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Inter-comparison of network measurements of non-methane organic compounds with model simulations

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HIGHLIGHTS

- Total PAMS species accounted for approximately 70% of the total ambient NMHCs.
- Total PAMS simulations agreed well with observations.
- AQS NMOCs tend to underestimate VOC levels due to lower sensitivity towards OVOCs.

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ABSTRACT

Ambient levels of total non-methane organic carbons (NMOCs) at air quality stations (AQSs, called AQS NMOCs) are compared with the summed concentrations of 56 NMHCs obtained from the Photochemical Assessment Monitoring Stations (called total PAMS). For mutual validation of the two networks, the total PAMS were compared with the AQS NMOCs at four sites on the island of Taiwan for the period 2007–2012. The inter-comparison of total PAMS and AQS NMOCs has been discussed previously, which reported that the total PAMS accounted for approximately 30% of the AQS NMOCs on average (Chen et al., 2014b). In this study, both the observed total PAMS and AQS NMOCs were further compared with the emissions and model simulations for mutual validation.

A three-dimensional Eulerian air quality model was used to simulate total PAMS and total VOCs, which were then inter-compared with the observed total PAMS and AQS NMOCs, respectively. We found closely agreeing results between the observed and simulated total PAMS, affirming that the treatment of meteorology and VOC emissions in the model was sufficiently robust. Further, although the modeled VOC data agreed with the AQS NMOC observations for the sites in urban settings, a significant discrepancy existed for the industrial sites, particularly at the concentration spikes. Such a discrepancy was presumably attributed to high emissions of OVOCs from industrial complexes compounded by the lower sensitivity of AQS measurements for OVOCs compared with hydrocarbons. Consequently, using AQS NMOCs to represent ambient VOC levels should be limited to environments where the amounts of OVOCs are relatively small relative to total VOCs.

1. Introduction

The secondary production of ozone (O_3) can affect air quality in high-density urban or industrial areas (Akimoto and Narita, 1994; Jacobson, 2005; Seinfeld and Pandis, 1998; Streets et al., 2003; Wayne, 2000). Nitrogen oxides (NO_x) and volatile organic compounds (VOCs) are precursors of ozone, especially under

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sufficiently high temperatures and strong solar radiation as well as low wind speed (Akimoto and Narita, 1994; Atkinson, 2000; Banta et al., 2011; Carter, 1994; Seinfeld and Pandis, 1998). In addition to playing the role of ozone precursors, VOCs also participate in the formation of organic nitrates and secondary organic aerosols (Dumanoglu et al., 2014). Certain VOCs are also known to be either toxic or carcinogenic (Clarke and Ko, 1996). Nevertheless, it is likely that only a small fraction of species are recognized in the entire pool of VOCs (Harley et al., 1993), and the majority of studies addressed VOCs only as total amounts (Cai et al., 2010; Dunker et al., 2002; Harley et al., 1997; Marr and Harley, 2002; Pratt et al., 2004; Scheff and Wadden, 1993).

Due to the complexity in the sources of VOCs and their reactivities, assessment by the means of total VOCs are often adopted for predicting photochemical oxidant formation (Hoshi et al., 2008). Because the total hydrocarbon (THC) analyzers used in air quality stations (AQSs) respond not only to non-methane hydrocarbons (NMHCs), but also to compounds with carbon atoms bound to oxygen, nitrogen, or halogens, these compounds are usually referred to as non-methane organic compounds (NMOCs) to be distinguished from NMHCs (EPA, 1997). Here, the term “NMOCs” is used to mean the actual instrumental response from the AQS THC analyzer, which has a different meaning from the true total VOC level. In other words, unless all VOCs are measured with an equal molar response, NMOCs can only approximate VOCs.

The establishment of the Photochemical Assessment Monitoring Stations (PAMS) in the U.S. since 1990 (EPA, 1997) and in Taiwan since 2002 (Yang et al., 2005a), with their hourly measurements of 56 target NMHCs, has significantly improved the understanding of VOC species-specific source-receptor relationships and their individual contribution to ozone formation. Other countries have also implemented similar monitoring programs (Dann and Wang, 1995; Hoshi et al., 2008). Over the past decade the addition of further techniques to measure a large variety of VOCs at trace levels (in addition to the target PAMS NMHCs) has led to an even more complete understanding of the VOC speciation profiles in the environment, even though accurate quantification of relevant species is still an ongoing endeavor (Apel et al., 2010; de Gouw et al., 2003; Goldstein and Galbally, 2007; Legreid et al., 2007a, 2007b; Lewis et al., 2000).

