, M., Liu, Y. Y. Y., William, K., Paul, G., Li, X., et al. (2007). Impact of biomass burning on urban air quality estimated by organic tracers: Guangzhou and Beijing as cases. *Atmospheric Environment*, *41*(37), 8380–8390. https://doi.org/10.1016/j.atmosenv.2007.06.048

Warneke, C., McKeen, S. A., de Gouw, J. A., Goldan, P. D., Kuster, W. C., Holloway, J. S., et al.et al. (2007). Determination of urban volatile organic compound emission ratios and comparison with an emissions database. *Journal of Geophysical Research Atmospheres*, *112*(10). https://doi.org/10.1029/2006JD007930

Wisthaler, A., Hansel, A., Dickerson, R. R., & Crutzen, P. J. (2002). Organic trace gas measurements by PTR-MS during INDOEX 1999. *Journal of Geophysical Research Atmospheres*, *107*(19), 1–11. https://doi.org/10.1029/2001JD000576

Wu, C., Wang, C., Wang, S., Wang, W., Yuan, B., Qi, J., et al. (2020). Measurement Report: Important contributions of oxygenated compounds to emissions and chemistry of VOCs in urban air. *Atmospheric Chemistry and Physics*, 1–37. https://doi.org/10.5194/acp-2020-152

Yan, C., Zheng, M., Sullivan, A. P., Shen, G., Chen, Y., Wang, S., et al. (2018). Residential coal combustion as a source of Levoglucosan in China. *Environmental Science and Technology*, *52*(3), 1665–1674. https://doi.org/10.1021/acs.est.7b05858

Yokelson, R. J., Burling, I. R., Gilman, J. B., Warneke, C., Stockwell, C. E., De Gouw, J., et al. (2013). Coupling field and laboratory measurements to estimate the emission factors of identified and unidentified trace gases for prescribed fires. *Atmospheric Chemistry and Physics*, *13*(1), 89–116. https://doi.org/10.5194/acp-13-89-2013

Yuan, B., Liu, Y., Shao, M., Lu, S., Streets, D. G., Yuan, B., et al. (2010). Biomass burning contributions to ambient VOCs species at a receptor site in the Pearl River delta (PRD), China. *Environmental Science and Technology*, *44*(12), 4577–4582. https://doi.org/10.1021/es1003389

Yurdakul, S., Civan, M., & Tuncel, G. (2013). Volatile organic compounds in suburban Ankara atmosphere, Turkey: Sources and variability. *Atmospheric Research*, *120–121*, 298–311. https://doi.org/10.1016/j.atmosres.2012.09.015

References From the Supporting Information

Afif, C., Jambert, C., Michoud, V., Colomb, A., Eyglunent, G., Borbon, A., et al. (2016). NitroMAC: An instrument for the measurement of HONO and intercomparison with a long-path absorption photometer. *Journal of Environmental Sciences (China)*, *40*, 105–113. https://doi.org/10.1016/j.jes.2015.10.024

Wang, B. L., Liu, Y., Shao, M., Lu, S. H., Wang, M., Yuan, B., et al. (2016). The contributions of biomass burning to primary and secondary organics: A case study in Pearl River Delta (PRD), China. *Science of the Total Environment*, *569–570*, 548–556. https://doi.org/10.1016/j.scitotenv.2016.06.153

Yuan, B., Hu, W. W., Shao, M., Wang, M., Chen, W. T., Lu, S. H., et al. (2013). VOC emissions, evolutions and contributions to SOA formation at a receptor site in Eastern China. *Atmospheric Chemistry and Physics*, *13*(17), 8815–8832. https://doi.org/10.5194/acp-13-8815-2013