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In Situ Measurements of Hydrogen Peroxide, Nitric Acid and Reactive Nitrogen to Assess the Ozone Sensitivity in Pingtung County, Taiwan

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ABSTRACT

This study was aimed to investigate the concentration of hydrogen peroxide (H_2O_2), nitric acid (HNO_3) and reactive nitrogen (NO_y) at three sites in Southern Taiwan during 2003–2004. The mean H_2O_2 concentrations were 1.0–2.7 ppbv, 1.6–2.8 ppbv and 1.0–2.6 ppbv at Pingtung, Chao-Chou and Kenting, respectively. Meanwhile, the mean HNO_3 concentrations were 2.7–5.5 ppbv at Pingtung, 1.9–4.6 ppbv at Chao-Chou and 1.2–3.0 ppbv at Kenting. The NO_y mean concentrations were 61.0–85.0 ppbv, 16.0–75.0 ppbv and 4.2–12.0 ppbv at Pingtung, Chao-Chou and Kenting, respectively. The hourly data of H_2O_2, HNO_3, NO_y and O_3 were then used to determine the ratio of H_2O_2 to HNO_3, O_3 to HNO_3, O_3 to NO_y and the extent of reaction (E) in Smog Production Model (SPM) to evaluate the NO_x and VOC sensitivity of ozone formation in Southern Taiwan. The results show that Pingtung city was primarily VOC-sensitive regime in four seasons. At Chao-Chou, the percentages of VOC-sensitive regime exceed those in NO_x-sensitive regime in H_2O_2/HNO_3 and O_3/NO_y in four seasons; but O_3/HNO_3 indicates NO_x-sensitive regime in autumn, winter and spring. Kenting was mainly dominated by NO_x-sensitive by use of three indicators in four seasons. The SPM results are consistent with those determined by the photochemical indicator ratios although the percentages of dominance may vary among these analyses.

Keywords: Hydrogen peroxide; Nitric acid; Reactive nitrogen; Ozone sensitivity; Smog production model.

INTRODUCTION

Ground-level ozone is a secondary pollutant produced from its precursors of nitrogen oxides (NO_x) and volatile organic compounds (VOC) via complex photochemical reactions in sunlight. Former studies have shown that the relationships between ozone and its precursors, VOC and NO_x, are non-linear (Liu, *et al*., 1987; Milford *et al*., 1994; Sillman, 1999). The ozone–VOC–NO_x sensitivity can be determined directly from measurements and from models. (Peng *et al*., 2006; Kumar *et al*., 2008; Tseng *et al*., 2009a; Tseng *et al*., 2009b; Lee *et al*., 2010) However, three-dimensional photochemical model simulations for evaluations of ozone–VOC–NO_x sensitivity are difficult because of the uncertainties of model assumptions, e.g., emission inventory and meteorology (Fujita *et al*., 1992; Sillman, 1995; Bishoi *et al*., 2009). Several alternative approaches have been developed to determine the ozone sensitivity. One approach is to use photochemical indicator species or species ratios, such as hydrogen peroxide and reactive nitrogen species (Milford *et al*., 1994; Sillman *et al*., 1997). Comparisons between model predictions and measured values for the indicator species would also provide a test of the accuracy of model sensitivity predictions (Sillman, 1995, Peng *et al*., 2006). Another approach is to use the ambient data of ozone and reactive nitrogen oxides to estimate the extent of reaction, the so-called smog production model (SPM), to predict whether ozone formation is VOC- or NO_x-sensitive (Johnson, 1984; Chang and Suzio, 1995; Chang *et al*., 1997; Blanchard, 2000; Blanchard and Fairley, 2001).

Atmospheric chemistry of H_2O_2 and its contribution to the formation of free radicals have been studied intensively over the pass years (Sakugawa and Kaplan, 1990; Das and Aneja, 1994; Jackson and Hewitt, 1996; Sauer *et al*., 2003). The major routes to H_2O_2 are: (a) recombination of HO_2• (Kleinman, 1991; Clavert and Stockwell, 1983), (b) reaction of ozone and biogenic hydrocarbons like isoprene and isobutane in water droplets, without radicals (Sauer *et al*., 1999). HNO_3 is an odd nitrogen trace specie and the end product of reactive nitrogen compounds such as NO, NO_2, and N_2O_5. In the atmosphere, HNO_3 may originate from (a) the homogeneous reaction of NO_2 with •OH, (b) Hydrolysis

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of N_2O_5 and (c) hydrogen abstraction by NO_3• from aldehydes and hydrocarbons. Reactions a and b constitute the dominant route to HNO_3 during the daytime and night time, respectively (Kitto and Harrison, 1992).

Pingtung County is in the southern end of Taiwan with around 0.91 million inhabitants and an area of 2,775 km^2 (Fig. 1). It is mainly agricultural, with touring and sightseeing (e.g. Kenting town). The air pollutants of Pingtung County most come from traffic sources (Lin *et al*., 2005; Lin *et al*., 2007; Lin *et al*., 2008; Lin *et al*., 2009) and some densely populated areas in Pingtung city (Northern part) and Chao-Chou town (Central part), with several small-sized industrial parks. Pingtung County belongs to Kao-Ping air basin which has the worst air quality, in Taiwan. This is mainly because the northern and central parts of Pingtung County are south of, and thus downwind of, the Kaohsiung areas (Kaohsiung City and Kaohsiung County), whenever a northerly or north-easterly wind prevails, such as in autumn and winter (Chen *et al*., 2003, 2004). Photochemical simulations by Chen *et al*. (2003) showed that around 49–57% of the ambient ozone in Pingtung County were transported from and/or contributed by Kaohsiung area, depending on the season. The simulations also showed that most of concentrations of the ambient ozone in Kaohsiung City and Pingtung City were sensitive to the reduction of VOC emissions. However, no direct measurement has been made to evaluate the ozone-VOC-NO_x sensitivity in southern Taiwan.

