Reconciling discrepancies in the source characterization of VOCs between emission inventories and receptor modeling

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ABSTRACT

Emission inventory (EI) and receptor model (RM) are two of the three source apportionment (SA) methods recommended by Ministry of Environment of China and used widely to provide independent views on emission source identifications. How to interpret the mixed results they provide, however, were less studied. In this study, a cross-validation study was conducted in one of China's fast-developing and highly populated city cluster- the Pearl River Delta (PRD) region. By utilizing a highly resolved speciated regional EI and a region-wide gridded volatile organic compounds (VOCs) speciation measurement campaign, we elucidated underlying factors for discrepancies between EI and RM and proposed ways for their interpretations with the aim to achieve a scientifically plausible source identification. Results showed that numbers of species, temporal and spatial resolutions used for comparison, photochemical loss of reactive species, potential missing sources in EI and tracers used in RM were important factors contributed to the discrepancies. Ensuring the consensus of species used in EIs and RMs, utilizing a larger spatial coverage and longer time span, addressing the impacts of photochemical losses, and supplementing emissions from missing sources could help reconcile the discrepancies in VOC source characterizations acquired using both approaches. By leveraging the advantages and circumventing the disadvantages in both methods, the EI and RM could play synergistic roles to obtain robust SAs to improve air quality management practices.

Key Words: Source characterization; VOCs; Emission inventory; Receptor models; Discrepancy

1. Introduction

Air pollution has emerged as a serious concern for many rapidly developing nations such as China. The premise of effective air pollution control is reliable source identification (Zhong *et al.*, 2013). To guide the emission source characterization, Ministry of Environment of China issued the guideline for emission source apportionment and recommended three methods, i.e., emission inventory (EI), receptor model (RM) and numerical methods such as the Comprehensive Air-quality Model with extensions (CAMx) (MEP, 2012). These three methods track down the emission sources from different perspectives and subsequently, provide varied results on source identification. In particular, EI and RM are widely used due to the complexities and higher data demand of numerical methods. The question on how to interpret the mixed results EI and RM generate and leverage the advantages of both methods, therefore, emerges with practical importance to support the policy-making process for air pollution control.

EI and RM quantify the emission sources from different angles. Typically, EI follows the bottom-up methodology to estimate the primary emissions for a given averaging time and geographic area. It involves estimation using statistics of activity level data (e.g., fuel consumption, product output, population of vehicles) and emission factors. For each source category, the bulk inventory (total emissions of a pollutant) for a given pollutant is typically based on the product of an emission factor and an activity factor. For some pollutants comprised by multiple species such as $PM_{2.5}$ (particulate matter with dynamic diameter less than 2.5 µm) and volatile organic compounds (VOCs), speciated inventory will be developed combining the bulk inventory with speciated source profiles (The percentage of different species in a source's emission). The established bulk or speciated inventory can be further refined to different temporal and spatial resolutions using surrogate data such as the temporal profiles of traffic flow, industrial activities and the spatial location of enterprise, road network and population density. The overall uncertainty in the inventory depends on the precision, accuracy, and representativeness of activity level data, emission factor, source profiles as well as the temporal and spatial surrogates (NARSTO, 2005; Miller *et al*., 2006).

RM, by contrast, generally follows the top-down based methodology. It statistically apportions the measured ambient air pollutant concentrations, for multiple time periods at one or multiple monitoring sites, to the emission sources according to some pre-knowledge of their emission characteristics (primarily their chemical characteristics). The site- and time-specific ambient VOC species measurements are subject to sampling and analytical errors and to meteorological variability (Karagulian & Belis, 2012; Belis *et al*., 2015). Uncertainties in statistical inferences regarding source apportionment arise as a result of tracer elements that are common to multiple sources, lack of locally-representative emission source profiles, adoption of different receptor models, effects of reaction loss on different species, and judgment regarding interpretation of results (Hopke, 1991; Watson *et al*., 2001; Morino *et al*., 2011; Yuan *et al*., 2012; Ling & Guo, 2014; Ou *et al*., 2015a).

Due to their different ways to track down emissions and sources of uncertainty, it is not surprising that they can produce mixed results for source apportionment (Leuchner & Rappenglück, 2010; Morino *et al*., 2011; Wang *et al*., 2014). For example, quite a few of studies compared VOCs emission source identification results between the emission inventory and receptor models, and found significant inconsistencies in source contributions, especially for solvent use, Liquefied Petroleum Gas (LPG) uses, and biogenic sources (e.g., Fujita *et al.*, 1995; Scheff *et al.*, 1996; Watson *et al.*, 2001; Morino *et al.*, 2011; Wang *et al.*, 2014). In China, Zheng *et al*. (2009a) compared the source apportionment by EI with receptor modelling by Liu *et al*. (2008). General consistency was gained on the high contributions from gasoline vehicles, coating and solvents, but large discrepancies were observed in the contribution of LPG, and some specific areas featured by high local emission loadings. Despite of the observed discrepancies, the question of how to interpret the mixed and sometimes conflicting answers for source identification remains less studied. Reasons responsible for the discrepancies scattered in different studies and they were proposed and studied in a somewhat biased way with the underlying assumption that one of the methods is more reliable and the discrepancies are mainly attributed by the limitation or flaw of the other. For studies focused on EI, representativeness of sampling time and sites, photochemical loss and the tracers used in RM were questioned (Zheng *et al*., 2009a). As for studies based on RM, they argued that EI may fall short of the data quality of activity level data, emission factor and potentially missing sources that lead to under- or over-estimations (Wang *et al*., 2014). The variations between EI and RM results call for a more systematic study with an objective view on the limitations and uncertainties of both methods in order to leverage their advantages to support robust air pollution control policy formulation.

