



Validation of ozone precursor measurement through inter-comparison with NO_x and CO measurement

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Abstract

Continuous hourly measurement of non-methane hydrocarbons (NMHCs) from C_3 to C_{12} was performed by an automated gas chromatographic (GC) system in downtown Taipei between 20 March 2000 and 12 May 2000. To test the performance this automated GC synchronous measurement of NMHCs with NO_x was conducted sharing a common air inlet. Excellent agreement in temporal variation between NMHCs and NO_x was observed suggesting that the automated GC measurement was accurately reflecting ambient concentrations of ozone precursors.

On two occasions during the monitoring period, abrupt increase in concentrations of gaseous pollutants due to nocturnal radiational inversion occurred at night under stable weather conditions. Improved correlation between different NMHC species for data within these two episodes suggested better air mixing than in other periods. These two events of concentration enhancement driven by temperature inversion were also registered in CO measurement in all EPA air quality stations scattered around Taipei metropolitan area. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Ozone precursors; Volatile organic compounds (VOCs); Non-methane hydrocarbons (NMHC); Automated gas chromatographic system

1. Introduction

Air pollution of high surface ozone arising from photochemical formation and accumulation has plagued many regions worldwide (Grennfelt and Schjoldager, 1984; Voltz and Kley, 1988). In the presence of volatile organic compounds (VOCs) and nitrogen dioxides ($\text{NO} + \text{NO}_2 = \text{NO}_x$), ozone is photochemically produced and can accumulate to hazardous level in favorable weather conditions (Davidson, 1993; Wakamatsu et al., 1996). In order to reduce ambient ozone concentrations, anthropogenic VOC emissions, which predominantly consist of non-methane hydrocarbons (NMHC) have been the subject of extensive control programs in many countries. Accurate characterization of ozone precursors, mainly NMHCs, is extremely important for understand-

ing tropospheric ozone formation and accumulation, and crafting effective control strategies to better address ozone air quality management issues. In accordance with the 1990 Clean Air Act Amendments [Section 182(C)(1)], US EPA developed rules for the initiation of photochemical assessment monitoring stations (PAMS) located in ozone non-attainment areas measuring a list of 56 NMHCs (EPA, 1994). Given the high complexity and low abundance nature associated with ambient NMHCs, the chromatographic methods are preferred for their efficient separation and detection capability over other analytical means (Maeda et al., 1995; Oliver et al., 1996; Dewulf and Langenhove, 1999; Helmig, 1999).

To investigate the high ozone problems in several areas of Taiwan, a project has recently been undertaken in an attempt to identify the source characteristics of ozone precursors and ultimately form effective control strategies to reduce ozone. As a result, an automated chromatographic system has been developed for this

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project and has been under intensive field tests for examining its overall performance. In this study a field test conducted by simultaneously running this system with other instruments of different working principle in an urban environment in which the source for most species of NMHCs, NO_x , and CO is the same, namely the vehicular exhaust.

2. Experimental

2.1. Instrumental

This self-developed system used dual trap and dual column to cope with the wide volatility range of the components by employing one column for the gaseous compounds and the other for the higher boiling ones. A PLOT $\text{Al}_2\text{O}_3/\text{KCl}$ column (30 m; 0.32 mm; $df = 8$ m,

Hewlett-Packard, San Fernando, CA, USA) was connected to one of the two sorbent traps for separating light VOCs from C_3 to C_7 . A DB-1 column (60 m \times 0.32 mm; $df = 1.0$ m, J&W Scientific, Folsom, CA, USA) was connected to the other trap for separating C_6 – C_{12} compounds. Detailed technical aspects concerning the system's design and analytical performance can be referred to our earlier publication (Wang et al., 1999, 2000). We have recently modified the system by adding a thermoelectrical cooling device to quantitatively enrich the 3 C_2 species, i.e., ethane, ethylene, and acetylene, which will be discussed in our future publication.