In model simulation, VOCs are often lumped into groups according to their chemical reactivities to simplify calculation and to increase computational speed (Carter, 2010; Gery et al., 1989; Lazar et al., 1990; Stockwell et al., 1997; Zaveri and Peters, 1999). However, these lumped groups used in all air quality models cannot be compared directly with results from monitoring stations such as PAMS, aircraft campaigns or field experiments with regard to evaluation of individual species.

With the extended chemical mechanisms and the advent of air-quality models for simulating selected individual species, it has become possible to make a direct comparison with speciated observations such as PAMS (Chen et al., 2014c, 2010; Doraiswamy et al., 2009; Harley and Cass, 1995; Liu et al., 2012; Ying and Li, 2011). A literature search found that the earliest pioneering work of simulations individual VOCs began in 1995, but these simulations could not be validated and subsequently optimized due to the lack of robust VOC monitoring data (Harley and Cass, 1995). Not until 2010 was a so-called PAMS-AQM developed with a complete transport and chemical mechanism to permit direct comparison with the detailed hour-to-hour variations of 56 PAMS NMHC observations (Chen et al., 2010). Since 2010, the near-explicit Master Chemical Mechanism (MCM) photochemical mechanism in the Community Multi-scale Air Quality (CMAQ) model was also developed to simulate a large number of primary pollutants (Ying and Li, 2011), of which the 4642 species were far more than could be compared with existing VOC monitoring data. Because the state-of-the-art model developments and measurement techniques for the speciated VOCs were integrated, the temporal variations of selected VOC released from various sources could be clearly identified (Chen et al., 2014c, 2010; Chung et al., 2003; Legreid et al., 2007a, 2007b; Seigneur et al., 2003; Ying and Li, 2011).

Prior to the availability of the systematic measurements of total/speciated VOCs and modeling capabilities, no studies were found in the open literature to describe the relationship between the total amounts and the speciated VOCs. Chung et al. (2003) investigated the relationship between the measured total NMOCs, the sum of speciated hydrocarbons and carbonyls in the Los Angeles air basin. The ratios of the total NMOCs and the speciated VOCs were mainly used to indicate the excess VOCs not detected by routine measurements. Recently, the annual trends of total oxygen-containing VOCs (OVOCs) and non-methane organic compounds (NMOCs) in mid-town Atlanta (Jefferson Street), Georgia, were compared to reflect their tends in the emission estimates of the county (Blanchard et al., 2010). Despite sporadic efforts in the past, very rarely can one find a given geographic domain with monitoring stations including both total and speciated NMOCs measurements as densely deployed and meticulously operated as in Taiwan. In our previous study, we found that hourly observations of the NMOCs obtained from real-time instruments at air quality stations (dubbed AQS NMOCs) exhibited very synchronous variations as did the PAMS data from summing 56 target NMHCs (dubbed total PAMS) at four sites in Taiwan based on five years of continuous hourly data, despite the fact that both techniques differ considerably in their working principles (Chen et al., 2014b). Although the synchronicity was superb, the total PAMS NMHCs values were consistently smaller than the values of AQS NMOCs by approximately 30% on average, due presumably to the fact that relatively limited species were covered by the PAMS observations (only 56 NMHCs were targeted), whereas the THC response that gives rise to AQS NMOC values is contributed measured numerous VOCs, including all species of NMHCs.

The mutual validation of the two types of observations, AQS NMOCs vs. PAMS, in the field, which has been previously reported (Chen et al., 2014b), provides the needed quality assurance of the observed data which can, in turn, be coupled with model simulations to validate the performance of the model. The objectives of this study were: firstly, to exploit, to our knowledge, two of the most explicit long-term datasets of PAMS and AQS NMOCs to inter-compare with model simulations of total PAMS and total VOCs with adequate resolution; secondly, to test the adequacy of using AQS NMOCs to represent ambient levels of VOCs through examining the role of OVOCs.

2. Observations and model setup

2.1. Observation site map and monitoring techniques

There are currently 74 AQS across Taiwan reporting hourly concentrations (as mixing ratios) of NO_x, SO_2, CO, PM_{10} and O_3. Of these AQSs, 36 sites also have NMOC measurements. In addition to the AQS network, the PAMS network sites have been established since 2002, and the network has grown to include nine stations over the last decade (Yang et al., 2005b) to cover four different areas: northern, central, southwestern and southern Taiwan, with each area having two or three stations to form a sub-network (Chen et al., 2014c). Of the nine PAMS sites, four sites (S1 to S4) had nearby AQS with NMOC observations (Fig. 1). As a result, inter-comparison of the two types of analyzers became possible.

Both AQS and PAMS use the flame ionization detection (FID)