By cross-validating SAs of EI and RM, it is possible to elucidate factors contributing to the discrepancies, to figure out ways for better interpretation, and finally to have a scientifically more plausible source apportionment. In this study, the SA cross-validation was demonstrated in the Pearl River Delta (PRD) region of China. The region is chosen for case study since it has a routinely updated regional-scale highly resolved EI for VOC species and a speciated ambient VOC measurement dataset generated from a region-wide gridded sampling campaign. The EI in the PRD provides hourly emission information for every 3×3km^2 grid. The RM is based upon VOCs measurement simultaneously conducted at 84 stations across the PRD, which overcomes limited spatial representation by a small number of monitoring sites that most of previous RM works were based upon (Louie *et al*., 2013). The high-resolution speciated EI and gridded VOC measurement campaign for the exactly same area provided us a good opportunity to systematically examine the underlying factors responsible for the discrepancies between two methods and to further explore ways to negate their impacts for more scientifically plausible determinations of SAs.

2. Data and Methods

2.1 Study region

As mentioned above, the PRD was selected as the study region due to the availability of highly resolved speciated VOC EIs and an extensive VOC ambient measurement campaign (the location of the study area is shown in Fig. S-1 in the Supporting Information (SI)). As one of the fastest developing regions in China, the PRD suffers from air pollution problems characterized by haze and serious photochemical smog episodes due to its dense population and intense economical activities (Zheng *et al*., 2009ab; Louie *et al*., 2013). Additionally, a variety of VOC emission sources in this region, e.g., vehicle exhaust, industrial and household solvent use, combustion, fuel evaporation, marine vessels, biomass burning, and biogenic emissions (Lau *et al*., 2010;

Ou *et al.*, 2016), leads to further complexity in the source characterization. Hot and humid weather favors photochemical reactions over the PRD, and the atmospheric chemistry also plays an important role in shaping the VOC loadings and compositions in the atmosphere therein. Such complex emission and atmospheric chemistry characteristics in conjunction with the available high-resolution EIs and gridded ambient VOC measurements make the PRD an ideal place to conduct an SA cross-validation study to elucidate the possible factors causing the inconsistencies between the EI and RM.

2.2 Emission inventory

High-resolution VOC bulk EIs (i.e., aggregated emissions of VOC species) in the PRD region from 2008 and 2009 were adopted in this study (Zheng *et al.*, 2009b). These bulk EIs from 2008 and 2009 were employed because a gridded ambient VOC measurement campaign (see details in Section 2.3) was conducted over those two years. These bulk EIs include anthropogenic emissions from 7 categories in addition to over 40 sub-categories and biogenic emissions estimated by the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther, 2006). With source-specific temporal and spatial allocation surrogates (CUHK, 2015), these bulk EIs have a spatial resolution of 3×3 km^2 and an hourly temporal resolution. On the basis of the bulk EIs, the speciated VOC EIs with approximately 300 VOC species were developed using local VOC source profiles (Zheng *et al.*, 2009a; Ou *et al.*, 2015b; HKPU& SCUT, 2016); meanwhile, only 30 VOC species were used in previous RMs. The reliabilities of the bulk and speciated EIs have been demonstrated in previous studies (Zheng *et al.*, 2009ab; Ou *et al.*, 2015b), and they are widely used in air quality modeling endeavors (Liu *et al.*, 2008; Ou *et al.*, 2016).

2.3 VOC grid study and receptor modeling

A gridded VOC sampling campaign (hereafter as "VOC grid study") with eight sampling events was conducted at 5 am and 10 am on four days (29 October 2008 and 1 March, 26 September and 5 December 2009). The PRD was equally divided into 100 grids with the grid size of 20×20 km^2, and both VOC and oxygenated VOC (OVOC) samples were simultaneously collected at 84 on-land grids. A total of 672 samples were collected and analyzed using gas chromatography (GC) with a multi-detector system and high-pressure liquid chromatography (HPLC) with a photodiode array detector for VOCs and OVOCs, respectively. Details of the sampling and analysis methods utilized in the VOC grid study can be found in Louie *et al*. (2013).

Because the SA for this VOC speciated dataset has been reported previously (Yuan *et al*., 2013), only a brief description is given here. The SA was performed using a positive matrix factorization (PMF) model (version 3.0). The uncertainties were determined following the protocol of Polissar *et al*. (1998). Twenty base runs and 100 bootstrap runs were performed to select the best solution and estimate the stability and uncertainty of the SA. Nine factors were identified, after which they were mapped onto the emission sources according to the abundances of various tracers, i.e., combustion, diesel exhaust, gasoline exhaust, gasoline evaporation, liquefied petroleum gas (LPG)-related sources, mixed solvents, industrial emissions, biogenic emissions and secondary and aged air masses. Details about the PMF modeling procedure can be found in Yuan *et al*. (2013).