2.2. Field measurement

Between 20 March 2000 and 12 May 2000 this automated GC system was placed in an air quality

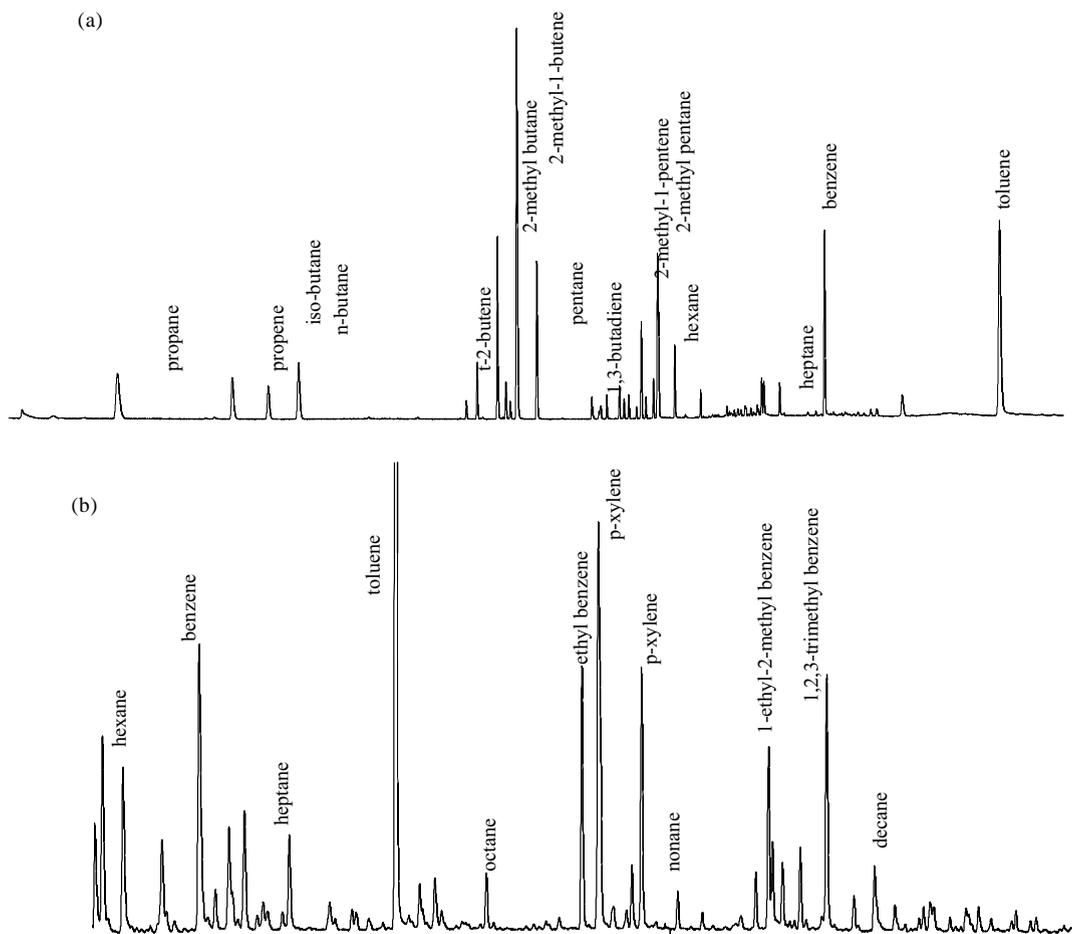


Fig. 1. A typical ambient air sample analyzed by the dual trap dual column GC system with selected peaks labeled for indicating carbon number range, (a) lighter hydrocarbons eluting from the PLOT column, and (b) heavier hydrocarbons eluting from the DB-1 column.

monitoring station on the rooftop of a 7 floor building in downtown Taipei. The automated GC system was run in parallel with the existing instruments in the station measuring SO_x , NO_x , O_3 , and PM_{10} by sharing the same air inlet. All instruments and the automated GC took hourly measurements. Fig. 1 shows a typical hourly measurement result of $\text{C}_3\text{--C}_{12}$ in this field study. Meteorological data, e.g., wind speed, wind direction, temperature, and humidity, were also measured on 10 min basis. Since the automated GC shared the same inlet with other instruments, as a result, the stability and overall performance can be viewed by comparing with the results obtained from other parallel running instruments. One of the major purposes of conducting parallel measurement with species such as NO_x was to validate the performance of the automated GC by a different instrument. Fig. 2 shows the parallel measurement results between the car exhaust type of compounds, such as benzene, measured by our automated GC, and NO_x measured by the chemiluminescence method. Excellent agreement was observed between NMHCs of vehicular origin and NO_x despite the fact that these two instruments have completely different working principles, indicating the performance of the automated GC was sound and actually reflecting the true ambient concentrations of NMHCs. Note that we deliberately conducted this parallel measurement in an urban