This work measures the concentrations of hydrogen peroxide, nitric acid and reactive nitrogen in the ambient air in Pingtung County in four seasons during 2003–2004. The three photochemical indictor ratios were calculated and the extent of reaction in the SPM was estimated. The VOC- or NO_x-sensitive regime to the formation of ozone was identified in each region.

EXPERIMENTAL

Sampling Sites and Periods

Three sampling sites, Pingtung, Chao-Chou and Kenting in Pingtung County were chosen because they had air-quality monitoring stations operated by the Taiwan-EPA (Environmental Protection Administration). Therefore, hourly air quality and meteorological data, on O_3, NO_x, temperature, and/or wind, were available. The distances between the monitoring sites are approximately 18 km between Pingtung and Chao-Chou and 70 km between Chao-Chou and Kenting (Fig. 1).

Samplings were taken on five days in four seasons in 2003 and 2004. Samples of H_2O_2, HNO_3 and NO_y were collected concurrently for eight 1-h periods between 09:00 and 17:00 at Pingtung, Chao-Chou and Kenting in Pingtung County. Table 1 presents the meteorological conditions at the sampling sites, including temperature, wind speed, relative humidity and period of sunshine.

Sampling Methods

H_2O_2

Fig. 2(a) shows the H_2O_2 sampling apparatus. Gaseous samples were collected in two identical midget fritted glass bubblers (Supelco No. 6–438), each containing 15 mL of $TiOSO_4$ collecting solution. The inlet of the first bubbler had two ports: one port was connected to the inlet of the second bubbler, and the other was connected to the outlet

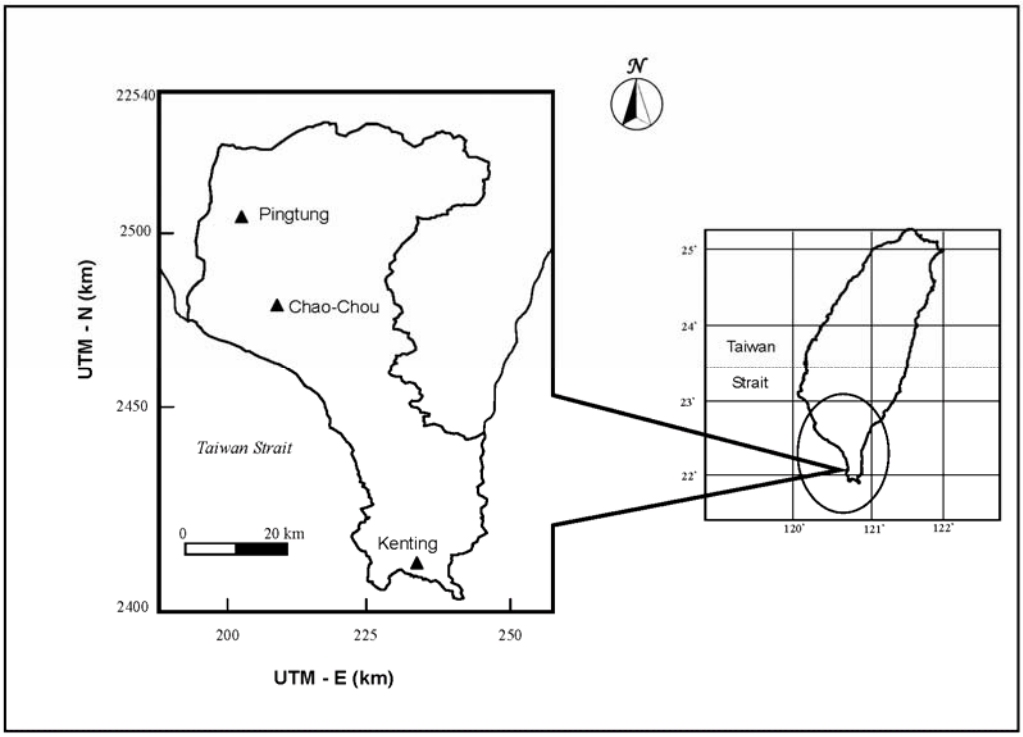

Fig. 1. Locations of the three measurement sites in Pingtung County, Southern Taiwan.

Table 1. Meteorological conditions at Pingtung (P.T.), ChaopChou (C.C.) and Kenting (K.T.).

Date	Temperature (°C)			Wind speed (m/s)			Period of Sunshine (h)			Relative Humidity (%)		
	P.T.	C.C.	K.T.	P.T.	C.C.	K.T.	P.T.	C.C.	K.T.	P.T.	C.C.	K.T.
8/7/2003	29.5	28.7	26.7	1.8	1.4	4.8	11.3	7.8	7.8	81.1	79.9	79.9
8/8/2003	29.7	28.9	27.0	1.5	1.1	6.1	9.5	9.1	9.1	78.2	78.5	78.5
8/9/2003	30.2	28.4	27.0	1.2	0.9	3.8	9.3	9.8	9.8	78.9	78.4	78.4
8/10/2003	30.5	28.9	27.0	1.3	0.8	2.9	6.6	8.0	8.0	80.3	77.0	77.0
8/11/2003	29.7	28.3	26.4	1.8	1.8	3.0	9.6	5.7	5.7	78.2	79.6	79.6
11/9 (20)/2003	26.5	28.0	26.6	0.8	0.8	3.6	9.2	7.7	8.7	77.8	76.8	75.0
11/10 (21)/2003	26.5	27.5	25.6	1.0	0.9	6.2	6.6	4.2	4	75.5	71.5	77.3
11/11 (22)/2003	24.9	22.4	24.1	0.9	0.8	12.9	3.2	0	6.2	70.4	81.7	68.7
11/12 (23)/2003	23.2	24.0	23.3	0.7	0.7	11.5	2.1	0	9.5	68.5	78.8	66.0
11/13 (24)/2003	23.0	25.7	22.8	0.6	0.7	11.0	8.2	7.7	7.3	7.23	75.4	67.4
1/13/2004	16.9	18.8	17.1	1.0	1.2	10.3	0.4	0.7	0.7	61.0	68.2	68.2
1/14/2004	18.7	20.0	18.7	1.0	1.0	8.0	9.3	5.4	5.4	65.0	60.8	60.8
1/15/2004	19.4	20.7	21.0	0.9	1.0	5.9	9.3	5.5	5.5	72.9	63.4	63.4
1/16/2004	21.2	22.9	22.6	1.6	1.8	3.6	8.9	5.7	5.7	69.4	69.5	69.5
1/17/2004	19.3	20.6	20.4	1.0	1.1	8.6	6.2	7.8	7.8	69.5	68.8	68.8
3/5/2004	20.4	22.0	20.3	1.4	1.4	5.5	8.1	7.0	7.0	58.4	63.3	63.3
3/6/2004	19.9	21.5	19.8	0.8	1.1	13.7	0.4	3.1	3.1	67.2	62.5	62.5
3/7/2004	18.7	20.3	16.5	0.8	0.9	13.0	0.6	0.4	0.4	66.4	60.9	60.9
3/8/2004	18.7	19.5	18.5	1.1	1.1	7.9	10.6	7.7	7.7	61.4	60	60
3/9/2004	20.0	21.2	19.5	1.2	1.0	5.1	10.6	8.9	8.9	67.3	64.9	64.9