2.4 Methods for comparison

To enable a comparison, the results obtained from both the EI and the PMF approaches were unified in terms of their source classification, sampling time, and temporal and spatial resolutions. Regarding the source classification, the bottom-up EI method incorporates a much more detailed source classification system, while the RM technique provides a general delineation of multiple sources based on the similarities among source profiles. Therefore, the deliberately classified sources in the EIs were grouped to match the 8 RM-based source categories, including combustion, gasoline exhaust, diesel exhaust, industrial processes, mixed solvents, LPG-related sources, gasoline evaporation and secondary and aged air masses. While secondary and aged air mass sources were classified within the RM, no primary emission source in the EIs was assigned to this category. The source mapping between the EI and RM and the unified source classification (see Table S-1) are detailed in the SI.

Hourly VOC emissions of the 8 sampling periods, i.e., 5 am and 10 am on 29 October 2008 and on 1 March, 26 September and 5 December 2009, were extracted from the EIs of 2008 and 2009 for comparison. To unify the spatial scale, the spatial surrogates used in the 3×3 km^2 EI were used to develop the 20×20 km^2 spatial factors for the emission allocation. The source characterization results acquired using the EIs and the PMF therefore had the same sampling time and spatial resolution and were ready for comparison in terms of source contribution percentages at both different temporal variations (i.e., hourly and annual) and different spatial scales (i.e., 20×20 km^2, 40×40 km^2, and 200×200 km^2).

3. Results and Discussion

3.1 Comparison of SAs using the EI and RM

Fig. 1 a-d show the source contribution percentages derived from the bulk EI and RM.

For the bulk EI with an aggregated emission of approximately 300 VOC species, mixed solvent usage was the dominant contributor (42%), followed by industrial processes (15%), biogenic emissions (15%), and gasoline exhaust (14%). In comparison, gasoline exhaust accounted for the largest fraction of VOCs (19%) in the RM, though it was only marginally higher than the contributions from mixed solvent (16%), industrial processes (15%) and LPG-related sources (15%). Gasoline evaporation (9%), combustion (8%), diesel exhaust (8%), and secondary and aged air masses (7%) also accounted for notable contributions. Biogenic emissions only contributed 3% on average.

A good agreement was found between the gasoline exhaust contributions in the EI and RM. The bulk EI generally provided much higher estimates of the mixed solvent and biogenic emission contributions and lower value for LPG-related sources. The contributions from mixed solvents and biogenic emissions in EI were 3 and 5-6 times those in RM, respectively. On contrast, the LPG-related source contribution estimated via the RM was 7 times the contribution in EI.

The diurnal variations of gasoline exhaust, combustion, diesel exhaust, gasoline evaporation and biogenic emission sources exhibited consistencies between EI and RM with higher contributions at 10 am than at 5 am (Fig. 1 a, c and Fig. S-2 in the SI). However, the RM results were also associated with significant seasonal variations (Fig. 1c) due to the large impacts of meteorological conditions and non-local transport mechanisms. Located along the southern coast of China, the PRD receives greater non-local contributions during the winter and spring with polluted continental air masses brought by the northeasterly monsoon; meanwhile, lower contributions are introduced during the summer and autumn with clean oceanic air masses brought by the southwesterly monsoon (Zheng *et al*, 2009b). In contrast, the EI reflected only local emissions within the PRD with slight seasonal variations. This constitutes an inherent cause of the discrepancies discussed below in Section 3.2**.**

3.2 Factors contributing to the insistencies between the EI and RM

To investigate the possible reasons leading to the notable discrepancies between the RM and EI approaches, we perform a SA cross-validation in this section to identify the major factors that impact the source characterization results by EI and RM and explore possible ways to reconcile those discrepancies.

3.2.1 Number of VOC species

The bulk EIs utilized in this study contained approximately 300 VOC species, while only 30 VOC species were consistently detectable by the instrument for the RM. The number of VOC species detectable within the ambient air is commonly much less than the number of VOC species detectable from emission sources because of their lower concentrations and the chemical loss of some reactive species. To eliminate the impacts of differences in the number of species, we constructed a speciated EI that contained the same species as those in the RM. Fig. 1 e-f show the source contribution percentages derived from the speciated EI. The largest source in the speciated EI was industrial processes (23%), followed by gasoline exhaust (21%), mixed solvents (20%), and biogenic emissions (17%). The predominant contribution from mixed solvents in the bulk EI was significantly weakened relative to that in the speciated EI. The contributions from industrial processes, gasoline exhaust and mixed solvents to VOCs in the speciated EI were comparable to those in the RM.

The differences in the contribution patterns in the bulk EI and speciated EI can be attributed to the proportions of the 30 RM species within the total VOC mass from a particular source. As shown in Fig. 2, the 30 RM species only accounted for 29% of the mixed solvent emissions, while they explained 85%, 76% and 74% of the emissions from combustion, gasoline exhaust and industrial processes, respectively. As a result, the contribution of mixed solvents dropped significantly in the speciated EI, thereby becoming more similar to those in the RM. Larger differences (i.e., reaching an order of magnitude) between the mixed solvent contributions from the bulk EI and RM were also reported in previous studies (Wang *et al*., 2014; Watson *et al*., 2001). These differences might be significantly reduced if an EI with the same species as a RM was used for comparison. This finding highlights the importance of species consensus when comparing SAs determined via EIs and RMs. Therefore, for the remainder of this study, comparisons were conducted between the speciated EI and the RM based upon the same 30 VOC species.