environment because both NMHCs and NO_x most likely share a common source of car exhaust. The monitoring site placed on top of a 7 floor building ensures the surface air reaching this altitude has been well mixed. If either of these two types of species has other important exclusive sources, such as in industrial areas where NMHCs and NO_x have their own characteristic emissions, then one may not expect to see such a seamless correlation as in Fig. 2. In that case, it would not be justifiable to validate NMHCs with NO_x measurement.

During the measurement period the prevailing winds were mild northeasterlies with wind speed varying from 0 to 7 m/s. Precipitation was common in this season. These weather conditions did not favor the accumulation of air pollutants and, as a result, the concentrations of NMHCs were rather low most of the time. On two occasions, when the strength of northeasterlies was subsiding and the precipitation paused, the much stable weather conditions manifested in the abrupt increase in the concentrations of air pollutants, as seen in Fig. 3 indicated by the enclosed portions.

We further investigated the mixing of compound affected by the wind conditions, which could be revealed by the correlation between compounds. Since the major source of NMHCs in Taipei is vehicular exhaust, concentrations of various compounds originated from tailpipes ought to exhibit high correlation in ambient air. As expected, excellent correlation was found among most measured compounds with R^2 better than 0.9, except with propane, iso-butane, and butane, which have other sources such as the liquefied petroleum gas (LPG). Fig. 4 illustrates relationship between the abundance of benzene and 3-methyl hexane, both of which are typical car exhaust compounds in urban environment. In Fig. 4a hourly data in the entire measurement period show good correlation between the two compounds with $R^2 = 0.94$. To illustrate how weather conditions affected air mixing the data points covered by the two episodes were isolated from the rest of the observation data. In Fig. 4b, the correlation within the episodes improves to $R^2 = 0.95$ compared to $R^2 = 0.94$ for the whole data set. By contrast, the data points outside the episodes exhibit much poorer correlation with $R^2 = 0.75$, see Fig. 4c.

Not only was the improvement in correlation observed for compounds of a common origin, compounds arising from different sources were also found to have similar results. For instance, propane, whose source is mainly the leakage of LPG used as a household fuel in certain parts of the city, exhibited poor correlation with most of the NMHCs. Nevertheless, the relationship between propane and benzene, which is a typical car exhaust compound, also showed improvement in correlation during the episodes with $R^2 = 0.78$ compared to $R^2 = 0.50$ for data outside the episodes, see

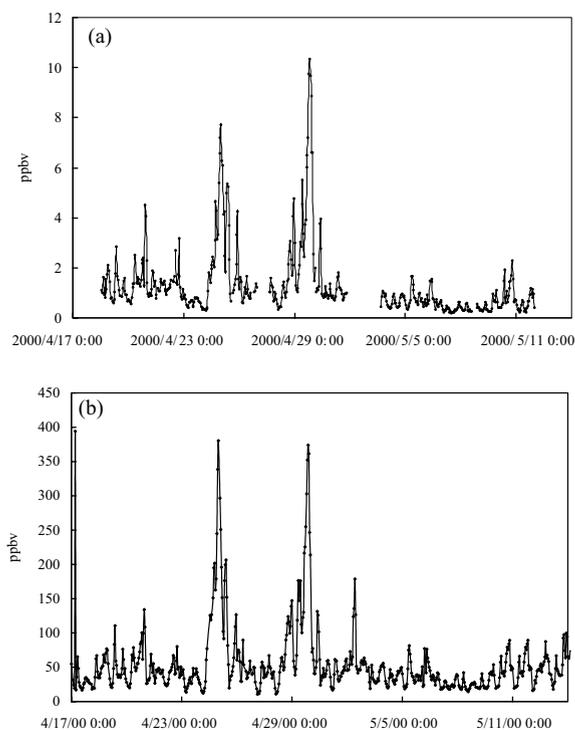


Fig. 2. Synchronous variation between (a) car exhaust type of NMHCs, e.g., benzene and (b) NO_x .

