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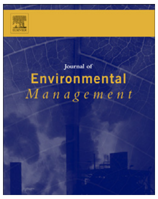

Research article

Vertical stratification of volatile organic compounds and their photochemical product formation potential in an industrial urban area

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ABSTRACT

High emissions of volatile organic compounds (VOCs) from the petrochemical industry and vehicle exhaust may contribute to high ozone formation potential (OFP) and secondary organic aerosol formation potential (SOAFP). In this study, the vertical profiles of VOCs were created for the southern Taiwan industrial city of Kaohsiung. Vertical air samples were collected up to 1000 m using an unmanned aerial vehicle (UAV). In Renwu District, VOC distribution was affected by the inversion layer up to 200 m height. Total VOCs (36–327 ppbv), OFP (66–831 ppbv) and SOAFP (0.12–5.55 ppbv) stratified by height were the highest values at 300 m. The VOCs originated from both local and long-distance transport sources. These findings can be integrated into Kaohsiung's future air quality improvement plans and serve as a reference for other industrialized areas worldwide.

1. Introduction

Kaohsiung city, the most industrialized area in southern Taiwan, has suffered greatly from air pollution in the past decades. For 131 days a year (36%), the air quality index (AQI) values fell into unhealthy category (101–150) in Kaohsiung, the highest rate in Taiwan (TAQMN, 2018). Due to the rapid development of petrochemical industry, the concentrations of volatile organic compounds (VOCs) in the ambient air have always been a great concern. In Kaohsiung the petrochemical industry and vehicular exhaust are the two major sources of VOCs (Chen et al., 2012).

VOCs, e.g. benzene, toluene, trichloroethene, and styrene, are highly toxic compounds, reported to cause diseases of the respiratory, blood, and central nervous systems (WHO, 2000; Kampa and Castanas, 2008; Sahu et al., 2016a). More importantly, VOCs are the precursors of other toxic photochemical products, including ozone and secondary organic aerosols (SOAs) (Sahu et al., 2017a). In the atmosphere, the reactions involving VOCs and NO_x under solar radiation lead to the formation of ozone and a variety of carbonyl compounds (Koppmann, 2010; He et al., 2017). The alkyl nitrates and peroxyacetyl nitrate (PAN) are known as secondary pollutants in photochemical smog. In the presence of NO, these secondary pollutants are formed from the oxidation of VOCs by OH radicals, which are formed through the photo-dissociation of ozone under ultraviolet radiation. The lifetime of alkyl nitrates varies from several days to one month depending on their chain length. PAN is thermally unstable so it can decompose into NO_x and peroxyethanoyl radicals (Sahu, 2012). More importantly, PAN serves as a carrier for NO_x into cleaner areas and also to elevated altitudes, leading to ozone formation worldwide.

Surface ozone formation due to high concentrations of ozone precursors is a serious air pollution problem in industrialized areas (Sahu et al., 2016b). Regulatory programs and state implementation plans have been conducted in many countries (e.g. the United States, Europe, Taiwan, etc.) in past decades to reduce exposure to ground-level ozone. However, many areas continue to exceed the

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national ambient air quality standard for ozone (TAQMN, 2018). With regard to Taiwan, surface ozone concentrations have consistently been increasing since 2012 (TAQMN, 2018). VOC emissions are reported to be the main cause of increasing surface ozone concentrations there (Li et al., 2010; Kuo et al., 2014). SOAs make up a major part of fine particular matter (PM), known to negatively impact human respiratory and cardiovascular systems (Solomon and Hopke, 2008; Kim et al., 2018). Approximately 95% of the wintertime daily average $PM_{2.5}$ in Kaohsiung exceeds the 24-hour limit mean value ($25\ \mu g\ m^{-3}$) issued by the World Health Organization (Lai, 2016). Many studies have investigated ozone and SOA formation by measuring spatial and temporal VOC distribution at ground-level (Tsai et al., 2012; Olajire and Azeez, 2013; Kuo et al., 2014; Garzón et al., 2015; Zhang et al., 2017). These studies have found that insignificant correlation between VOCs and OFP (Kuo et al., 2014). High TVOC concentration may not necessarily contribute to high OFP (Garzón et al., 2015). While OFP may be high, SOAFP may not be (Zhang et al., 2017). Their findings suggest that each VOC contributes differently to ozone formation. However, variation of TVOC concentration and changes of dominant VOCs depend on sampling period, observation height, area studied and source of emissions (Tsai et al., 2012; Zhang et al., 2017). Most of VOC monitoring programs used in these studies were conducted on the ground. Few of them were conducted at elevated locations. Thus, to date our understanding regarding the vertical profile of VOCs and their effects on ozone and SOA formation remains incomplete. For effective emission control strategies, it is necessary to obtain vertical VOC profiles and identify the most abundant compounds contributing to high ozone concentrations and identify their important emission sources.