3.2.2 Temporal and spatial resolutions

After reconciling the number of species that used for comparison, different scales of temporal and spatial resolutions also explained part of the discrepancies between the two methods.

Starting with the finest temporal and spatial resolution, i.e., instant sample for the 20×20 km^2 grid, we illustrated the SA results by EI and RM in two sampling periods (2^{nd}: 10am, 1 March 2009; 6^{th}: 10am, 26 September 2009) for the selected cells to represent urban (Grid 74), industrial (Grid 66), suburban (Grid 54), upwind rural (Grid 99) and downwind rural (Grid 14) areas in PRD in Fig. 3. Noteworthy is that, the two sampling periods were of the same local time but different seasons (March for spring, and

September for late summer in PRD).

As shown in Fig. 3, SA by EI was generally stable during these two seasons, and its source contributions generally coincided with the local emission characteristics. Industrial processes, mixed solvents and gasoline exhaust dominated in urban and suburban grids. Industrial processes contributed the most significantly in the industrial grid, while biogenic emissions overwhelmed in the two rural grids. By contrast, SA by RM was much sampling event-specific, and the resolved contributions deviated significantly to their EI counterparts. For example, industrial processes contributed to 40% of VOCs in the urban grid in the 2nd event and 14% in the 6th event, both differed much from 30% and 23% in the EI. In two rural grids, RM resolved much lower biogenic contributions. The upwind rural grid was associated with higher contribution of secondary & aged air mass from long-range transport. Its source contribution patterns also varied as the prevailing wind changed from weak north-easterly in the 2nd event to moderate easterly in the 6th event. The downwind rural gird was dominated by high contributions of mixed solvents and remained stable despite the shift of prevailing winds. Significant mixed solvents may come from nearby upwind emissions, as Grids 24 and 25 to the north and northeast of the downwind rural grid were characterized by high emissions of mixed solvents.

The above selected cells showed how the SA results from EI and RM might be different from cell to cell and period to period, if we summarized their discrepancies for all the 84 grids over the 8 sampling periods, we found that the discrepancies were quite large. As shown in Fig. 4a, 57% of the results between two methods varied more than 3 times, i.e., the EI result was more than 3 times of RM or the other way around (RM result was more than 3 times of EI). 24% of the estimations even had differences greater than 15-fold, and almost all source categories contributed to these extreme values. Therefore, such disagreements were independent of source categories.

If comparisons were made in larger temporal and spatial resolutions, e.g., combined the 8 sampling periods as annual average or combined every 4 grids to a bigger grid of 40×40 km^2, the discrepancies between the two methods seemed to be smoothed in some degrees. As Fig. 4b illustrated, the percentage for those with variations more than 3 times decreased to 46% when comparison was made for annual average in 20×20 km^2 resolution. Similarly, when the grid size was increased to 40×40 km^2, the percentage dropped to 46% (Fig. 4c). If both spatial and temporal enhancements were adopted, only 38% of the results remained in the range of more than 3 times, i.e., 62% of the results fell in the range between 1/3 and 3 (Fig. 4d). If the grid size further increased to cover the entire PRD region and samples in all eight events averaged, 78% of the percentage ratios (7 out of 9 sources) fell in the range between 1/3 and 3 (Fig. 4e). Only biogenic emission and LPG-related sources still had percentage ratios greater than 3, implying other factors may contribute larger to discrepancies for the two categories. We shall address them in later sections.

The reasons why the EI and RM results can be reconciled by spatial and temporal averaging enhancements might due to the fact that RM results were sampling event-specific. As discussed in Fig. 3, the source contributions of EI were generally more stable while the results by RM tended to fluctuate from different sampling times and were subject to meteorological conditions and the upwind sources. For example, under different wind patterns, hotspots of toluene concentration were at different grids (as shown in Fig. S3-a&b of SI) and sometimes could be 40-60 kilometers away from the in-situ emission hot spots (Fig. S3c&b of SI). As inter-grid transport can be reflected by RM but cannot by EI, averaging in a larger area over a longer period of time is a possible way to ease this inherent discrepancy. Hence, in order to make a scientifically sound cross-validation between EI and RM, sampling should be conducted over a large area during a long period of time, preferentially a year, to minimize the impact by meteorology and inter-grid transport.

3.2.3 Chemical loss

Even after reconciling the spatiotemporal resolution as discussed above, substantial disagreements still existed for biogenic emissions and LPG-related sources. Though similar diurnal variations were presented by EI and RM, the biogenic emission contribution resolved by the EI was 5.7 times that by RM. Intriguingly, the biogenic emission estimates from the EI and RM had a high correlation (r=0.77), suggesting that both estimates were robust in terms of their temporal variations. The significant difference in the absolute mass contributions is therefore believed to be largely due to the high reactivity of isoprene, the tracer used to identify biogenic emissions in an RM. An inherent assumption of an RM is that all samples in a source profile are constant during the analysis, and the high reactivity of isoprene certainly violates this assumption (Harley and Cass, 1995). Since the reactivity of isoprene is one to two orders higher than those of other species in an RM (Harley and Cass, 1995), it was removed at a faster rate in the atmosphere, thereby distorting the ambient VOC profiles for interpretation using the RM and resulting in much lower biogenic contributions.