Note: 1. Autumn samplings in Chao-Chou were made on 20–24 November in 2003 due to the EPA monitoring site in Chao-Chou was undergoing maintenance on 9–13 November in 2003.

of an air sampler, via silica gel tubes. Desiccants were packed in the tube between the first bubbler and an air pump (SKC Model 210–1000s) operated at a flow rate of 500 mL/min. The sampling and analytical procedures complied with US-OSHA (Occupational Safety and Health Administration) Method VI-6 (OSHA, 1978). The Ti-H_2O_2 solution was analyzed in the laboratory using a spectrophotometer (Shimadzu UV-160) at a wavelength of 410 nm. No breakthrough of the species occurred in the test tubes. Calibrations were conducted using seven concentrations of standard samples, with a coefficient of determination, R^2, of above 0.997. The detection limit was 0.12 ppbv.

HNO_3

HNO_3 sampling apparatus is shown in Fig. 2(b) Gaseous samples were collected using silica gel adsorption tubes (SKC No. 226-10-03) of length 11 cm and outer diameter 7 mm, containing a 400-mg front section and a 200-mg backup section of washed silica gel, with flamed-sealed ends with plastic caps. The adsorption tube was connected to a pump (SKC No. 210-1002MH) operated at an airflow rate of 250 mL/min. No breakthrough of the compounds occurred in the tubes. The sampling and analytical procedures complied with US-NIOSH (National Institute for Occupational Safety and Health) Method 7903 (NIOSH, 1994). The samplers were analyzed in the laboratory using ion chromatography (DIONEX Model DX-100) with an AS-4ASC separator column of 4 mm. Calibrations were conducted using seven concentrations of standard samples, with a coefficient of determination, R^2, of above 0.997. The detection limit was 1.55 ppbv.

NO_y

NO_y sampling apparatus is shown as Fig. 2(c) NO_y refers to total reactive nitrogen including NO, NO_2, HNO_3, HNO_2, PAN and alky nitrates. Ambient NO_y was converted to NO via molybdenum catalyst converter at 350°C with low influence from NH_3 or other species (Williams, 1995; Honrath and Jaffe, 1990; Fehsenfeld *et al*., 1987). The instrument detection limit was 0.1 parts per billion volume (ppbv) for both NO and NO_y (Delany *et al*., 1982; Dickerson *et al*., 1984). The ground molybdenum was put in a glass tube (length = 15 cm, D = 3 cm) with quartz wool in both end and heated to 350°C by temperature controller. Inlet NO_y will be converted to NO under the molybdenum catalysis. Outlet NO gaseous was connecting to an ambient NO detector (Ecotech, 1070). The convertibility of NO_y to NO in this study is 93.8%.

Data Analysis Using Smog Production Model

Blanchard *et al*. (1999) reformulated the algorithm to compute the "smog produced" (SP), originally proposed by Johnson (1984) according to two alternative equations:

$$SP(t) = O_3(t) + DO_3(t) - O_3(0) + NO(i) - NO(t) \quad (1)$$

or,

$$SP(t) = \beta\,[NO_x(i) - NO_x(t)]^{\alpha} \quad (2)$$

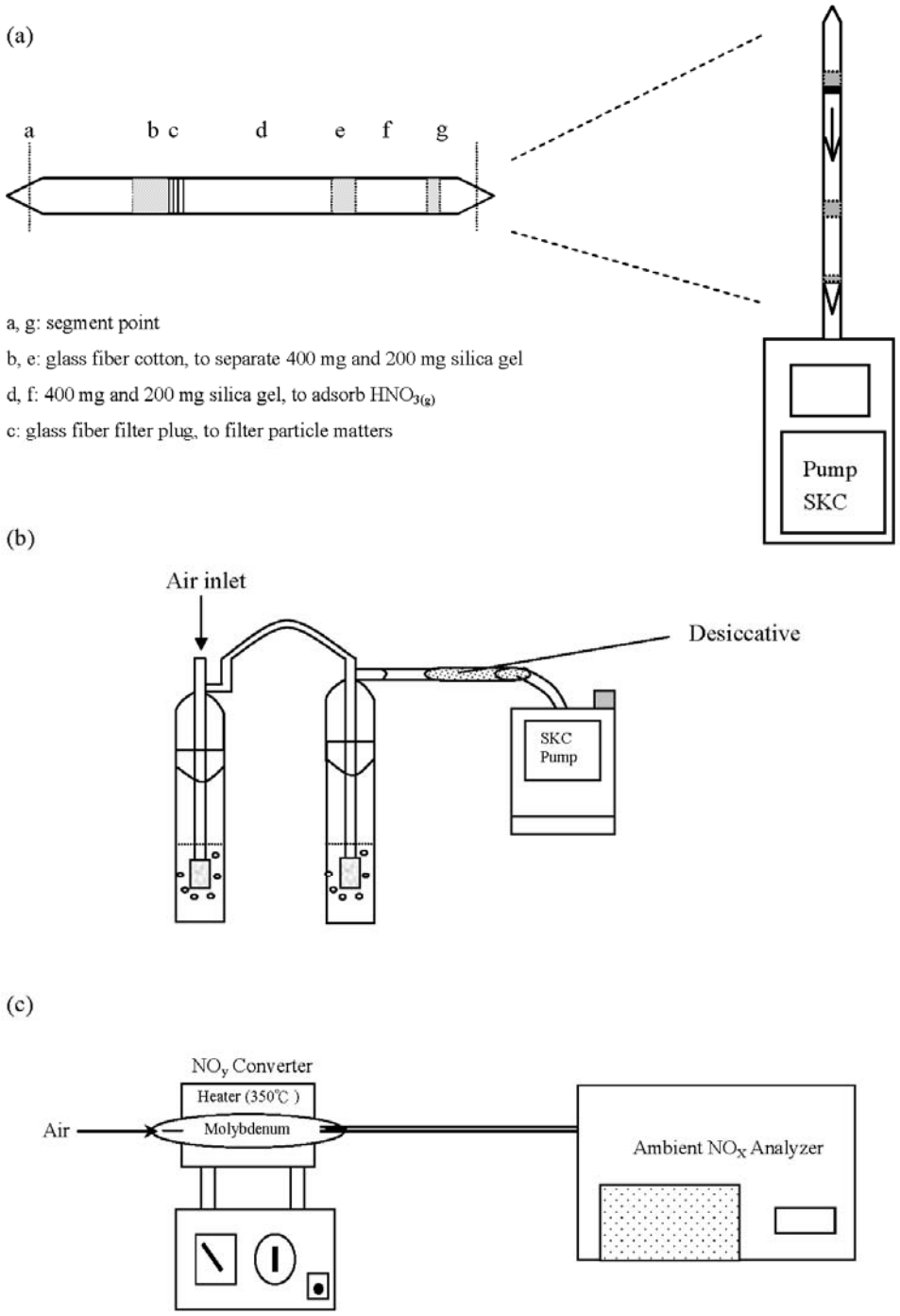

Fig. 2. Sampling apparatus of (a) HNO_3, (b) H_2O_2 and (c) NO_y.

where DO_3 is the accumulated deposition losses of ozone. Furthermore, the maximum potential SP is given by

$$SP_{max} = \beta\,[NO_x(i)]^{\alpha} \tag{3}$$

The extent of reaction, $E(t) \equiv SP/SP_{max}$, can thus be obtained by

$$E(t) = \frac{O_3 + DO_3(t) - O_3(0) + NO(i) - NO(t)}{\beta\,[NO_x(i)]^{\alpha}} \tag{4}$$

or,

$$E(t) = \left[1 - \frac{NO_x(t)}{NO_x(i)}\right]^{\alpha} \tag{5}$$

In evaluating E, the instantaneous data of $O_3(t)$, $NO(t)$, and/or $NO_x(t)$ must be measured. Also, those unmeasured quantities, including $DO_3(t)$, $O_3(0)$, $NO(t)$, $NO_x(i)$, and others must be estimated. Detailed descriptions on estimating relevant parameters are given in Blanchard *et al*. (1999), in which the default values were used here.

Furthermore, the intermediate values of $E = 0.6 – 0.8$ used in Blanchard and Stoeckenius (2001) were adopted here such that a value of E lower than 0.6 indicates a VOC-sensitive regime, while a value of E higher than 0.8 indicates a NO_x-sensitive regime.

RESULTS AND DISCUSSION

Seasonal Variations of H_2O_2, HNO_3 and NO_y Concentrations

Fig. 3 shows the box plots of measured ozone sensitive species concentrations, namely H_2O_2, HNO_3 and NO_y, at Pingtung, Chao-Chou and Kenting in four seasons. The box plots indicate the percentiles (5th, 10th, 25th, 50th, 75th, 90th and 95th) and means of the data. The distance between 25th and 75th in the box plot represents the data divergence. In addition to spring, H_2O_2 concentration trends show Chou-Chao > Pingtung > Kenting in summer, autumn and winter. Typically, H_2O_2 is lower inside in an urban plume relative to the rural area (Weinstein-Lloyd *et al*., 1998). The concentration trends of HNO_3 are consistent with the NO_x, show Pingtung > paperChao-Chou > Kenting in four seasons. Summertime box plot shows NO_y concentration at Pingtung was much higher than that in Chao-Chou and Kenting.

Table 2 statistically summarizes the H_2O_2, HNO_3 and NO_y concentration in mean, maximum, minimum and standard deviation (S.D.) at three sites over the entire study period. The mean H_2O_2 concentrations were 1.0–2.7 ppbv, 1.6–2.8 ppbv and 1.0–2.6 ppbv at Pingtung, Chao-Chou and Kenting, respectively. According to the S.D concentrations, we can realize that the H_2O_2 concentration varies slightly in four seasons. Peng *et al*. (2006) has investigated the H_2O_2 and HNO_3 concentration in urban Kaohsiung and Pingtung County. The mean H_2O_2 concentrations were 1.76–1.79 ppbv at Nan-Chie and Hsiung-Kong in Kaohsiung City and