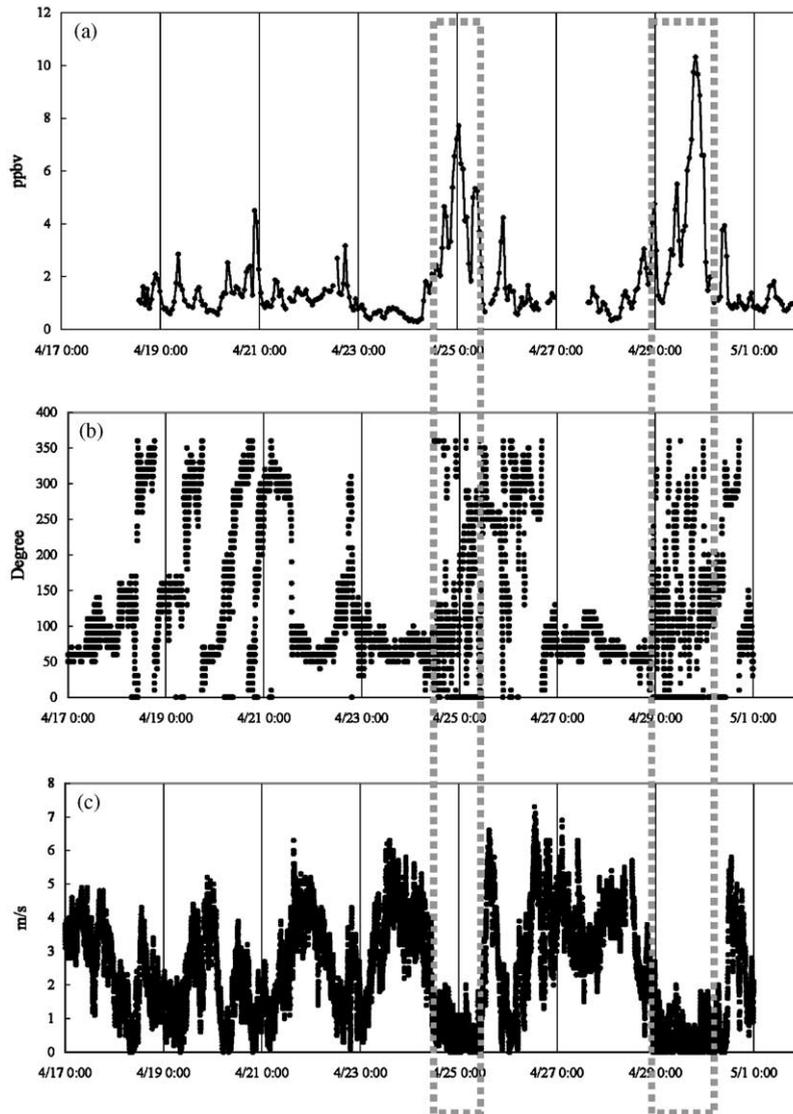


Fig. 3. Correlation of (a) benzene with (b) wind direction and (c) wind speed. Two pollution episodes are encircled by the dotted line.

Fig. 5. This improved mixing during the episodes was the result of weak turbulence as suggested by low wind speeds and random wind directions during these two time periods. Since the emissions were near the surface, the emitted compounds were given time to mix by the weak turbulence before reaching our observation site, ~ 30 m above the surface. By contrast, the higher wind speeds and more uniform wind directions outside the episodes translated into faster transport towards our site and hence less blending with air masses aside from their pathways and, consequently, poorer correlation.