The discrepancy between the SAs acquired using the EI and RM correlated well with the source reactivity. By combining the reactivity (k_{OH}) of different VOC species with their proportions in a source, the source reactivity can be estimated (details are provided in the "Estimation of source reactivity" material of the SI). As shown in Fig. 5, biogenic emissions (point 9) in the upper-right corner constituted the most reactive source, and it was associated with the largest difference between the EI and RM. As the source reactivity decreased, the relative differences of source contributions by EI and RM declined as well, with the exception of LPG-related sources and secondary and aged air masses. Secondary sources exhibited the lowest reactivity, as it is composed of long-lived species. Since a secondary source cannot correspond to any source in an EI, its associated discrepancy was expected to be high. If LPG-related sources and secondary and aged air masses were removed, the source reactivity showed a positive relationship with the relative differences of two methods (r^2=0.59). Therefore, chemical loss constituted the single most important factor in the disagreement between EI and RM. Accordingly, some adjustment methods have been developed to account for the chemical losses of VOC species in the atmosphere to reconcile the SAs acquired using EIs and RMs (Na and Kim, 2007; Yuan *et al.*, 2012).

3.2.4 Potential missing sources in the EI and tracers used in the RM

The above factors failed to explain the significant discrepancy in the contribution of LPG-related sources. Its source contribution estimated using the RM was 15 times that by EI. The disagreement in the LPG-related source contributions from EI and RM has been reported elsewhere in China (Zhang *et al.*, 2009; Zhao *et al.*, 2012), Japan (Morino *et al.*, 2011) and North America (Blake and Rowland, 1995; Fujita *et al.*, 1995), suggesting that this discrepancy is globally pervasive. Two reasons might be blamed for it.

One is the usage of propane and *i/n*-butane in the RM as unique tracers of LPG sources. Propane and *i/n*-butane are ubiquitous in the atmosphere and generally make up large portions of the measured VOCs. For a long time, these species were treated as tracers of LPG sources due to their higher percentages in the source profiles (percentage of a species in a source's emission). Propane and *i/n*-butane each comprises 40%, 4% and 9% of the VOC emitted from LPG exhaust (Ou *et al*., 2015b; HKPU&SCUT, 2016), much higher than their percentages in other sources. With the measurements of high concentrations of propane and *i/n*-butane in ambient samples and the underlying assumption that propane and *i/n*-butane came dominantly from LPG sources, LPG was constantly apportioned with high source contribution by RM. However, if the emission intensity was considered, industrial processes, which dominated the emissions in PRD, would contributed 47%, 29% and 54% of the total propane and *i/n*-butane emissions in the PRD according to the EI (as shown in Fig. S-4 in SI). Regardless of whether these percentages were accurate or not, we need to be cautious on treating propane and *i/n*-butane as the tracers of LPG. More efforts are needed to measure the local source profiles, especially the presence of propane and *i/n*-butane, in a wide variety of industrial processes.

Another possibility is underestimation of LPG emissions in the current EI. A previous study suspected that usage of LPG might result in significant leakage (Blake & Rowland, 1995), with leakage rate of 1-5% depending on the boundary conditions. Evaporative emissions from LPG usage and gasoline evaporation during vehicle movement and parking were absent in the current EI. A recent study in China highlighted that vehicular evaporative emissions (predominantly from gasoline) constituted a missing yet significant part of VOC emissions in EI, and estimated that one vehicle in China emitted 1.6 kg of VOC emissions per year (Liu *et al*., 2015). If these two potentially missing sources were taken into account in EI, the source contributions by EI would change as those shown in Fig.6. It was noted that the large discrepancy in LPG-related sources was reconciled by inclusion of vehicular evaporative emissions and 2% LPG leakage rate. This highlighted that the need to review and improve emission estimations from evaporative sources in EI. Nevertheless, cross-validation on SAs between EI and RM revealed the necessity to improve both methods.

3.3 Implications for reconciling the inconsistencies between the EI and RM

The characterization of VOC sources is challenging due to the complexity in emission sources and species. The EI and RM represent two widely used VOC SA techniques that approach VOC from different perspectives, i.e., EIs focus on emission sources (bottom-up) while RMs emphasize pollutant levels in the environment (top-down); therefore, it is natural that these two methods may generate intrinsically different SA results. Given their inherent limitations, the SAs determined using either the EI or the RM could deviate from the ‘real’ source contributions, implying that control strategies based on either the EI or RM separately can be easily biased. This study identified the factors contributing to these discrepancies and provided ways to address these factors. The work shown here could help negate their impacts to obtain a more plausible SA, thereby generating a more robust control strategy.

The first implication of this study was that a consensus of species in cross-validating the results from the EI and RM is a prerequisite for reducing their discrepancies. The species included within RM generally present with high concentrations in the ambient air and low instrumental detection limits, while species in EIs are detectable in source profile measurements. As emission sources have high loadings of various species, higher quantities of species are more often detected and thus included in speciated EIs than in RMs. Inconsistencies in such species generally lead to lower estimations of some source contributions such as mixed solvent in RMs. These discrepancies can be even larger if the SA by an RM is simply compared with the EI of a total pollutant amount (e.g., bulk VOCs). It is therefore improper to use RM results based on a limited number of species to infer the control measures for a bulk amount of pollutants.

