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Research article

Investigating the differences between receptor and dispersion modeling for concentration prediction and health risk assessment of volatile organic compounds from petrochemical industrial complexes

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ABSTRACT

Receptor and dispersion models both provide important information to help understand the emissions of volatile organic compounds (VOCs) and develop effective management strategies. In this study, differences between the predicted concentrations of two models and the associated impacts on the estimated health risks due to different theories behind two models were investigated. Two petrochemical industrial complexes in Kaohsiung city of southern Taiwan were selected as the sites for this comparison. Although the study compares the approaches by applying the methods to this specific area, the results are expected to be adopted for other areas or industries. Ninety-nine VOC concentrations at eight monitoring sites were analyzed, with the effects of diurnal temperature and seasonal humidity variations being considered. The Chemical Mass Balance (CMB) receptor model was used for source apportionment, while the Industrial Source Complex (ISC) dispersion model was used to predict the VOC concentrations at receptor sites. In the results of receptor modeling, 54% ± 11% and 49% ± 20% of the monitored concentrations were contributed by process emissions in two complexes, whereas the numbers increased to 78% ± 41% and 64% ± 44% in the results of dispersion modeling. Significant differences were observed between two model predictions ($p < 0.05$). The receptor model was more reproducible given the smaller variances of its results. The effect of seasonal humidity variation on two model predictions was not negligible. Similar findings were observed given that the cancer and non-cancer risks estimated by the receptor model were lower but more reproducible. The adverse health risks estimated by the dispersion model exceeded and were 75.3%–132.4% of the values estimated by using the monitored data, whereas the percentages were lowered to the range from 27.4% to 53.8% when the prediction was performed by using the receptor model. As the results of different models could be significantly different and affect the final health risk assessment, it is important to carefully choose an appropriate model for prediction and to evaluate by monitoring to avoid providing false information for appropriate management.

1. Introduction

Volatile organic compounds (VOCs) are easily emitted into the atmosphere and are of concern for two main reasons. A number of VOCs are precursors that form secondary air pollutants through chemical and photochemical reactions (Simpson et al., 1999; Brock et al., 2003; Schwarzenbach et al., 2003). These pollutants include tropospheric ozone that affect the atmospheric chemistry and halogenated greenhouse gases that adversely cause the stratospheric ozone depletion (Fenger, 1999; Chang et al., 2005). The concentration of hydroxyl radical, a major oxidizing agent in the troposphere, is also influenced by VOC emissions (Simpson et al., 2013). More importantly, many VOCs are considered as hazardous air pollutants (HAPs) posing risks to the public health (Guo et al., 2004; Chang et al., 2010; Yang et al., 2012). For instance, BTEX is the abbreviation of benzene, toluene, ethylbenzene, and xylene, which are four compounds often found together in petroleum

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products. Exposures to BTEX have been associated with toxicological effects on human health such as central nervous system depression and diseases of respiratory and blood systems (Aguilera et al., 2008; Durmusoglu et al., 2010).

Anthropogenic sources of VOC emissions contain mobile and stationary emissions, as the stationary emissions are sub-classified into stationary and fugitive sources. Receptor and dispersion models represent two examples widely used to identify possible emission sources and to understand the transport of pollutants in the atmosphere, respectively. Different theories and mechanisms are involved behind two models. Receptor models employ the concentration distributions of compounds from sources and those observed at receptors to quantify different source contributions to receptor concentrations. Dispersion models use mathematical equations to simulate the atmospheric behaviors of pollutants emitted by known sources. As both models are popular tools to solve air quality problems, the influences of choosing different models on predicting the VOC concentrations in the environment and the associated public health risk assessment were limitedly known and could be underestimated. Other factors such as diurnal temperature and seasonal variation may further affect the impact of this concern.

Petrochemical industry plays an important role in economic development in Taiwan. However, its influences on air quality by VOC emissions also attract public attention. Kaohsiung city is the largest industrial city in southern Taiwan and more than 2.8 million people are living in the city. While it is an important hub for national industrial development, many industries are located in the north region of the city and affect the local air quality. More than one hundred VOCs including alkanes, alkenes, aromatics, and halogenated VOCs have been detected in our early monitoring studies (forty of which were considered to be HAPs) (Yang et al., 2013; Liu et al., 2014). The VOC concentrations observed were significantly higher than those detected in other non-industrial areas (Chang et al., 2005). The VOC concentrations in these areas were also contributed by vehicular sources (Liu et al., 2008, 2014). In the Taiwan Emission Data System, which was developed by the Taiwan Environmental Protection Agency (Taiwan EPA) to monitor air qualities in major metropolitan areas (http://edw.epa.gov.tw/ENG/topicAirEN.aspx), vehicular combustions and fugitive sources could account for nearly or more than 50% of the total annual non-methane hydrocarbon emissions in Kaohsiung city. The effects of emission height and air humidity on the VOC distributions were not negligible and were further impacted by the physicochemical properties of VOCs including their molecular structures, photochemical resistances, and atmospheric lifetimes.

