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Evaluating the applicability of the ratio of $PM_{2.5}$ and carbon monoxide as source signatures

Meng Xiu [a], Rohan Jayaratne [a], Phong Thai [a, b], Bryce Christensen [a], Isak Zing [a], Xiaoting Liu [a], Lidia Morawska [a, c]*

[a] International Laboratory for Air Quality and Health, Queensland University of Technology, 4000, Brisbane, Australia

[b] Queensland Alliance for Environmental Health Science, The University of Queensland, 4102, Brisbane, Australia

[c] Global Centre for Clean Air Research (GCARE), Department of Civil and Environmental Engineering, Faculty of Engineering and Physical Sciences, University of Surrey, Guildford GU2 7XH, United Kingdom

Corresponding Author:

*Distinguished Professor Lidia Morawska, International Laboratory for Air Quality and Health, Institute of Health and Biomedical Innovation, Queensland University of Technology, Brisbane, Queensland 4001, Australia. Email: l.morawska@qut.edu.au

Abstract

Air pollution is among the top risk faced by people around the world, and therefore combating it is among the top priorities. It begins with identifying the sources that contribute the most to local air pollution to prioritize their control. There are advanced methods for source identification and apportionment, but such methods are not available in many low-income countries and not everywhere in all high-income countries. We propose a simplified method by using source the signatures to help obtain information about the local source contribution if no other methods are available. Using low-cost monitors, particle mass ($PM_{2.5}$) and carbon monoxide (CO) concentrations were measured and the ratio of CO/$PM_{2.5}$ was determined. We investigated outdoor and indoor sources, including vehicular exhaust, combustion of biomass, incense and mosquito coil burning, and cigarette smoking. The results show that the ratios differed significantly between certain pollutant sources. Compressed natural gas (CNG) engines have a high ratio (mean value of 972 ± 419), which is attributed to relatively low $PM_{2.5}$ emissions, while ship emissions and cigarette smoke recorded a relatively low ratio. Most traffic emissions recorded higher ratios than those of bushfire emissions, and ratios of most outdoor pollutant sources were much higher than those of indoor pollutant sources. There is a clear trend for ratios to decrease from high to low for CNG, petrol, diesel for buses, and fuel for ships. Our results suggest that the ratio of CO/$PM_{2.5}$ can be used as an effective method to identify pollution sources.

Keywords: air pollution; carbon monoxide; $PM_{2.5}$; traffic emissions; pollution sources.

1. Introduction

With growing concerns over increasing air pollution, it is of critical importance to identify combustion sources that contribute to pollution of the local environments. The availability of source signatures can be used as a support tool to obtain information on contributions from specific local sources and to develop appropriate air quality management and control strategies(Morawska and Zhang, 2002).Source signatures may be used to aid source apportionments. Zhang et al. (2003) investigated enrichment factors of inorganic chemical elements and chemical compositions in $PM_{2.5}$, which provided an effective method to distinguish local sources from external sources such as dust. Similar studies, using the source profiles of organic compounds or elements in atmospheric particulate matter, have been reported by Choi et al. (2001), Gilman et al. (2013), and Manoli et al. (2002). The number or mass size distribution of PM (particulate matter) and organic species can be a good parameter for distinguishing between PM from different emission sources. For instance, the fine particle size fraction (diameter < 2.5 μm) is typically dominated by combustion sources (Kleeman et al., 2008; McDonald et al., 2003), and in urban areas where vehicle emissions are one of the main sources, about 80% are in the ultrafine range (diameter < 0.1 μm) (Morawska et al., 1998). Another study by Morawska et al. (2006) suggested that the particle size distribution can be considered as a source signature, because the size distribution of an industrial facility is distinct from that of vehicle emissions. The ratio of compounds, elements or isotopes can also be considered as a source signature. For example, polycyclic aromatic hydrocarbon (PAH) molecular diagnostic ratios can be used to distinguish natural from anthropogenic emissions (Jautzy et al., 2013); the ratios of elemental carbon (EC) and organic carbon (OC) can differentiate fossil and non-fossil sources (Szidat et al., 2009), δ15N values of the N mixture in atmospheric samples can identify the difference between coal combustion and urban transportation (Wang et al., 2017), and ratios of metallic isotopes can discriminate between urban PM sources (Souto-Oliveira et al., 2018). In addition, the gas-to-particle ratio ($SO_2/PM_{2.5}$, $CO/PM_{2.5}$, and $NO_x/PM_{2.5}$) was applied for the first time to split the source apportionment of gasoline and diesel vehicles (Marmur et al., 2005). Overall, however, the strategies outlined above are difficult and complex; some are dependent on long-term monitoring data, some on emission inventories and/or dispersion models, and some on detailed knowledge of sources and emission profiles. Therefore, a simple way to distinguish pollutant sources by using a suitable source signature could be a very useful tool.

