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Characterization of non-methane hydrocarbons and their sources in an industrialized coastal city, Yangtze River Delta, China

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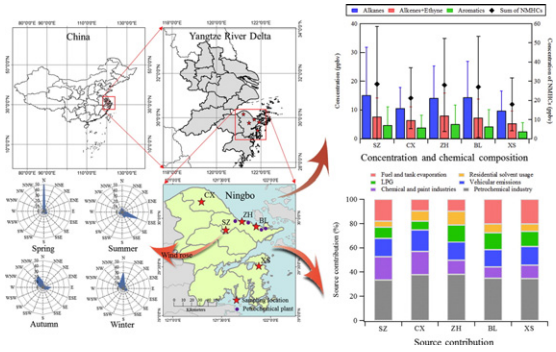
HIGHLIGHTS

- First measurements of NMHCs in Ningbo, an industrialized coastal city in the YRD, China, are reported.
- Diagnostic ratios were used to analyze the chemical evolution of NMHCs.
- Conditional probability function (CPF) was used to facilitate the determination of PMF-resolved factors.
- Seasonal variations of source contributions should be considered when formulating the NMHC abatement strategy.

GRAPHICAL ABSTRACT



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ABSTRACT

Ningbo is a highly industrialized city in the coastal area of the Yangtze River Delta (YRD), China. Large emissions and transport of non-methane hydrocarbons (NMHCs) may contribute to regional ozone (O_3) and particulate matter (PM) pollution; however, the concentrations and sources of ambient NMHCs have not yet been investigated in Ningbo. In this study, ambient NMHCs were measured at two residential (SZ and CX) and two industrial (ZH and BL) sites and one suburban (XS) site over ten consecutive days in each season (10–20 December 2012 in winter, 14–23 April 2013 in spring, 15–24 July 2013 in summer, 22–31 October 2013, in autumn). A positive matrix factorization (PMF) model using multiple site data was deployed to explore the source contributions and their spatial and seasonal characteristics. The measurement results showed obvious seasonal variations in ambient NMHC concentrations (ranging from 17.89–28.48 ppbv); chemical compositions were similar among the five sampling sites. PMF analysis showed that the petrochemical industry was the largest contributor (an average of 35.64%) to ambient NMHCs, while contributions of smaller sources (i.e., chemical and paint industries [14.34%], fuel and tank evaporation [16.02%], and residential solvent usage [7.24%]) showed spatial variations. Liquefied petroleum gas and fuel and tank evaporation contributed more in summer and autumn, while the contribution of the chemical and paint industries was greater in spring and winter. An evaluation of the ozone formation potential and secondary organic aerosol potential suggested that petrochemical and solvent-related sources were key parameters in mitigation of secondary pollutant formation. Seasonal variations in source contributions should be considered when formulating an effective NMHC abatement strategy.

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1. Introduction

The Yangtze River Delta (YRD), located in Eastern China, has undergone rapid development and urbanization. It encompasses a cluster of large cities such as Shanghai (a municipality of China), Nanjing (the capital of Jiangsu Province), Hangzhou (the capital of Zhejiang Province), Suzhou, Ningbo, and Wuxi. Along with economic growth and industrial development, this area has been suffering from severe air quality deterioration (Deng et al., 2011; Hu et al., 2014). High levels of particulate matter (PM) and ozone (O_3) are frequently observed (Cheung and Wang, 2001; Fu et al., 2008; Tie et al., 2006). The YRD was identified as an emission hotspot in the emission inventory of China (Bo et al., 2008; Zhang et al., 2009). In this region, volatile organic compounds (VOCs) play an important role in the formation of secondary pollutants (i.e., O_3 and secondary organic aerosols [SOA]) (Geng et al., 2007; Volkamer et al., 2006). Non-methane hydrocarbons (NMHCs), a specific subset of VOCs, can account for a large proportion of total ambient VOCs in urban areas (Watson et al., 2001). Thus, it is essential to identify the sources of NMHCs and formulate efficient abatement strategies to address serious air pollution.

Receptor models are widely used to apportion the source contributions of ambient NMHCs (Henry et al., 1984). Chemical mass balance (CMB), positive matrix factorization (PMF), principal component analysis/absolute principal component scores (PCA/APCS), and the UNMIX receptor model have been utilized to investigate NMHC source characteristics in various cities, such as Beijing (Song et al., 2008), Shanghai (Cai et al., 2010) and Nanjing (An et al., 2014) in China, Los Angeles (Brown et al., 2007) and Houston (Buzcu and Fraser, 2006) in the United States (US), and Dunkerque in France (Xiang et al., 2012). It has been shown that vehicular emission is the major source in urban areas (e.g., Lau et al., 2010; Song et al., 2008) while industry-related activities (e.g., petrochemical and solvent usage) are the largest contributors in industrialized areas (e.g., Buzcu and Fraser, 2006; Dumanoglu et al., 2014). In addition, the source characteristics show significant seasonal and spatial variations. For example, evaporative emission contributes more in summer due to high volatility at high temperatures and sites in close proximity to industrial emissions are more heavily impacted (Dumanoglu et al., 2014).