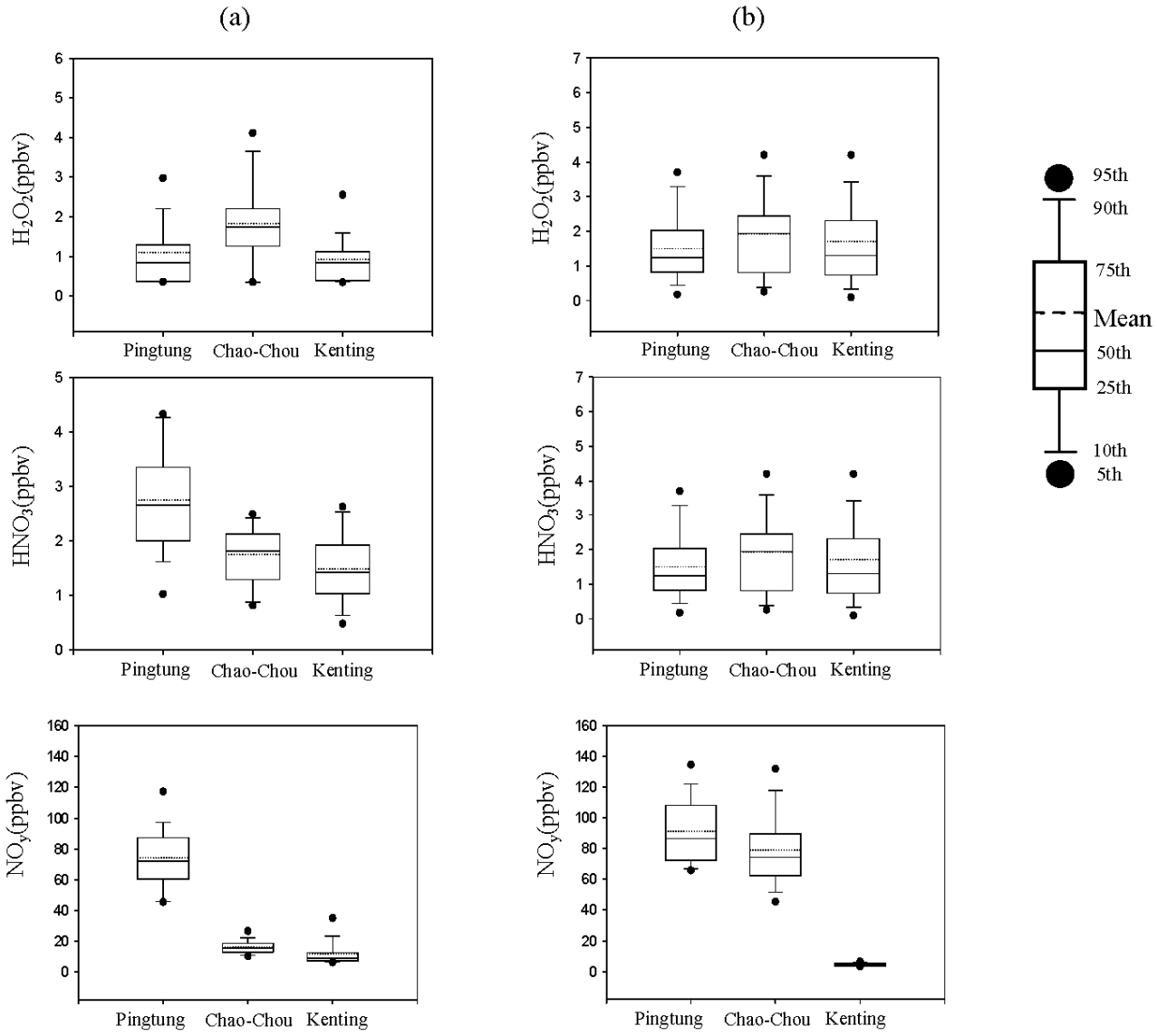

Fig. 3. Concentrations of H_2O_2, HNO_3 and NO_y using box plots at Pingtung, Chao-Chou and Kenting in (a) summer, (b) autumn, (c) winter and (d) spring in 2003–2004.