In recent years, the increased focus on ambient air pollution has led to the emergence of many low-cost sensors for air quality monitoring. The application of sensors has burgeoned due to their low cost, portability, and enormous capability for information processing (Kumar et al., 2015; Morawska et al., 2018). Low-cost sensors make it possible for widely distributed rural or remote regions to obtain monitoring data. The objective of this work was to propose a source signature that can be detected by low-cost sensors and can be used for source identification and apportionment. We show that this can be achieved with mass concentration ratios of CO to $PM_{2.5}$ ($CO/PM_{2.5}$). Our ratio results provide scientific guidance for distinguishing a range of combustion sources.

2. Methods

In this project, low-cost monitors were used to measure CO and $PM_{2.5}$ concentrations from different sources, including vehicle emissions, ship emissions, bushfires, household biomass combustion, cigarette smoke, and combustion emissions from incense and mosquito coils, in the field and in the laboratory, in Australia and overseas.

2.1. Instrumentation

The KOALA (Knowing Our Ambient Local Air-quality) monitor is a stand-alone monitor powered by a solar panel and built-in battery unit, with two low-cost sensors (a Plantower PMS1003 sensor and an Alphasense CO-B4) that measure PM and CO concentrations, respectively (Liu et al., 2020; Jayaratne et al., 2021). The Plantower PMS1003 sensor monitors particle mass with a minimum detectable particle size of 0.3 μm. It operates on a laser light scattering principle for the detection of particles. The particle number is measured and reported in six particle size fractions between 0.3 and 10 μm, and particle mass concentrations are reported in three size classes (PM_1, $PM_{2.5}$, and PM_{10}) expressed in units of $\mu g\, m^{-3}$. The Alphasense CO-B4 sensor is a passive device using the principle of electrochemical sensing to determine the CO concentration in units of parts per million (ppm). The performance of the two sensors in the KOALA air quality monitor has been extensively evaluated both in the laboratory and in the field. The results are reported in detail in our earlier publications (Jayaratne et al., 2020a,b, 2021; Liu et al., 2020; Kuhn et al., 2020). A built-in SIM card enables real-time data to be transmitted

from the sensor units to a central in-cloud database through the 3G/4G network. The data can also be stored on an SD card for later download and analysis.

2.2. Measurement

A number of KOALA monitors have been installed and operated successfully over the past 3 years, both in Australia and overseas. Much of the data analysed in this paper were derived from these monitors, complemented by data from several of our laboratory studies.

2.2.1. Field measurement

The field study was carried out in nine sites in Australia, China and the Solomon Islands. In Australia, we selected several representative locations. The data were downloaded from the in-cloud database for analysis. Detailed information about the locations and monitoring periods is shown in Table S1. Briefly, Charlotte Street and Ipswich Road are two urban streets in Brisbane, Australia, with high vehicle traffic and with light-duty vehicle emissions being the main pollutant source. The Mater Hill busway station in Brisbane is not influenced by vehicle emissions other than from compressed natural gas (CNG) and diesel buses. During the monitoring period, bus types and stop times were recorded manually. The Gap is a north-western suburb in Brisbane. The Blue Mountains region is located west of Sydney in New South Wales, where the air quality is sometimes affected by bushfires. Station Pier, located at Port Melbourne in Australia, serves as a transport hub for passenger and cruise ships. The Northern 5th Ring Road in Beijing, China, is a busy street right through the day and night. In the Solomon Islands, air pollution is enhanced by biomass combustion especially during cooking times.

2.3. Laboratory measurements

We conducted a series of studies in a laboratory chamber using emissions from cigarette smoke, mosquito coils and incense. These are recognized as important sources of indoor air pollution. The chamber had a volume of 0.1 m^3 with dimensions of 47 cm × 37 cm × 54 cm (H × L × D). The Koala unit was placed on the floor near the center of the chamber. A NOVA SDL607 mini-low-cost PM sensor with a digital display was placed next to it to give an instantaneous indication of the $PM_{2.5}$ for practical

purposes only. Before each trial, the chamber was left open for at least 30 min and then flushed with clean air for several minutes to remove pollutant residues from the previous trial. The pollutants were introduced by inserting the combustible source through a hole in the chamber for approximately 1 s.