These two episodes were mainly the result of nocturnal radiational inversion. The rapid radiation of

heat off the ground creates temperature inversion near the surface in stable weather condition, which prevents the ventilation of gaseous pollutants emitted from the surface at night, resulting in concentration enhancement. The inversion top elevates and finally breaks up as the sunlight continues to heat up the surface in daytime until the inversion disappears completely in the afternoon, which dilutes pollutants to their minimum levels near noon time. Not only was this inversion registered in the NMHC and NO_x data, but also observed by the CO measurement in other 5 Taiwan EPA air quality stations, which are scattered around Taipei metropolitan area of about 400 km^2 , as illustrated by Fig. 6 for the CO measurement from 3 selected stations.

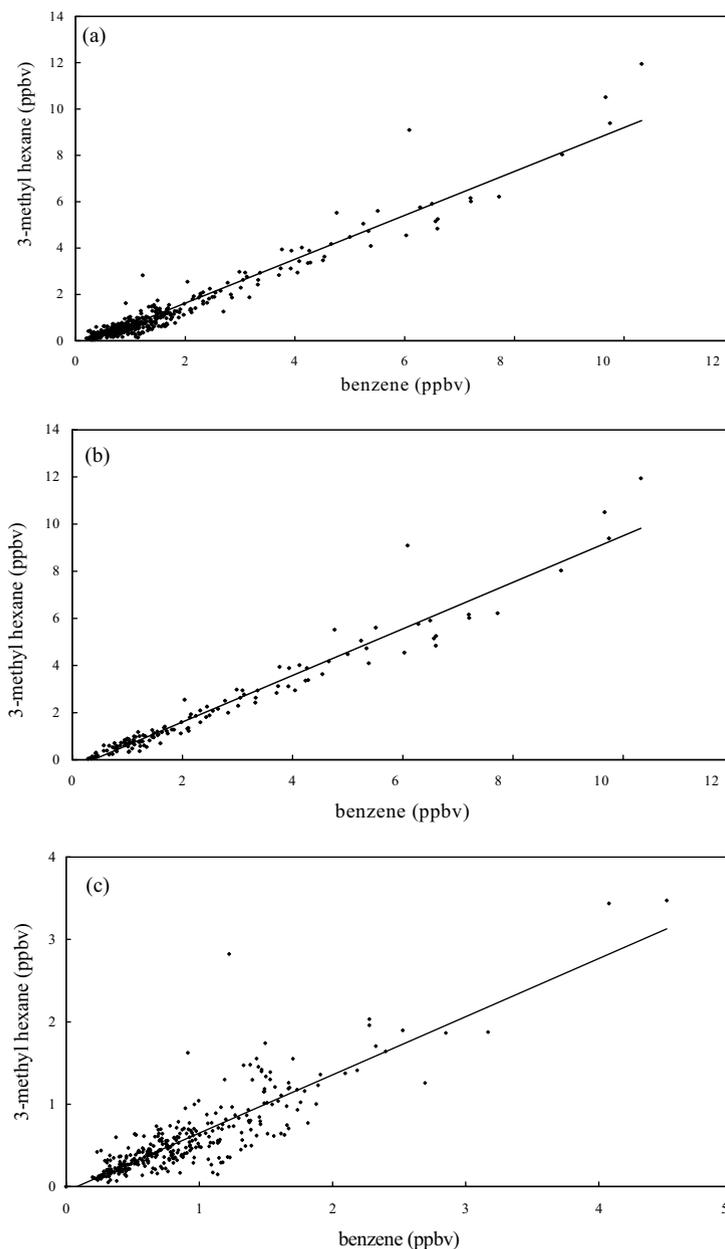


Fig. 4. Correlation between 3-methyl hexane and benzene in different time slots, (a) entire measurement period encompassing about 500 data points with $R^2 = 0.936$, (b) within the episodes encompassing about 150 data points with $R^2 = 0.946$, (c) outside the episodes encompassing about 350 data points with $R^2 = 0.749$.

3. Conclusion

To validate the ozone precursor measurement we synchronized an automated GC system with a NO_x instrument to perform continuous hourly measurement in downtown Taipei. The excellent agreement between NMHCs and NO_x observation effectively substantiated the quality of ozone precursor measurement.

