



C₂–C₅ HYDROCARBON CONCENTRATIONS IN CENTRAL OSAKA

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Abstract—Hourly measurements of nine C₂–C₅ hydrocarbons (HCs) were made over a period of 15 months in the center of Osaka City, Japan. The measurements were made by using an automated system consisting of a combination of a gas preconcentrator and a gas chromatograph. The concentrations of all components were high in early winter and low in summer. The highest concentration was of C₂H₄, while C₃H₆ showed the lowest concentration throughout the year, and was rarely detected in summer. There were small annual variations in the concentrations of C₄–C₅ HC. The chemical reactions that affect HC concentrations were also examined. The seasonal C₂H₄/C₂H₂ and C₃H₆/C₂H₂ ratios were compared, taking into account that C₂H₄, C₂H₂, and C₃H₆ are mainly from vehicles and the differences in their reactivities. Despite the high reactivity of C₂H₄, the C₂H₄/C₂H₂ ratio was low in winter and high in summer, with the result that the C₂H₄ consumption by chemical reaction seemed small in the center of the city. The behavior of C₃H₆/C₂H₂ is opposite to that of C₂H₄/C₂H₂, illustrating the more reactive characteristics of C₃H₆. Regarding the effect of photochemical reactions, it was observed that HC's levels drop as NO₂/NO_x increases. Though the slope does not show a direct proportionality to HC reactivity, reactivity of C₃H₆, which is the most reactive HC among the nine measured HCs, showed the largest declines. The ratio of C₄–C₅ HC to the C₂–C₅ HC rose with increase in ambient temperature, while the ratio of C₂–C₅ HC to the nonmethane hydrocarbons decreased. This phenomenon was correlated with ambient temperature, indicating higher emissions of higher molecular weight HCs in summer. © 1998 Elsevier Science Ltd. All rights reserved

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1. INTRODUCTION

Atmospheric HCs are closely related to both photochemical oxidant formation and to high concentrations of NO₂ (nitrogen dioxide) which appear in winter or spring in urban areas of Japan. It has been indicated that HCs play an important role in aerosol formation and acid rain. In addition, some HCs such as benzene and 1,3 butadiene are toxic.

In Japan, atmospheric HCs are being monitored as nonmethane hydrocarbon (NMHC) at 358 air pollution monitoring stations and 179 automobile exhaust monitoring stations (1994). In the central Tokyo and Osaka areas, the annual average of NMHC between 0600 and 0900 LST decreased from 0.77 to 0.41 ppmC at air monitoring stations, and from 0.83 to 0.42 ppmC

at automobile exhaust monitoring stations from 1983 to 1994 (Environment Agency, Japan, 1995a, b). At the same time photochemical oxidant levels have not shown much improvement for several years and high levels of photochemical oxidants were monitored on the outskirts of metropolitan areas (Wakamatsu *et al.*, 1996) as well. Wakamatsu *et al.* attribute this to the wide spread of emission sources, increments of NO_x (nitrogen oxides) emissions and decrease of the NMHC/NO_x ratio. However, it is also important to note that changes in the components of NMHC change the reactivity of NMHC, which influence photochemical reactions in the atmosphere (Dodge, 1984).

Recently, long-term observations of individual HC levels were made by many researchers in both urban and remote area (e.g. Boudries *et al.*, 1994; Bottenheim and Shepherd, 1995). The biggest monitoring program is the Photochemical Assessment Monitoring Station (PAMS) network program, which was started by the U.S. Environmental Protection Agency. Continuous measurements of pollutants

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including individual volatile organic compounds (VOCs) have been started to provide information on the role of oxidant precursors, pollutant transport, and local meteorology in the photochemical process (Gerald, 1994).

However, for Japanese urban areas, the sampling periods have not been sufficiently long. The longest continuous measurement of individual HCs (C_2 – C_4) was made during 35 d in summer and during 40 d in winter by Kayashima and Aoki in the Tokyo Bay area (1989). The distributions of HC components differ from those in cities and reflect characteristics of the areas. Each HC component has shown large variations in concentration, diurnally and seasonally. To clarify the time behavior of individual HC in each metropolitan area is a very important step in solving pollution problems in urban areas.