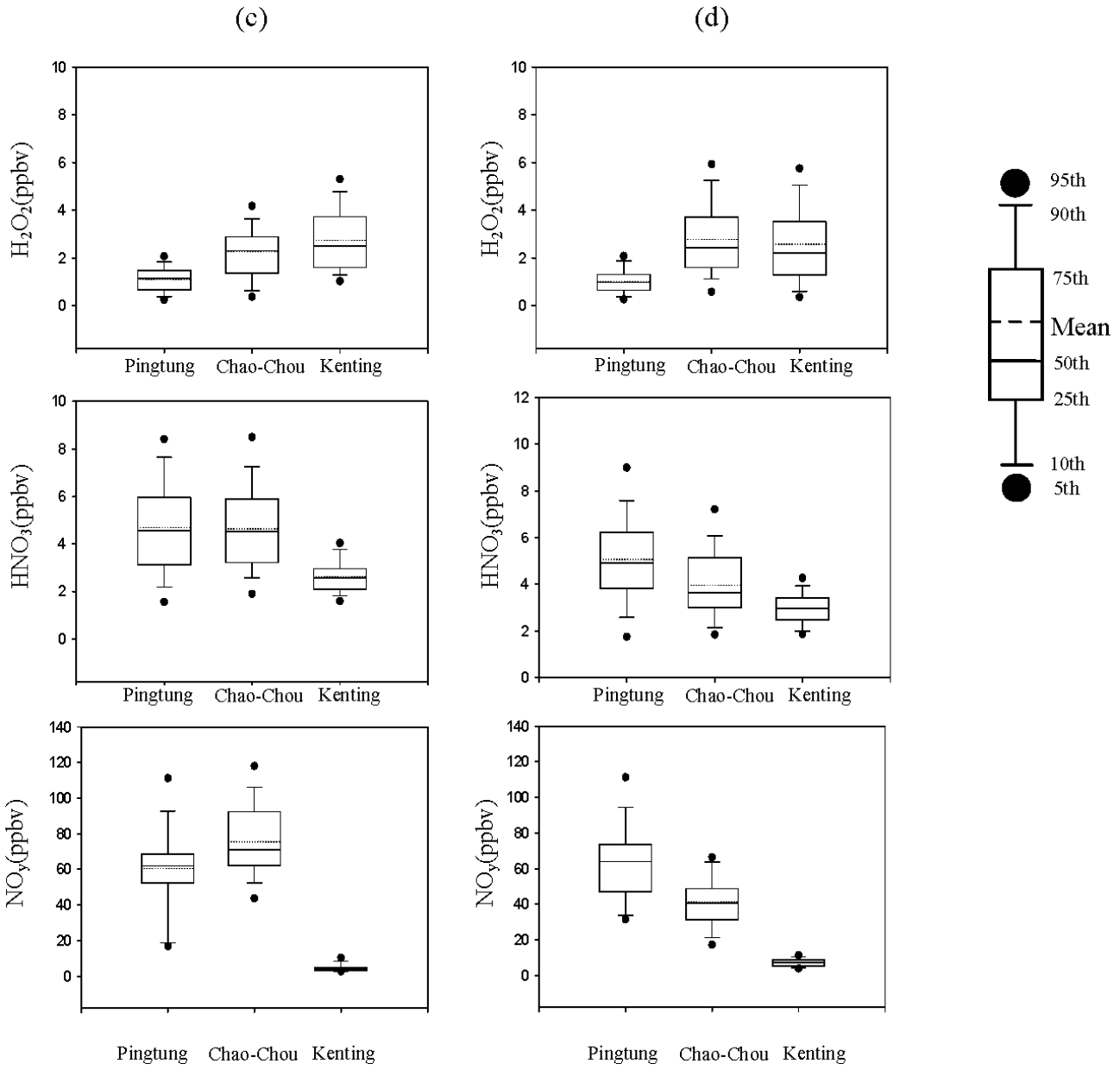

Fig. 3. *(continued).*

1.40–1.76 ppbv at Pingtung and Chao-Chou in Pingtung County. The present results are in the range of the reported ambient H_2O_2 concentrations of 0.1 to 3.5 ppbv. For example, the concentration of H_2O_2 ranged in 0.1 to 0.3 ppbv in downtown Raleigh of North Carolina (Das and Aneja, 1994), at a forest site in Portugal (Jackson and Hewitt, 1996), and in downtown Seoul, Korea (Kang *et al.*, 2002), whereas the concentrations of other pollutants such as O_3 and NO_x were also much lower than those here. Additionally, the present results are close to 0.86–2.04 ppbv observed in Los Angeles (Sakugawa and Kaplan, 1989 and 1990).

During the whole measurements, HNO_3 concentration ranged from 2.7–5.5, 1.9–4.6 and 1.2–3.0 at Pingtung, Chao-Chou and Kenting, respectively. The concentrations of gaseous HNO_3 here are lower than 6.11–7.79 ppbv in Kaohsiung City and 3.78–4.92 ppbv in Pingtung County (Peng *et al.*, 2006) but much higher than 1.55 ppbv at a rural site in Pennsylvania (Buhr *et al.*, 1990), 0.67 ppbv in the central Piedmont region of North Carolina (Aneja *et al.*, 1996), and 0.02–2 ppbv in the upper troposphere above Ellington Field in Texas (Neuman *et al.*, 2001).

NO_y mean concentrations were relatively high (all above 61.0 ppbv) at Pingtung and Chao-Chou, but were low at Chao-Chou during the summer times (16.0 ppbv) and at Kenting in four measurement periods (4.2–12.0 ppbv). This may due to Pingtung is a sub-urban city with more vehicles exhausts than that at Chao-Chou and Kenting. The range of NO_y concentrations was 14.2–136.0 ppbv, 6.0– 142.0 ppbv and 2.3–38.0 ppbv at Pingtung, Chao-Chou and Kenting, respectively. NO_y concentrations, that are similar to other air pollutants in Kenting, were low in four seasons because of

Table 2. Statistical data of H_2O_2, HNO_3 and NO_y measured at Pingtung, Chao-Chou and Kenting in 2003–2004.

Sites		Pingtung			Chao-Chou			Kenting		
Species		H_2O_2	HNO_3	NO_y	H_2O_2	HNO_3	NO_y	H_2O_2	HNO_3	NO_y
Summer	Max.	3.5	4.7	135.0	5.1	3.6	40.0	2.6	2.7	38.0
	Mean	1.1	2.7	70.0	1.6	1.9	16.0	1.0	1.4	12.0
	Min.	0.3	1.0	42.0	0.3	0.4	6.0	0.3	0.4	6.0
	S.D.	0.7	0.9	20.2	1.1	0.6	5.4	0.5	0.6	7.7
Autumn	Max.	3.9	10.7	136.0	6.3	8.1	142.0	5.9	2.0	6.5
	Mean	1.1	5.5	85.0	1.9	4.3	75.0	1.0	1.2	4.2
	Min.	0.1	2.3	60.0	0.2	1.7	42.0	0.2	0.3	2.9
	S.D.	0.4	0.8	14.8	1.1	0.8	12.7	1.1	0.1	0.6
Winter	Max.	5.8	8.4	116.0	7.8	8.9	123.0	2.4	3.4	14.0
	Mean	2.7	4.7	61.0	2.5	4.6	68.0	1.2	1.2	4.7
	Min.	1.0	1.3	14.2	0.1	0.4	42.0	0.2	2.7	2.3
	S.D.	0.6	1.9	23.6	1.2	1.7	22.7	1.3	0.7	2.5
Spring	Max.	2.8	9.1	115.0	8.0	7.3	67.0	8.0	4.6	12.6
	Mean	1.0	5.1	63.9	2.8	4.0	41.2	2.6	3.0	7.1
	Min.	0.3	1.0	30.0	0.5	1.0	16.0	0.3	1.7	3.9
	S.D.	0.6	2.0	20.7	1.6	1.5	13.6	1. 7	0. 8	1.5

no emission sources surrounded, and with strong wind speed (see Table 1.). The NO_y concentrations in southern Taiwan, Pingtung County, were similar to 0.3–110 ppbv on the Augustine's campus near the downtown Raleigh, North Carolina (Aneja *et al*., 1997) but higher than 0.56–9.29 ppb in eastern Canada (Zhang *et al*., 2008). The present results are somewhat lower than 156–222 pptv in the Azores Island, Portugal where the mean NO_x concentrations were ranged from 26–37 ppbv during the measurement period (Martin *et al*., 2008). Table 3 shows the results of H_2O_2, HNO_3 and NO_y measurements found in the literatures together with the results from this paper. These ozone relative species were then used to evaluate the sensitivity of ozone formation in the ambient air, namely photochemical indicators, discussed in the coming section.