2.4. Data analysis and calculations

$PM_{2.5}$ concentrations were reported in units of μg m^{-3}. The CO values were converted from ppm to μg m^{-3}, assuming a pressure of 1 atmosphere and a temperature of 25 °C using the following relationship:

Concentration (μg m^{-3}) = 0.0409 × concentration (ppm) × molecular weight × 1000

As the same with the unit of $PM_{2.5}$, at each interval, the ratio of $PM_{2.5}$ and CO concentrations was calculated for each experiment.

At Brisbane CBD (CBD), Woolloongabba (WG) and Beijing (BJ), the ratios were derived from the concentrations observed in the general environment. At the Mater Hill busway station, we considered matching PM and CO spikes as buses traveled past the platform. When spikes overlapped from different buses, these events were discarded. Bus types (diesel or CNG) were identified by noting their ID numbers. Cases where a bus travelled too fast to determine the bus type or two buses passed very close to each other were discarded. A similar method was adopted at Port Melbourne. Generally, $PM_{2.5}$ and CO spikes were observed when ships docked or left the port (Jayaratne et al, 2020). For the other locations—biomass combustion in Brisbane CBD (bushfire), The Gap (bushfire), the Blue Mountains (bushfire) and Honiara (home heating and cooking)—we studied elevated concentrations: $PM_{2.5}$ concentrations above 25 μg m^{-3} (national air quality standards in Australia for $PM_{2.5}$ in the ambient environment) and the corresponding CO concentrations over the entire sampling period for data analysis. In the laboratory studies, all data for $PM_{2.5}$ and CO concentrations were used for the calculation of ratios.

All statistical analyses were performed with R Version 2.5.1 (R foundation for Statistical Computing, www.r-project.org, Vienna, Austria). P-values of less than 0.05 were considered statistically significant.

3. Results and discussion

The ratio results (mean, IQR and 5% and 95% percentiles) are shown graphically in Figure 1. Of the vehicle fuels, CNG had the highest ratio, followed by petrol and diesel, and the ratio for biomass combustion was at a similar level to diesel. Different types of incense emitted different levels of $PM_{2.5}$ and CO concentrations, which is confirmed in many studies (Jetter et al., 2002; Lee and Wang, 2004; Ongwandee and Pipithakul, 2010). Nevertheless, it is interesting that the ratios of these indoor pollutant sources were similar. Overall, we can see clearly that land traffic emissions in particular had higher ratios than other combustion processes.