In this study, nine atmospheric species of C_2 – C_5 HC were measured continuously (every hour), during a year and three months. It was the longest measurement period in Japan. The results were analyzed to determine the behavior of each HC. Also, the relationship between HC and other atmospheric pollutants was examined to clarify the effects on photochemical pollution, considering meteorological influences.

2. METHODOLOGY

The Konohana ward air pollution monitoring station located on the rooftop of the Konohana Ward office, Osaka Metropolitan Area, was chosen as the monitoring point. This is an industrial area, about 4 km from Osaka Bay. A map of the monitoring station location is shown in Fig. 1. Two trunk roads, National Highway Root 43 and Hokkou street pass near the station, intersecting 130 m southeast of the monitoring point. The sampling period was from October 1992 to December 1993, except from April 17 to May 31 1993, when the roof of the building was being repaired.

This area is strongly affected by land and sea breezes, and the frequency of winds from the north–northeast (north–northeasterly winds; land breezes) is high from midnight to morning. The frequency of winds from the west (westerly winds; sea breezes) is high from noon to evening. The frequency of southeasterly winds is under 1% of all winds throughout the year. The other pollutant concentrations (e.g. NO_x) and meteorological data were obtained from the routine air monitoring program at Konohana Air Pollution Monitoring station. To show the air quality level of the Konohana area, the monthly average pollutant concentrations monitored at the station are listed in Table 1. The meteorological conditions are also listed in Table 1.

The contribution to NMHC levels from different sources at the monitoring point was estimated by Tanaka *et al.* (1993) using a chemical balance element air pollution model. Tanaka *et al.* indicated vehicle emissions were the dominant source of NMHC, 43.1% in summer and 44.3% in winter.

The continuous measurements of atmospheric C_2 – C_5 HCs were made by an automatic system, which was a combination of a gas preconcentrator and a gas chromatograph. Air was sampled in a trap in the preconcentrator (DKK, Model Gas-10L) which was cooled to 0°C by an electric cooler with a flow rate of 50 ml min⁻¹. The trap consisted of two stainless-steel columns connected in series, and packed with activated alumina (i.d. 2 mm × o.d. 3 mm × 4 cm, 60–80 mesh) and activated carbon (i.d. 3 mm × o.d. 4 mm × 4 cm, 60–80 mesh), respectively. The trapped components were thermally desorbed at 250°C into the temperature-programmed gas chromatograph equipped with a flame ionization detector (Shimadzu GC-9A) by the carrier gas stream (N_2 , flow rate 45 ml min⁻¹). The analytical column used a glass column packed with activated alumina (i.d. 2 mm × o.d. 3 mm × 2 m, 60–80 mesh). The column oven temperature program was started with an isothermal period of 4 min at 50°C, followed by 7°C min⁻¹ heating to 180°C. The target concentration limit of compounds for this study was set at 0.1 ppbV, and a 400 ml sample of air was employed at this detection limit. Considering the sampling volume, a total analytical run time was determined to be 45 min on the measurement system shown in Fig. 2.

The components identified in this study were: C_2H_6 , C_2H_4 , C_2H_2 , C_3H_8 , C_3H_6 , $n-C_4H_{10}$, $i-C_4H_{10}$, $n-C_5H_{12}$, and

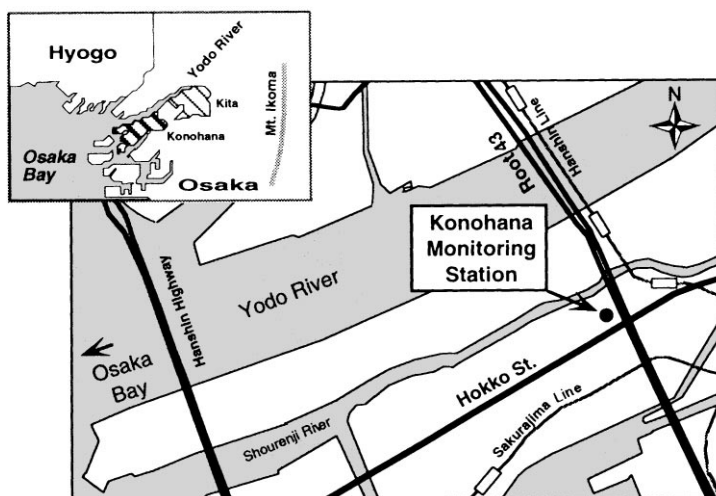


Fig. 1. The location of the measurement site.

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