This study also highlighted the importance of reconciling the EI and RM SA results in a larger spatial coverage and longer time span. As pollutants in the air may originate from both local and non-local (i.e., areas outside the EI coverage) sources, an enhanced spatial coverage could downgrade the impact of non-local sources, thereby improving the consistency between the SAs from EIs and RMs. Meanwhile, longer time spans could improve the SAs determined by both methods. In an EI, temporal allocation surrogates are often used to allocate the total annual emission into months, days and hours; however, this can introduce additional uncertainties into these surrogates and therefore impact the emission estimates at any specific time. The influences of such uncertainties can be reduced if SAs are constructed with a longer time span, e.g., seasonally or annually. In RM, a longer time span would cover a wider range of synoptic conditions and thereby increase the temporal variability in the source contributions. In particular, a sampling interval spanning at least one year is suggested in areas dominated by a monsoonal climate to avoid any biases in SAs produced from limited directions of prevailing winds.

Third, addressing the impacts of chemical losses by employing receptor models for SAs could help reconcile the discrepancies between EIs and RMs. Chemical losses might be the single most important factor in SA discrepancies with regard to reactive pollutants, e.g., VOCs. Reactive species decay rapidly in the atmosphere and can drop to low or even undetectable levels if the receptors are far from their emission sources. Therefore, RMs most likely underestimate the contributions of sources with high abundances of reactive species and accordingly overestimate the contributions of sources with low reactivity. The significant decay of a reactive species could therefore distort the conclusions and implications for emission controls, reactive-based controls or health-based controls derived from an RM. For example, many studies have used maximum incremental reactivity (MIR)-weighted factor loadings from RM to indicate the ozone forming potentials (OFPs) of different VOC sources (Carter, 2008; Ou *et al*., 2015b). However, such OFPs only account for the post-receptor ozone production capacity; meanwhile, they neglect ozone that was produced by the decay of VOCs prior to reaching the receptor. As a result, the OFPs for sources with high abundances of reactive species are underestimated, and the degree of underestimation depends on the reactivity of the species and the proximity of the receptor to its source. Indeed, although they are used widely, MIR-weighted VOC factors in RM are scientifically inaccurate when estimating source-specific OFPs, as they generate misleading scientific conclusions and control-oriented implications. Hence, the impacts of chemical losses must be quantitatively addressed before they are used for cross-validation and policy formulation.

There are several types of RMs, in which PMF and the Chemical Mass Balance

(CMB) are the two most popular ones. In this study, only PMF is used for comparison with EI. This is due to the higher requirement of input data in CMB, such as the actual number of emissions sources and their source profiles, which requires a comprehensive pre-knowledge of all the significant sources and their speciated characteristics (Na and Kim, 2007; Lau *et al*., 2011; Teixeira *et al*., 2015). Previous studies showed that different RMs have general consistencies in the major emission sources. Specific variations in certain sources vary from sites and the VOC species in calculation. For example, Song *et al*. (2008) found the contribution of gasoline-related sources using CMB was higher than PMF for 31 VOC species (not including polycyclic aromatic hydrocarbons (PAHs)) in Beijing. On contrast, Teixeira *et al*. (2015) reported that PMF attributed a slightly greater amount of PAHs to the gasoline and diesel sources in Brazil. Differences in the theoretical approaches of RMs, the site-specific atmospheric chemistry and reactivity of VOC species might contribute to the variations of model performances. Though the variations between different RMs were much less than the discrepancies between PMF and EI in this study, cross-validation between different RMs and emission inventories is recommended to better understand the source characteristics of a region.

Last but not least, speciated EIs of reactive species are associated with significant uncertainties. Studies have shown that uncertainties in bulk VOC emission estimates sometimes reach or exceed 100% (Wei *et al*., 2008; Zheng *et al*., 2009b), and these estimates may be even higher for reactive species (Simpson *et al*., 1995). These uncertainties could be enhanced when a speciated EI is inferred by multiplying bulk emissions with speciated source profiles that are either measured or borrowed from an established source profile database such as SPECIATE from the U.S. Environmental

Protection Agency (EPA). Considering significant uncertainties in the SA of a reactive species using both EI and RM, cross-validation and reconciliation can shed light on directions for further improvement in both methods. For example, the large discrepancies in LPG-related sources indicate one or both of the methods call for critical review. Vehicular evaporation emissions and LPG leakage might be underestimated or missing in the current EI, while the tracers of propane and *i/n*-butane in RMs need to be reviewed to address the issue of overlapped tracers. In this regard, the EI and RM both play as synergistic roles in improving the confidence of SA results by both methods.

4. Summary and Conclusions

Source identification and apportionment are fundamental for the formulation of air pollution control measures. The two most widely used source characterization approaches are the bottom-up-based EI and the top-down-based RM; however, these two techniques often provide inconsistent SA results due to their inherent differences and limitations. In this study, we utilized the high-resolution, speciated VOC emission inventory and the region-wide VOC gridded measurement campaign for the PRD as a case study to perform a detailed examination of the factors leading to SA discrepancies and to explore possible ways to reconcile those discrepancies. The consensus of species included in the analysis, the temporal and spatial resolutions of the data for comparison, chemical losses of reactive species, potential missing sources in EIs and some tracers used in RMs were identified as the important factors responsible for the SA discrepancies between EIs and RMs. Therefore, ensuring a consensus of the species used in the EI and RM, employing a larger spatial coverage and longer time span, addressing the impacts of chemical losses by using receptor models, supplementing emissions from missing sources and selecting proper source tracers will help to reconcile the discrepancies among VOC source characterizations generated using EIs and RMs.