Ozone Sensitivity Determined by Indicator Ratios

The ranges of H_2O_2/HNO_3, O_3/HNO_3 and O_3/NO_y based on the present measurements were used to assess the conditions of NO_x-sensitive and VOC-sensitive regimes to ozone formation. Table 4 summaries the results of NO_x-sensitive and VOC-sensitive regimes to ozone at the four sites in four seasons. Here, the threshold ratios of H_2O_2/HNO_3 = 0.3–0.6, O_3/HNO_3 = 12–16 and O_3/NO_y= 6–7 were adopted (Sillman 1995; Sillman *et al*., 1997), in which a lower value than the threshold ratio indicates a VOC-sensitive regime, a higher value than the threshold ratio indicates a NO_x-sensitive regime, and otherwise indicates an intermediate (or a transition) regime.

Table 4 shows the percentages of VOC-sensitive and NO_x-sensitive regimes to ozone formation at the three sites in four seasons in 2003 and 2004, based on measurements of photochemical indicators. Pingtung city was primarily VOC sensitive regime in four seasons by the percentage of 44.6–72.2%, 60.7–88.7% and 100% in H_2O_2/HNO_3, O_3/HNO_3 and O_3/NO_y, respectively. At Chao-Chou, the percentages of VOC-sensitive regime exceed those in NO_x-sensitive regime in H_2O_2/HNO_3 and O_3/NO_y in four seasons; but O_3/HNO_3 indicates NO_x-sensitive regime in autumn, winter and spring. Kenting site was mainly dominated by NO_x-sensitive by use of three indicators in four seasons. Notably, Pingtung City is an urban area and close to the pollution sources in the Kaohsiung area, whereas Chao-Chou and Kenting are rural regions that are farther away from the source regions. Therefore, the present results are consistent with the fact that freshly emitted pollutants are typically characterized by VOC-sensitive chemistry (such as in Pingtung City) and evolve towards NO_x-sensitive chemistry (as in Chao-Chou town and Kenting town) as the air mass moves downwind (Sillman, 1999; Peng *et al*., 2006).

Comparisons of Ozone Sensitivity between Indicator Ratios and SPM Results

Fig. 4 illustrated the SPM result which shows VOC sensitive, intermediate, and NO_x-sensitive regimes at the four sites in summer, autumn, winter, and spring. The VOC-sensitive regime dominated at Pingtung in all four seasons. Chao-Chou was primarily VOC-sensitive regime except for summer season. The percentages of NO_x-sensitive occupy more than 94.65% at Kenting in all the analyzed episodes. Castell *et al*. (2009) applied MM5-CAMx model system to explore the relationships between various photochemical indicators and ozone sensitivity. Results show that O_3/NO_y and *E* have similar behavior on evaluating ozone sensitivity, i.e., *E* parameter shows good correlation in VOC sensitive conditions (Blanchard and Stoeckenius, 2001; Sillman and He, 2002; Castell *et al*., 2009). In this study, the SPM results are consistent with those determined by the indicator ratios, discussed in the preceding section, although the percentages of dominance may vary among these analyses.

Table 3. Comparison of measurements of H_2O_2, HNO_3 and NO_x in this study and previous studies.

Reference	Concentrations	Year	Site	O_3 sensitivity
H_2O_2	*(ppbv)*			
Sakugawa and Kaplan, 1990	0.86–2.04	1986	Los Angeles and its vicinity, USA	VOC-sensitive
Das and Aneja, 1994	0.1–0.3	1991	Raleigh in North Carrolina, USA	VOC-sensitive
Jacob *et al*., 1995	0.13–0.86	1990	Shenandoah National Park, Virginia, USA	
Jackson and Hewitt, 1996	< 0.025–0.63	1994	Portugal	
Weinstein-Lloyd *et al*, 1998	1.5–3.5	1995	Nashville in Tennessee, USA	NO_x-sensitive
Kang *et al*., 2002	< 0.01–0.38	1998–1999	Seoul, South Korea	
Dommen *et al*., 2002	0.9–2.7	1998	Milan, Italy	VOC-sensitive
Sauer *et al*., 2003	0–1.2	2000	California, USA	
Peng *et al*., 2006	0.24–3.94	2002–2003	Kaohsiung City, Taiwan	VOC-sensitive
	0.61–3.93	2002–2003	Pingtung County, Taiwan	VOC-sensitive
Acker *et al*., 2008	< 0.05–6.2	2004	Zagreb in Croatia	
This study	0.1–8.04	2003–2004	Pingtung County, Taiwan	VOC-sensitive
HNO_3	*(ppbv)*			
Buhr *et al*., 1990	> 1.55	1998	Pennsylvania, USA	
Aneja *et al*., 1996	0.67[a]	1992	North Carolina, USA	VOC-sensitive
Neuman *et al*., 2001	0.02–0.2	1999	Upper troposphere in Texas, USA	
Khoder, 2002	1.14[*]–6.70[*]	1999–2000	Cario, Egypt	
Sauer *et al*., 2003	0–26	2000	California, USA	
Peng *et al*., 2006	0.60–20.40	2002–2003	Kaohsiung City, Taiwan	VOC-sensitive
	1.10–8.47	2002–2003	Pingtung County, Taiwan	VOC-sensitive
This study	0.3–10.65	2003–2004	Pingtung County, Taiwan	VOC-sensitive
NO_y	*(ppbv)*			
Fahey *et al*., 1986	0.5–1.4	1984	Niwot Ridge, USA	
Singh *et al*., 1994	0.24–1.4	1990	Eastern Pacific	
Atlas *et al*, 1992	0.7–0.934	1988	Hawaii, USA	
Sandholm *et al*., 1994	0.06–1.01	1988–1990	Arctic Boundary Layer	
Singh *et al*., 1996	0.1–0.8	1991	Western Pacific	
Aneja *et al*., 1997	0.3–111	1991	North Carolina, USA	VOC-sensitive
Harrison *et al*., 1999	1.8–29.1	1993–1995	Norfolk, UK	
Singh *et al*., 2007	1.781[a]	2004	North America	
Zhang *et al*., 2008	0.56–9.26	2001–2005	Canada	
Martin *et al*., 2008	156[b]–222[b]	2002–2005	Portugal	
This study	2.3–142	2003–2004	Pingtung County, Taiwan	VOC-sensitive

Note: *: unit in $\mu g/m^3$; a: mean concentration, b: mean concentration in pptv.