Ambient NMHC sources are associated with energy consumption, urban development, and industrial structures in particular regions. Ningbo, one of the urban cores in the YRD, is a coastal and highly industrialized city, consisting of a large industrial complex with petroleum, organic chemical, and painting plants. There is a diversity of petroleum and chemical products such as gasoline, diesel fuel, liquefied petroleum gas (LPG), and acrylonitrile–butadiene–styrene (ABS). Equipment leakage, fugitive evaporation, and exhaust discharge are all potential sources of NMHC emissions in this area. However, there is still limited understanding of the characteristics of NMHCs in Ningbo; the source structure of NMHCs and their spatial and seasonal characteristics have not yet been determined. Nevertheless, this information is urgently needed for local governments and policymakers to formulate efficient NMHC abatement policies.

Recently, the characteristics of industry related sources were investigated in Ningbo (Mo et al., 2015; Mo et al., 2016). However, it is difficult to employ a CMB model for source apportionment due to the limited availability of source profiles. In contrast, a PMF model is more favorable because only ambient data is required (Paatero and Tapper, 1994). In this study, ambient samples of NMHCs were collected from five sites (including two residential and two industrial sites, as well as one suburban site) in Ningbo. The spatial and seasonal characteristics of ambient NMHCs were investigated, and their source contributions were determined using a PMF model. A conditional probability function was used to facilitate source identification. Ozone formation potential (OFP) and secondary organic aerosol potential (SOAP) were evaluated for the development of effective pollution control strategies. This study gives an example of PMF source apportionment using multiple site data for four seasons from different regions, and advances our understanding of NMHC source contributions in a coastal and highly industrialized city.

2. Methodology

2.1. Sampling program

Ambient samples were collected in 3.2-L fused silica-lined stainless steel canisters (Entech Instrument, Inc., Simi Valley, CA, USA) simultaneously at five sites in Ningbo: Shizhan (SZ), Cixi (CX), Zhenhai (ZH), Beilun (BL), and Xiangshan (XS), as shown in Fig. 1. Taking SZ as a reference point, CX, ZH, BL, XS are approximately 40 km northwest, 20 km northeast, 30 km east, and 55 km southeast of SZ, respectively. The sampling sites were selected with the aim of collecting ambient samples away from the immediate influence of localized pollution sources, such as roadside vehicle exhausts and industrial emissions. Sufficient separation for the generally long-lived NMHCs considered here was achieved using sites located at the tops of buildings, five to eight stories in height. All of these sites belonged to the air quality monitoring stations established by the local governmental environmental monitoring center; the sites were easily accessible for canister sampling and were located at an appropriate distance so as to avoid direct smoke stack emission or other industrial outputs nearby. This was to ensure that the samples were representative of well-mixed air. Hourly measurements were conducted for the criteria pollutants sulfur dioxide (SO_2), nitrogen dioxide (NO_2), carbon monoxide (CO), ozone (O_3), and $PM_{2.5}$. Specifically, SZ (area: 271 km^2; population: 819,000) and CX (area: 1,361 km^2; population: 1,042,000) are located in urban areas surrounded by residential buildings and traffic roads. ZH (area: 246 km^2; population: 228,000) and BL (area: 559 km^2; population: 383,000) are two industrial sites, around which a large petrochemical complex and chemical production factories are situated (Fig. 1). The suburban site XS (area: 382 km^2; population: 540,000) was also selected. Compared with ZH and BL, XS has less industry and no significant local sources. A terrain map of these areas is illustrated in Fig. S1 in Supplementary material.

Four sampling events were conducted during 10–20 December 2012, 14–23 April 2013, 15–24 July 2013, and 22–31 October 2013, representing winter, spring, summer, and autumn, respectively. The sampling dates were selected based on a forecast of meteorological conditions. All samples were collected on days that were predicted to have synoptic conditions with fine weather and calm winds. Each event lasted ten consecutive days, and the weather during the sampling days was generally fine and the wind speed calm, favoring pollutant accumulation and interaction. Time periods with such weather conditions were deliberately sought so as to maximize NMHC signals and increase the likelihood of successful identification of sources using PMF. It should be noted that sampling on the 19 December 2012 was stopped due to rain. For each sampling day, three samples were collected at 8:00, 13:00, and 21:00 from each site, which aimed to capture NMHC changes due to human activities, e.g., rush-hour traffic and industrial manufacturing. Note that due to the scale of industrial activities in this area, no significant variations in industrial emissions were observed between daytime and nighttime or between weekdays and weekends. Subatmospheric sampling was used. The evacuated canisters (<20 mTorr) were placed on the "roof platform" for 30-min sampling. No sources (e.g., air conditioning systems) immediately influenced the sampling. A filtered grab sampler (39-RS-0, Entech Instrument, Inc.) was used with a pre-calibrated flow regulator (CS1200; Entech Instrument, Inc.) at a flow rate of about 1.8 mL s^{-1}. A pressure gauge was used to check the completion of each sample collection (~atmospheric pressure). A total of 600 samples were collected across the sampling events.