This study also highlighted the fact that high-resolution, speciated EIs and large-scale gridded monitoring campaigns are essential for a plausible source comparison between an EI and an RM. By leveraging the advantages and circumventing the disadvantages in both methods, EIs and RMs could play as synergistic roles in producing reliable source characterizations, especially those for reactive species such as VOCs. The work shown in this study could be used to more accurately characterize the sources of $PM_{2.5}$ emissions. The approach outlined herein could thus be promulgated to other regions in China and other developing countries with intense and complex emissions sources to more accurately characterize source impacts on the ambient pollution and ultimately to improve the efficacies of pollution control strategies.

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SUPPORTING INFORMATION AVAILABLE

Four figures, one table and additional information are available for the following: (1) the locations of the PRD region and the VOCs grid sampling campaign; (2) the source categories in the EI and their grouping relative to the RM sources; (3) the diurnal variations in the RM and EI region-wide estimates; (4) the spatial distribution of ambient toluene under different wind patterns and the spatial locations of its major sources-industrial solvent and industrial processes; (5) the proportions of propane and *i/n*-butane in the source profiles and the total emission budget; and (6) the estimation of the source reactivity.

References

Blake, D. R.; Rowland, F. S. Urban leakage of liquefied petroleum gas and its impact on Mexico city air quality. *Science*, 1995, 269, 953–6.

Carter WP. Reactivity estimates for selected consumer product compounds. Final Report to the California Air Resources Board Contract 2008: 06-408.

Karagulian, F.; Belis, C.A. Enhancing source apportionment with receptor models to foster the air quality directive implementation. *Int. J. Environment and Pollution* 2012, 50, 190-198.

Belis, C.A.; Pernigotti, D.; Faragulian, F.; Pirovano, G.; Larsen, B.R.; et al. A new methodology to assess the performance and uncertainty of source apportionment models in intercomparison exercises. *Atmos. Environ.* 2015, 119, 35-44.

Hong Kong Polytechnic University and South China University of Technology (HKPU& SCUT). Characterization of VOC sources and Integrated Photochemical Ozone Analysis in Hong Kong and the Pearl River Delta Region; Final Report, 2016.

Fujita, E. M.; Watson, J. G.; Chow, J. C.; Magliano, K. L. Receptor Model and Emissions Inventory Source Apportionments of Nonmethane Organic Gases in California'S San Joaquin Valley and San Francisco Bay Area. *Atmos. Environ*. 1995, 29, 3019–3035.

Guenther, A.; Karl, T.; Harley, P.; Wiedinmyer, C.; Palmer, P.I.; Geron, C. Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). *Atmos. Chem. Phys.,* 2006, 6, 3181-3210.

Lau, A.K.H.; Yuan, Z.; Yu, J.Z.; Louie, P.K.K. Source apportionment of ambient volatile organic compounds in Hong Kong. *Sci. Total Environ*. 2010, 408, 4138–49.

Leuchner, M.; Rappenglück, B. VOC source–receptor relationships in Houston during TexAQS-II. *Atmos. Environ*. 2010, 44, 4056-4067.

Li, Y.; Lau, A.K.H.; Fung, J.C.H.; Zheng, J.Y.; Zhong, L.J.; Louie, P.K.K. Ozone Source Apportionment (OSAT) to Differentiate Local Regional and Super-regional Source Contributions in the Pearl River Delta Region, China. *J. Geophys. Res.*, 2012, 117, D15305.

Ling, Z.H.; Guo, H. Contribution of VOC sources to photochemical ozone formation and its control policy implication in Hong Kong. *Environ. Sci. & Policy* 2014, 38, 180-191.

Liu, H.; Man, H.Y., Tschantz, M., Wu, Y., He, K.B., Hao, J.M. VOC from Vehicular Evaporation Emissions: Status and Control Strategy. *Environ. Sci. Technol*. 2015, 49, 14424–14431.

Liu, Y.; Shao, M.; Lu, S.H.; Chang, C.C.; Wang, J.L.; Fu, LL. Source apportionment of ambient volatile organic compounds in the Pearl River Delta, China: Part II. *Atmos. Environ*. 2008, 42, 6261-6274.

Louie, P.K.K., Ho, J.W.K.; Tsang, R.C.W.; Blake, D.R.; Lau, A.K.H.; Yu, J.; Yuan, Z.B.; Wang, X.M.; Shao M.; Zhong, L.J. VOCs and OVOCs distribution and control policy implications in Pearl River Delta region, China. *Atmos. Environ*. 2013, 76, 125–135.

Ministry of Environmental Protection of the People's Republic of China (MEP). Guidelines on source apportionment techniques of particulate matters (trail), 2012; Available via:

http://www.zhb.gov.cn/gkml/hbb/bwj/201308/t20130820_257699.htm.

Miller, C.A.; Hidy, G.; Hales, J.; Kolb, C.E.; Werner, A.S.; Haneke B, et al. Air Emission Inventories in North America: A Critical Assessment. *J. Air & Waste Manage. Assoc*. 2006, 56:1115–1129

Morino, Y.; Ohara, T.; Yokouchi, Y.; Ooki, A. Comprehensive source apportionment of volatile organic compounds using observational data, two receptor models, and an emission inventory in Tokyo metropolitan area. *J. Geophys. Res*. 2011, 116, D02311.