Towers (Lin et al., 2011), tethered balloons (Tsai et al., 2012), and aircrafts (Mak et al., 2013) have been widely used for vertical air sampling over the three past decades. Meteorological sensors can be attached to those sampling devices to record the variations in temperature, humidity, pressure, wind speed, etc. Tower-based sampling techniques are limited by the height and location of the tower (or sometimes building). The maximum height of air samples collected by these techniques has been recorded to be about 280 m (Mao et al., 2008; Lin et al., 2011). The tethered balloon technique, though able to sample up to 1000 m, requires large space and can only operate for short-flight distances limited by length of their anchoring cords (Tsai et al., 2012; Yang et al., 2013). Furthermore, this technique is limited by strong wind conditions (Mak et al., 2013). Tower-based and tethered balloon techniques are usually combined with the adsorbent cartridge (activated charcoal) or sampling bags (Teflon and Tedlar) to collect air samples. Although activated charcoal is an excellent material, its recovery for nonpolar compounds is relative low, impeding the accuracy of the contaminant measurement. Various sizes of commercial Teflon and Tedlar bags can be economically produced, but these bags can only be used for collecting relatively stable contaminants. VOCs, on the other hand, may not remain stable for more than 24 h, since they react with other chemicals in the air (Kumar and Víden, 2007); thus, the holding time for samples stored in the bags is limited. Another downside of these bags is that they are easily punctured, which causes loss of compounds due to leakage (Król et al., 2010). Vacuum stainless steel canisters are highly recommended for the collection of ambient air VOC samples. The interior surface of the canisters is coated with a thin silica layer to reduce surface activity, allowing air samples to be stored for several weeks without any significant loss or change in sample amount and composition (Dobrzyńska et al., 2010). Herrington (2014) reported that the VOC recoveries determined under a relative humidity of 93% vary from 85% to 88% over 30 days of storage in canisters. An aircraft equipped with a canister sampling device has been employed to overcome the limits of sample collection techniques as well as sampling height, and they can be used to collects samples up to 12 km in height (Baker et al., 2011; Mak et al., 2013; Sahu et al., 2017b). Yet, emission interferences from fuel-powered engines and the potential danger in flying at heights lower than 500 m (altitudes containing important information for air quality research) limit the application of aircraft to air sampling (Wespes et al., 2012).

Unmanned aerial vehicles (UAVs) have been widely applied in military surveillance, atmospheric studies, weather forecasting, observations of volcano activities, and forest conservation (Diaz-Varela et al., 2014; Li et al., 2017). Compared to other types of UAVs, rotary-wing UAVs have several prominent advantages such as being lightweight, having a simple structure, being able to hover and requiring small space for landing (Klemas, 2015). Moreover, the battery-powered rotors emit no air contaminants. UAV can be equipped with stainless steel canisters to perform VOCs collection in ambient air. Although they are only capable of collecting air samples up to 200 m in height, their use with canisters make them and an innovative approach and greatly suitable for three-dimensional environmental studies (Chang et al., 2016).

In the current study, rotary-wing UAV equipped with stainless steel canisters were employed to characterize the vertical profile of VOCs. Air samples were collected up to 1000 m in height at sites located in Renwu and Chaozhou Districts of Kaohsiung. The selected sampling sites are surrounded by the major industrial plants. We measured 101 VOC compounds selected according to the photochemical assessment monitoring station - PAMS (USEPA, 1996) and the urban air toxics monitoring program - UATMP (USEPA, 2003). The results of this study can help in the following ways: (i) assess whether inversion phenomenon exists through continuous monitoring of vertical variation in temperature and relative humidity; (ii) assess the effect of inversion layer on vertical VOC distribution; (iii) determine VOC emission sources and pathways; and (iv) assess the stratification of VOCs, OFP and SOAFP, and evaluate their effects on ambient air quality.

2. Materials and methods

2.1. Sampling

The sampling sites are shown in Fig. 1a. First sampling trip was conducted at the Yongda Institute of Technology (22.70° N, 120.35° E) in Renwu District. This site is surrounded by three major industrial plants of Kaohsiung, namely Nanzi export processing zone (NEPZ), Dashe industrial park (DSIP), and Renwu industrial park (RWIP) and also Renwu incinerator (RWIn). NEPZ, DSIP, and RWIP have been reported to be major VOC emission sources in Kaohsiung (Lin et al., 2004; Liu et al., 2008). At this sampling site, five air sampling flights were conducted at five targeting heights of 100, 200, 300, 500 and 700 m on February 12, 2017, from 14:00–16:00. A second sampling trip was conducted at Chaodong Elementary School (22.52° N, 120.56° E) in Chaozhou District, an agricultural and tourism oriented county. From daytime data collected by Taiwan Air Quality Monitoring Network, prevailing wind direction came from the Northwest in Kaohsiung during the study period. Thence, this site was located downwind of the Renwu site. Local air pollutant emission sources mainly include vehicular exhaust and agricultural combustion. In addition, some distant upwind emission sources (Dafa industrial park - DFIP, Linyuan industrial park - LYIP, Kaohsiung export processing zone - KEPZ and sources around Renwu site) might potentially affect the air quality at this site. Four air sampling flights were conducted at different heights of 100, 200, 400, and 1000 m on March 31, 2017, from 14:00–16:00. At each site, an additional sample was manually taken at ground-level (at 2 m from the ground) with a canister sampler. All samples were then