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Characteristics of C_2–C_{15} hydrocarbons in the air of urban Kaohsiung, Taiwan

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Abstract

The concentrations of 71 hydrocarbons (HC) from C_2 to C_{15} were measured simultaneously at two sites in Kaohsiung city in the morning (07–10), the afternoon (13–16), and the evening (18–21) on 14 days in spring 2003. A total of 84 3-h integrated air samples were collected using multibed stainless-steel thermal adsorption tubes and then analyzed using a GC/FID or a GC/ECD. The most abundant species of Kaohsiung's air is toluene (43.36–54.49 $\mu g\,m^{-3}$), followed by *i*-pentane, 1,2,4-trimethylbenzene, benzene, *n*-butane, propane and acetylene, in the range 10.36–17.11 $\mu g\,m^{-3}$. The concentrations of 14 halocarbons are in the range 0.25–4.57 $\mu g\,m^{-3}$. Alkanes (around 44.8%) represent the largest proportion of the total HC, followed by aromatics (35.1%), alkenes (15.5%) and halocarbons (5.4%). The afternoon HC concentrations are much lower than those in the morning and at night, due to relatively intense photochemical reaction and favorable dispersion conditions from noon to afternoon. Notable increases in daily HC concentrations are consistent with high temperature, and low HC concentrations on Sunday coincide with low traffic volume. Photochemical activity is investigated, and HC concentrations are found to decline as the NO_2/NO_x ratio increases. Correlation analyses imply that vehicle exhaust is the dominant source of atmospheric hydrocarbons in Kaohsiung.

Keywords: Hydrocarbons; Aromatics; Halocarbons; Urban air quality; Vehicle exhaust

1. Introduction

Vehicles, industries and energy production sources emit large amounts of anthropogenic hydrocarbons (HC) into the atmosphere. Most ambient hydrocarbon species are strongly associated with the formation of photochemical oxidants and elevated surface ozone levels in urban areas (Seinfeld and Pandis, 1997). Some hydrocarbon species, including benzene and chlorobenzene, are also known to be toxic.

Kaohsiung, just below the Tropic of Cancer (23.5°N) in southern Taiwan, is an industrialized and densely populated harbor city, with around 1.49 million inhabitants, 1,281,000 registered vehicles (380,000 cars, 886,000 motorcycles, and 15,000 trucks) and an area of 153.6 km^2. Dense traffic and industrial activities have made Kaohsiung city and the surrounding Kaohsiung County the source region of the most HC and the poorest quality of air in Taiwan (DEP, 2002). In southern Taiwan, the air has the poorest quality between the late winter and the middle spring, and in the autumn, largely due to increased ground-level ozone concentrations associated with unfavorable meteorological conditions (Chen et al., 2004). Although many control measures, including regulating stationary-source NO_x emissions form power stations and steel-making industries and hydrocarbon emissions from organic solvents, petrol-chemical industries, and mobile sources, have been implemented to improve the quality of air in Kaohsiung, most are based on the continuous monitoring of air-quality data, such as NMHC (total non-methane hydrocarbons), NO_x ($=NO+NO_2$) and ozone. No station for monitoring HC species, continuously or

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non-continuously, has been set up in Taiwan. Speciation and concentrations of atmospheric hydrocarbons are essential in evaluating the photochemical reactivity of individual species. They are also required inputs in source apportionment analysis, using either a receptor model (Scheff and Wadden, 1993; Watson et al., 2001) or a multivariate principal component/factor method (Derwent et al., 1995; Borbon et al., 2002), which helps to develop an effective means of reducing atmospheric HC levels.

This work presents the measurements of the concentrations of 71 HC species in Kaohsiung in the spring of 2003. Spatial and temporal variations of the atmospheric HC levels were investigated. Correlation analyses were conducted to assess the importance of vehicle exhaust to ambient HC levels. The effects of other sources on ambient HC levels and photochemical reactivity were also considered.