Na, K.; Pyo Kim, Y. Chemical mass balance receptor model applied to ambient C2-C9 VOC concentration in Seoul, Korea: Effect of chemical reaction losses. *Atmos. Environ*. 2007, 41, 6715–6728.

North American Research Strategy for Tropospheric Ozone (NARSTO). Improving Emission Inventories for Effective Air Quality Management Across North America: A NARSTO Assessment, 2005.

Ou, J.; Guo, H.; Zheng, J.Y.; Cheung, K.; Louie, P.K.K.; Ling, Z.H.; Wang, D. Concentrations and sources of non-methane hydrocarbons (NMHCs) from 2005 to 2013 in Hong Kong: A multi-year real-time data analysis. *Atmos. Environ*., 2015a, 103, 196–206.

Ou, J.; Zheng. J.Y.; Li, R.R.; Huang, X.B.; Zhong, Z.M.; Zhong, L.J.; Lin, H. Speciated OVOC and VOC emission inventories and their implications for reactivity-based ozone control strategy in the Pearl River Delta region, China. *Sci. Total Environ*. 2015b, 530–531, 393–402.

Ou, J.; Yuan, Z.B.; Zheng, J.Y.; Huang, Z.J.; Shao, M.; Li, Z.K.; Huang, X.B.; Guo, H,; Louie, P.K.K. Ambient Ozone Control in a Photochemically Active Region: Short-Term Despiking or Long-Term Attainment? *Environ. Sci. Technol*. 2016, 50, 5720–5728.

P.K. Hopke. Receptor Modelling for Air Quality Management. Elsevier Science Ltd, 1991, pp. 213-249.

Polissar, A. V.; Hopke, P. K.; Paatero, P.; Malm, W. C. & Sisler, J. F. Atmospheric aerosol over Alaska: 2. Elemental composition and sources. *J. Geophys. Res*. 1998, 103, 19045.

Scheff, P.A., Wadden, D.M., Kenski, J., Chung J., Wolff, G. Receptor model evaluation of the Southeast Michigan Ozone Study ambient NMOC measurements. *J. Air & Waste Manage. Assoc*, 1996, 46(11): 1048-1057.

Simpson, D, Guenther A, Hewitt CN, Steinbrecher R. Biogenic emissions in Europe: 1. Estimates and uncertainties. *Journal of Geophysical Research: Atmospheres*, 1995; 100: 22875-22890.

Song, Y., Dai, W., Shao, M., Liu, Y., Lu, S.H., Kuster, W., Goldan, P. Comparison of receptor models for source apportionment of volatile organic compounds in Beijing, China. *Environ. Pollut.* 2008, 156: 174-183.

Teixeira, E.C., Agudelo-Castañeda, D.M., Mattiuzi, C.D.P. Contribution of polycyclic aromatic hydrocarbon (PAH) sources to the urban environment: A comparison of receptor models. *Sci. Total Environ*. 2015, 538: 212-219.

Wang, M.; Shao, M.; Chen, W.; Yuan, B.; Lu, S.; Zhang, Q.; Zeng, L.; Wang, Q. A temporally and spatially resolved validation of emission inventories by measurements of ambient volatile organic compounds in Beijing, China. *Atmos. Chem. Phys*. 2014, 14, 5871–5891.

Watson, J. G.; Chow, J. C.; Fujita, E. M. Review of volatile organic compound source apportionment by chemical mass balance. *Atmos. Environ*. 2001, 35, 1567–1584.

Yuan, B.; Shao, M.; Gouw, J.; Parrish, D.D.; Lu, S.H.; Wang, M.; Zeng, L.M.; Zhang, Q.; Song, Y.; Zhang, J.B.; Hu, M. Volatile organic compounds (VOCs) in urban air: How chemistry affects the interpretation of positive matrix factorization (PMF) analysis. *J. Geophys. Res. Atmos*. 2012, 117, 1–17.

Yuan, Z.; Zhong, L.J.; Lau, A.K.H.; Yu, J.Z.; Louie, P.K.K. Volatile organic compounds in the Pearl River Delta : Identification of source regions and recommendations for emission-oriented monitoring strategies. *Atmos. Environ*. 2013, 76, 162–172.

Zhao, B.; Wang, P.; Ma, J.Z.; Zhu, S.; Pozzer A.; Li, W. A high-resolution emission inventory of primary pollutants for the Huabei region, China. *Atmos. Chem. Phys*. 2012, 12, 481–50.

Zheng, J.; Shao, M.; Che, W.W.; Zhang, L.J.; Zhong, L.J.; Zhang, Y.H.; Streets, D. Speciated VOC emission inventory and spatial patterns of ozone formation potential in the Pearl River Delta, China. *Environ. Sci. Technol*. 2009a, 43, 8580–8586.

Zheng, J.; Zhang, L.; Che, W.; Zheng, Z.; Yin, S. A highly resolved temporal and spatial air pollutant emission inventory for the Pearl River Delta region, China and its uncertainty assessment. *Atmos. Environ.* 2009b, 43, 5112–5122.

Zhong, L.J.; Louie, P.K.K.; Zheng, J.Y.; Yuan, Z.B.; Yue, D.L.; Ho, J.W.K. Science–policy interplay: Air quality management in the Pearl River Delta region and Hong Kong. *Atmos. Environ*. 2013, 76, 3–10.