Table 4. Percentages of VOC-sensitive and NO_x-sensitive regimes to ozone formation at Pingtung, Chao-Chou and Kenting in four seasons in 2003–2004.

Site	Season	H_2O_2/HNO_3		O_3/HNO_3		O_3/NO_y	
		VOC-sensitive (< 0.3)	NOs_x-sensitive (> 0.6)	VOC-sensitive (< 12)	NO_x-sensitive (> 16)	VOC-sensitive (< 6)	NO_x-sensitive (> 7)
Pingtung	Summer	44.6	26.8	60.7	12.5	100	0
	Autumn	72.6	11.7	66.0	14.0	100	0
	Winter	57.4	16.7	88.7	7.5	100	0
	Spring	72.2	7.4	88.4	9.6	100	0
Chao-Chou	Summer	15.1	67.9	40.0	49.1	16.1	19.6
	Autumn	30.2	30.2	44.4	27.8	100	0
	Winter	20.4	35.2	67.9	20.8	100	0
	Spring	13.8	43.1	54.0	38.0	100	0
Kenting	Summer	9.8	56.9	12.5	57.1	100	0
	Autumn	5.7	79.3	4.2	79.2	23.4	55.3
	Winter	1.9	75.0	16.2	51.4	15.4	76.9
	Spring	11.7	70.7	4.0	60.7	27.3	47.3

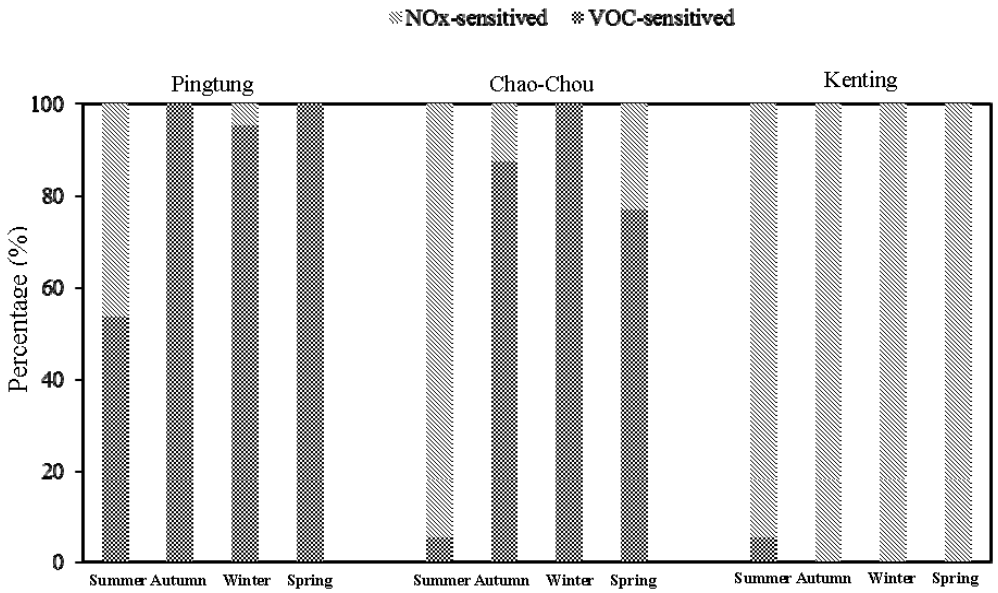

Fig 4. Percentages of VOC-sensitive and NO_x-sensitive regimes to ozone formation at Pingtung, Chao-Chou and Kenting in 2003 and 2004, based on SPM results

CONCLUSIONS

The gaseous H_2O_2, HNO_3 and NO_y were measured at three sites in Pingtung County, southern Taiwan, in summer, autumn, winter and spring during 2003–2004. The mean H_2O_2 concentrations were 1.0–2.7 ppbv, 1.6–2.8 ppbv and 1.0–2.6 ppbv in Pingtung, Chao-Chou and Kenting, respectively. Meanwhile, the mean HNO_3 concentrations were 2.7–5.5 ppbv at Pingtung, 1.9–4.6 ppbv at Chao-Chou and 1.2–3.0 ppbv at Kenting. The NO_y mean concentrations were 61.0–85.0 ppbv, 16.0–75.0 ppbv and 4.2–12.0 ppbv at Pingtung, Chao-Chou and Kenting, respectively. The hourly data were then used to evaluate VOC and NO_x sensitivity of ozone formation. The threshold values of H_2O_2/HNO_3 = 0.3–0.6, O_3/HNO_3 = 12–16 and O_3/NO_y = 6–7 indicate that Pingtung was dominant by VOC-sensitive in four seasons. Chao-Chou was VOC-sensitive chemistry dominant by use of both O_3/HNO_3 and O_3/NO_y indicators, but NO_x-sensitive chemistry was dominant by use of H_2O_2/HNO_3 indicator in four seasons. Meanwhile, Kenting was primarily NO_x-sensitive in all seasons. The VOC-sensitive and NO_x-sensitive regimes determined using the indicator ratios agree well with those obtained from the SPM using the threshold value E = 0.6–0.8.

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