With the air quality problems in Kaohsiung city, one of the next steps to develop effective control strategies is the use of appropriate air quality models to investigate/predict the VOC emissions from different sources and to assess the adverse health risks. In this study, possible differences between two model predictions and associated health risk assessments due to different theories behind two models were investigated. Two petrochemical industrial complexes in Kaohsiung city of southern Taiwan were selected as the sites for comparison. Although the study compares the approaches by applying the methods to this specific area, the results are expected to be adopted for other areas or industries. The VOC data observed at the monitoring sites were applied with a receptor model for source apportionment to determine the VOC concentrations contributed by the stationary sources in two petrochemical industrial complexes. On the other hand, the VOC emissions from these stationary sources were investigated and applied with a dispersion model to predict the VOC concentrations at the monitoring sites. The VOC data estimated by two models were compared with those observed by monitoring, followed by comparisons of the cancer and non-cancer risks that were calculated by using these monitored and predicted VOC concentrations. The effects of diurnal temperature and seasonal humidity variations on two model predictions were also discussed.

2. Experimental methods

2.1. Monitoring and sampling

This study focused on the vicinities of two petrochemical industrial complexes (Renwu and Dazher) in the north of Kaohsiung city in Taiwan. Two complexes together form Renda industrial park and both are well known for their VOC emissions. Renwu industrial complex contains petrochemical and some chemical and plastic industries, while Dazher industrial complex mainly contains petrochemical industries. The overall areas of Renwu and Dazher industrial complexes are 21 and 109 ha, respectively. Abbreviations of RW and DS are used to represent the names of Renwu and Dhazer Industrial Complexes, respectively. Four sampling sites including one upwind location and three downwind locations were selected to consider the possible effect of wind direction on VOC concentration distributions (Fig. 1). The Taiwan EPA's Taiwan Air Quality Monitoring Network provides the information for wind speeds and directions in these areas during the monitoring period (http://taqm.epa.gov.tw/taqm/en/default.aspx).

Our early study has indicated the influence of humidity variation on the VOC distributions near the areas of interest (Liu et al., 2014). The rainy season typically lasts from April to June every year. The samplings were conducted in January and June 2011 for VOC analyses in the dry and wet seasons, respectively. Each sampling lasted for two days. To investigate the effect of diurnal temperature variation on VOC concentrations, air samples were collected twice a day. The Taiwan Central Weather Bureau provides the meteorological information (http://www.cwb.gov.tw/V7/index.htm). The average monthly relative humidity were 72% (the minimum was 39%) and 75% (the minimum was 52%) in two samplings. Although the difference of the average relative humidity between two seasons was limited, the rainy season occurred between two samplings increased the humidity in the wet season (e.g., the minimum humidity in two seasons). The average temperatures in the dry and wet seasons were 17.5 °C (between 11.3 °C and 25.0 °C) and 27.2 °C (between 21.2 °C and 32.9 °C), respectively.

2.2. VOC analysis

The VOC concentrations were analyzed by following the U.S. Environmental Protection Agency's (USEPA's) TO-15 standard method (USEPA, 1999). Air samples were collected in specially-prepared canisters. All canisters were emptied and cleaned before sampling. A blank experiment was performed to ensure samples were not contaminated during collection. After sampling, the valves were close and the canisters were transported to the laboratory for VOC analysis by using gas chromatography coupled with mass spectrometry (GC/MS).

A GC/MS (HP 6890N) with a thermal desorption unit (ENTECH 7100A, TDU) was used for VOC analysis. Air sample was directed from a canister through a solid multi-sorbent concentrator. Water contents in air samples were removed by dry-purging with helium. The VOCs on the concentrator were desorbed by heating at 150 °C and were entrained in the carrier gas stream. The VOCs were then trapped on a small volume multi-sorbent trap, followed by being thermally desorbed and injected into the GC/MS. The GC was equipped with a 60 m × 0.25 mm I.D. DB-VRX capillary column (Chrompack, U.S.). Mass spectrometry was performed in electron ionization mode. The acquisition mode was set to scan in the range