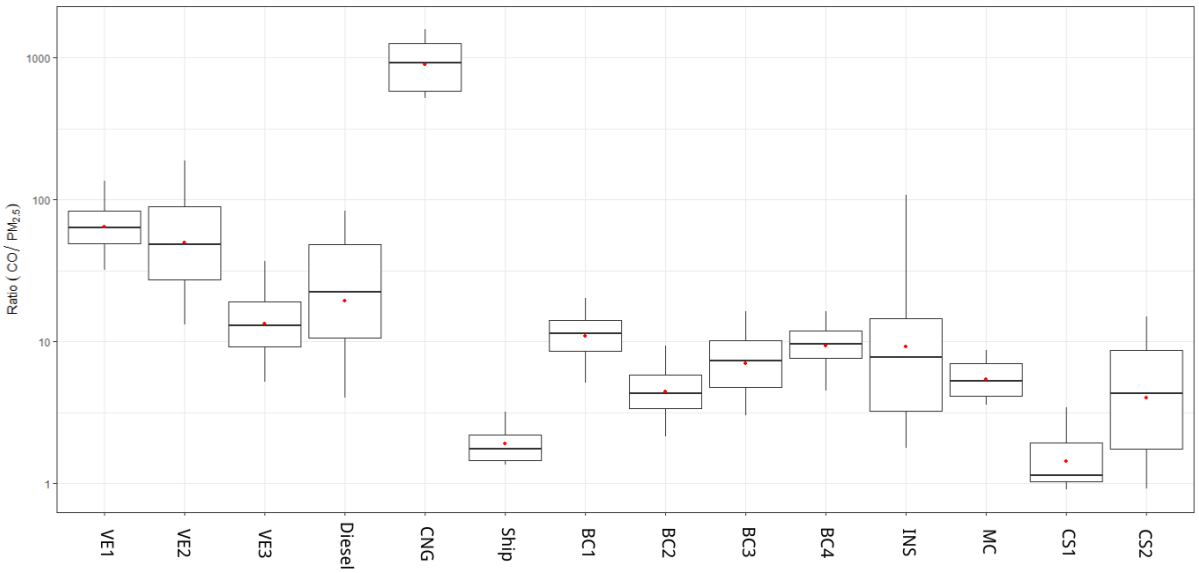

Figure 1. Boxplot with the mean, median, interquartile range (IQR), 5th percentile and 95th percentile of the ratio. (VE: vehicle emission; Diesel: diesel buses; CNG: compressed natural gas buses; Ship: ship emissions; BC: biomass combustion; INS: incense combustion; MC: mosquito coil combustion; CS: cigarette smoke). (VE1: Brisbane CBD vehicle; VE2: Woolloongabba; VE3: Beijing; BC1: The Gap; BC2: Brisbane CBD bushfire; BC3: Blue Mountains; BC4: Honiara; CS1: cigarette inserted in the chamber; CS2: cigarette smoke blown into the chamber)

Diesel engines are known to produce less CO (Hesterberg, Lapin et al. 2008) and more $PM_{2.5}$ (Schauer et al., 1996) (Dallmann et al., 2014) than petrol and CNG engines, reducing the ratio of $PM_{2.5}$ and CO concentrations substantially. As observed in this work, the ratio of diesel buses was much lower than that from internal combustion engines. Beijing, representing China's rapidly developing cities, has implemented a strict standard that diesel trucks are forbidden in urban areas. Therefore, as in Brisbane,

petrol vehicles are the main contributors to traffic emissions in Beijing. However, the ratio of VE3 was significantly different from VE1 and VE2, but close to Diesel, as shown in Figure 1, implying that the contribution of $PM_{2.5}$ emissions is complex in Beijing. We speculate that the higher $PM_{2.5}$ background concentration caused by larger scale air pollution led to a lower ratio in Beijing than in Brisbane. The average $PM_{2.5}$ concentration in Beijing in July 2018 was 47.9 $\mu g/m^3$. An extremely low ratio was observed for ship emissions at Port Melbourne, but in contrast with combustion emissions, the CO and $PM_{2.5}$ values of ship emissions were both low (Fig. S1), owing to the fuel type and engine system of ships. In general, among traffic pollutant sources, the signature for the emission from on-road motor vehicles and ships is evident. The pattern is $Ratio_{CNG} > Ratio_{petrol} > Ratio_{diesel} > Ratio_{ship}$. Additionally, from the perspective of outdoor and indoor pollutant sources, the ratios of all indoor pollutant sources in this study were lower than those of most outdoor pollutant sources.

Although the ratios of some of the sources overlap, thus making it difficult to unequivocally distinguish between the sources, there are many situations when the ratios are clearly different, such as those from diesel and petrol emissions. Use of the $CO/PM_{2.5}$ ratio to identify sources is of particular value when more sophisticated source identification techniques are not available. Other factors, such as elevated concentrations of NO_2 or SO_2 can be used to separately identify combustion sources. However, this method was outside the scope of this study, which was limited to CO only. Unlike other methods used to distinguish pollutant sources, the concentration of CO and $PM_{2.5}$ is much easier to obtain without complicated measurement techniques. Furthermore, the ratio of $CO/PM_{2.5}$ is reliable and not affected by measuring instruments. Although CO and $PM_{2.5}$ concentrations are affected by sources and combustion processes, our findings demonstrate that the ratios of $CO/PM_{2.5}$ from various pollution sources present distinct patterns. This study suggests a novel method to find a source signature. We propose that this method can be conveniently applied in various environmental conditions for identifying emission sources. It can be used in areas with serious air pollution, from traffic emissions, or even for bushfire emissions as well as the indoor environment.

4. Conclusion

Most ratios of traffic emissions are higher than those of general combustion emissions, such as burning of biomass, incense and mosquito coils. CNG engines have an extremely high ratio due to low $PM_{2.5}$ emissions and high CO emissions. In contrast, the high $PM_{2.5}$ emissions and low CO emissions from diesel engines result in a low ratio. In summary, obvious differences exist in the ratios for different sources, such as vehicle emissions vs biomass emissions, and CNG engines vs diesel engines. The findings from this work indicate that the $CO/PM_{2.5}$ ratio can be used as a novel source signature, and this ratio may be applied to identify combustion-generated pollutant sources and in turn help in source control.

CRediT author statement

Meng Xiu: Conceptualization, Investigation, Methodology, Writing- Original draft preparation**. Rohan Jayaratne:** Writing- Reviewing and Editing, Supervision. **Phong Thai**: Writing- Reviewing and Editing, Supervision. Bryce Christensen: Software. **Isak Zing**: Software. **Xiaoting Liu:** Writing- Reviewing and Editing. Lidia Morawska: Resources, Supervision, Writing- Reviewing and Editing, Funding Acquisition.

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