Concentration variation was better understood when taking into account of wind information. The concentration enhancement occurred on two nights with calm weather condition was the result of nocturnal radiational inversion, and also registered in the CO measurement in 5 EPA air quality stations distributed around Taipei basin. The extremely consistent results with the NO_x and CO measurement during the field test period

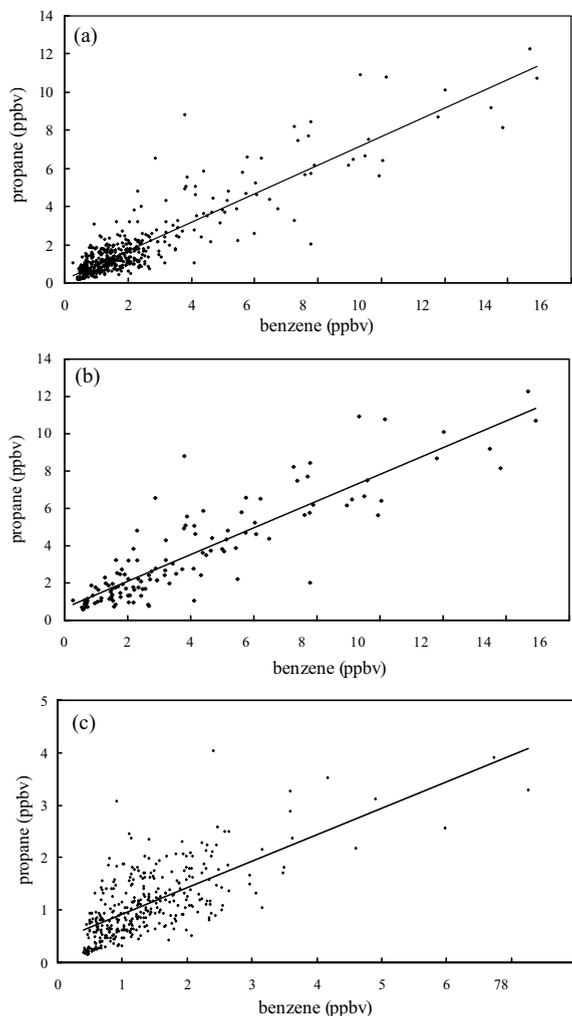


Fig. 5. Correlation between propane and benzene in different time slots, (a) entire measurement period with $R^2 = 0.798$, (b) within the episodes with $R^2 = 0.777$, (c) outside the episodes with $R^2 = 0.468$.

indicated that the automated GC system was adequate in monitoring ambient NMHCs.

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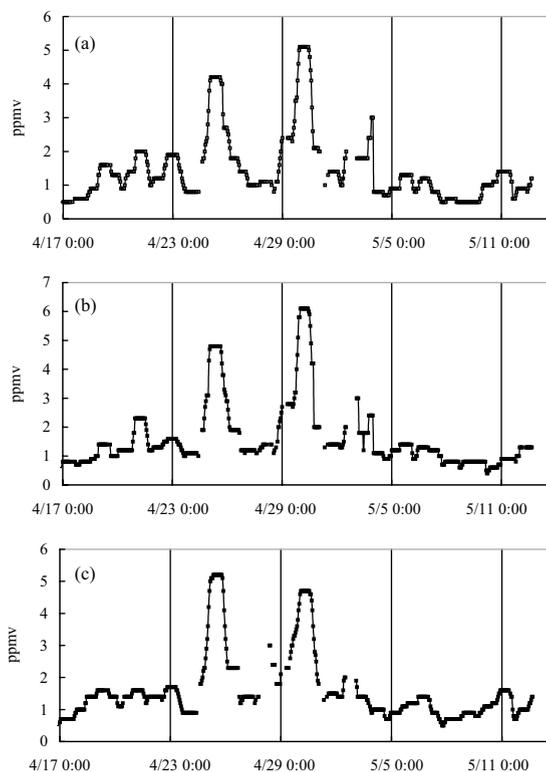


Fig. 6. CO measurement in 3 selected EPA air quality stations in Taipei metropolitan area. The three EPA stations (a), (b), and (c) are located southeast, west, and northeast of site, respectively, within 5–10 km to our site.

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