2. Experimental

2.1. Sampling sites and periods

This work selected two sampling sites, Nan-Chie and Hsiung-Kong, in the northern and southern parts of Kaohsiung city, respectively. These sites were selected because they include air-quality monitoring stations operated by the Taiwan-EPA (Environmental Protection Administration). Hence, hourly air-quality and some meteorological data, including NMHC, NO_x, temperature, wind speed and direction were available at these stations. As indicated in Fig. 1, Kaohsiung areas include six large industrial complexes, two in Kaohsiung city and four in Kaohsiung County. The distance between the Nan-Chie and Hsiung-Kong sites is approximately 20 km.

Sampling was performed over 14 days on 17–23 March and 21–27 April in 2003 concurrently at the two sites. Each day included three 3-h sampling periods— in the morning (07–10), the afternoon (13–16) and the evening (18–21). A total of 84 3-h integrated air samples were collected. Table 1 presents the meteorological conditions, including temperature, wind speed and the period of sunshine. Also, Fig. 2 displays the wind rose plots over the study period, during which the relative humidity ranged from 66.0% to 78.9%.

2.2. Methods of sampling and analysis

Gaseous samples were collected using multi-bed stainless-steel thermal adsorption tubes (Carbotrap 300, Supelco) and HC with widely different volatilities were simultaneously separated at each site, as described in Chen et al. (2003). Three adsorbent columns with an inner diameter (i.d.) of 5.3 mm are packed in the tube. The Carbosieve S-III column (60/80 mesh, 125 mg) is designed to separate out light HC from C_2 to C_5; the Carbotrap B column (20/40 mesh, 200 mg) is designed to separate out C_5–C_{10}, and the Carbotrap C column (20/40 mesh, 300 mg) is designed to separate out C_{12}–C_{20}. The thermal adsorption tube was connected to a pump (SKC Model 210-1000 s, SKC) operated at an airflow rate of 200 ml min^{-1}. The sampling method and procedures were complied with the US—Environmental Protection Agency (EPA) Methods TO-1 and TO-2.

Breakthrough tests were performed before and during the samplings at each site. Tests were conducted by joining another test adsorption tube to one end of the sampling tube. The minimum breakthrough time of each site was determined to be 4.5 h. For consistency, the sampling time was 3 h at each site. The two ends of the sampling tube were sealed after the samples were taken and analyzed in the laboratory. No breakthrough of the compounds occurred in the test tubes. Before sampling, the tube was conditioned using nitrogen gas at a flow rate of 40–70 ml min^{-1} and a temperature of 250–360°C for 2–5 h, and was then conditioned for 24 h after sampling.

HC were analyzed by cryo-focusing and capillary gas chromatography (GC), using a Tekmar 6000 thermal desorber unit and a Shimadzu GC-14B, fitted with a flame ionization detector (FID) for non-halocarbons and an electron capture detector (ECD) for halocarbons. The analytical column of the GC was a J & W Scientific DB-1 fused silica capillary column (0.249 mm i.d., 30 m long, 0.25 μm film thickness). The oven temperature program was 32°C for 6 min, followed by three heating stages. Heating began at a rate of 10°C min^{-1}–70°C, before being increased at a rate of 13°C min^{-1}–110°C, and then being finally increased at a rate of 10°C min^{-1}–230°C. A total of 71 HC species in C_2–C_{15} were identified, including alkanes, alkenes, aromatics and halocarbons (Table 2). The desktop computer and an integration analyzer analyzed all data and output plots. Note that the ideal gas law and the molecular weight of a compound were used to convert its mass concentration (μg m^{-3}) to its volume fraction (ppm), evaluated at 1 atm and 298 K (Seinfeld and Pandis, 1997). The organic concentration as carbon (ppmC) of a compound is the carbon number of the compound times its volume fraction (ppm), complying with the US-EPA Method 25A. Then, the concentration of NMHC (ppmC) was obtained by summing all individual organic concentrations as carbon.

Calibrations were conducted using six different concentrations of standard samples in clean tubes, all with a coefficient of determination, R^2, above 0.995. The lowest possible concentration of a compound above the noise value of the instrument was then analyzed repeatedly for seven times, from which the detection limit (DL) was determined by three times the standard