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# Effects of reactive hydrocarbons on ozone formation in southern Taiwan

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**Abstract**

Ambient air samples were collected at 13 air quality monitoring stations in Kaohsiung city, Kaohsiung county, and Pingtung county (KKP) to investigate the composition and spatial distribution of $C_2$–$C_{10}$ non-methane hydrocarbons (NMHCs) in southern Taiwan. Ozone formation potentials (OFPs) of NMHCs were estimated using maximum incremental reactivity (MIR) and $k_{OH}$ method (reactivity of NMHC with OH radical) to assess the relative effects of hydrocarbons on ozone formation. The measurements showed that mixing ratios of toluene, ethene, ethyne, ethane, isopantane and propane were the highest among all measured species at most of the sampling sites. Nevertheless, considering both the photochemical reactivities and mixing ratios of all the measured species, toluene, xylene, ethene and propene were calculated to have the highest OFPs and reactivities. The OFPs and reactivities assessed by the MIR and $k_{OH}$ methods for the four compounds accounted for 54.5% and 39.3% of all the measured species. Larger benefit margin of ozone abatement may be obtained by reducing emissions of a group of key species with high OFPs.

2,2-dimethylbutane (22DMC4) was used as an indicator of traffic emissions to distinguish traffic from non-traffic contributions of key species in Kaohsiung metropolitan area. It revealed that the contribution of non-traffic source was significant for toluene, whereas xylene was found to be primarily from the traffic source in Kaohsiung metropolitan area during the sampling periods.
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## 1. Introduction

Because of the rapid economic growth in Taiwan in the last few decades, increasing amounts of non-methane hydrocarbons (NMHCs) and nitrogen oxides ($NO_x$) are released into the atmosphere due to escalating consumption of fossil fuel burning and solvent usage. As a result, large amount of ozone is produced in urban as well as in downwind rural areas of Taiwan. Kaohsiung city, Kaohsiung county and Pingtung county (hereafter referred as KKP) located in southern Taiwan are particularly vulnerable to the ozone build-up in fall when the climate is favorable for intensive photochemistry (Taiwan EPA, 2002). Different from the other leading pollutant, i.e., $PM_{10}$, which has shown a decreasing trend in the last decade, ozone, on the other hand, showed an increasing trend, and since 1997 ozone

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has exceeded $PM_{10}$ and become the top pollutant in many areas of Taiwan.

It is well documented that the lower tropospheric ozone is directly linked to its precursors of NMHCs and $NO_x$ (Seinfeld and Pandis, 1998; Gong and Demerjian, 1997). The ozone isopleth concept gives a rough ideal in terms of determining whether a given environment is $NO_x$- or NMHCs-limited, which is crucial for ozone control. The three-dimensional model simulations on $NO_x$–NMHCs–ozone sensitivity in southern Taiwan suggested most areas appeared to be NMHCs-limited (Chang, 1998), which has become a strategy implemented by Taiwan's EPA to control ozone levels in southern Taiwan. NMHCs have various reactive potentials with respect to ozone formation (Carter and Atkinson, 1989; Carter, 1994). Several volatile organic compounds (VOCs) reactivity scales have been proposed for the quick and convenient evaluation of the ozone formation potentials (OFP). A common and useful reactivity scale is the approach of maximum incremental reactivity (MIR) developed by Carter (1994), which uses practical indices for quantifying ozone-forming impacts imposed by precursors in urban-suburban areas (Hsieh and Tsai, 2003; Yu, et al., 2000). Others have discussed $k_{OH}$ method, which is another means of referencing VOC's reactivities (Dimitriades, 1996). It entails experimental measurement of the rate at which each VOC is consumed by reacting with OH. The method is commonly used to measure a VOC's reactivity relative to that of a reference VOC species.

Successful smog abatement strategies require reasonable reactivity estimates for NMHCs and identify the more effective species to form ozone in a given area. Furthermore, appropriate methods to identify NMHCs sources for crafting control strategies are also needed for reducing surface ozone. In southern Taiwan, ambient NMHCs are not only contributed by vehicles, but also by various large industrial sources (Chang et al., 2003). Unlike common metropolitan areas where traffic is considered as the only major source of NMHCs, most of the country's heavy industries are packed in Kaohsiung of southern Taiwan. These industries include petroleum cracking plants, petrochemical plants, power plants, steel plants, shipyards, and other industries, all considered as heavy polluters. Owing to emission components and component proportions of these sources vary constantly, emission profiles of these sources are difficult to determine. In light of the complexity in emission sources, the chemical mass balance (CMB) receptor model becomes ineffective for the source apportionment of NMHCs (Chang et al., 2003). Therefore, we propose using 2,2-dimethylbutane (22DMC4) as a vehicular indicator for estimating traffic contribution of hydrocarbons based on the concentration ratios of VOCs to 22DMC4 (Chang et al., 2004).

In this investigation, MIR method and $k_{OH}$ method (reactivity of NMHC with OH radical) were used to estimate the degrees of ozone formation, which were then compared with the actually observed ozone mixing ratios. The objectives of this research are to investigate the composition and spatial distribution of NMHCs in southern Taiwan and to identify the most critical species to form ozone as well as to estimate source apportionments of these critical compounds.

## 2. Experimental methods

### 2.1. Sampling strategy

The registered vehicles and factories in KKP region (located in southern Taiwan) are 580 and 1.4 $km^{-2}$ (Taiwan EPA, 2001), and air pollution is generally considered to be the worst in Taiwan mainly due to its over loaded heavy industries and traffic. In order to understand the effect of atmospheric NMHCs on ozone formation in southern Taiwan, 208 flask samples were collected at 13 Taiwan EPA air quality monitoring stations. Fig. 1 shows the locations of 13 EPA monitoring stations scattered around the area of KKP. Collecting samples at air quality monitoring stations has an obvious advantage of obtaining $NO_x$, $O_3$, and wind data at the same time. In this study, the 13 stations were grouped into three categories, i.e., urban (nine stations in Kaohsiung metropolitan area), downwind (Ping-Tung, Chau-Jou and Mei-Nung stations), and remote (Heng-Chuen station) according to the wind pattern in this season. Because most of the ozone episodes in southern Taiwan occur in autumn with maximum ozone mixing ratios mostly appearing at 1:00 p.m.–3:00 p.m. during a day, in this study, two sampling campaigns were conducted for 8 days in two periods, 10–13 October and 25–28 October of 2002. Air samples were collected as simultaneous as possible at 9:30 a.m. and 11:30 a.m. to investigate NMHCs during the build-up phase of ozone.

### 2.2. Instrumentation

Ambient air samples were collected in 0.5-L glass flasks which were evacuated and humidified prior to sample collection. Upon analysis each aliquot of 403 mL was drawn from the flask through the cryogenic trap packed with fine glass beads cooled by liquid nitrogen for preconcentration. During injection the trap was heated with boiling water and a stream of high purity $H_2$ flushed the trapped NMHC onto gas chromatographic columns. An analytical system, which composed two gas chromatographs (GC) equipped with two flame ionization detectors (Hewlett-Packard 6890), was used to analyze NMHC of $C_2$–$C_{10}$ in all air samples. Two capillary columns, a PLOT (Chrompack; 30 m × 0.53 mm;

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