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PC2) Characteristics of NO-NO_2 System with Different Chemical Regimes during MIRAGE-Mex Field Campaign

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1. Introduction

As main precursors of O_3, the reactive nitrogen species(NO_x) in the atmosphere emitted mainly in the form of NO from road traffic. NO and NO_2(NO_x) are interconverted rapidly through following reactions:

$$NO + O_3 \quad NO_2 + O_2 \qquad (R1)$$

$$NO_2 + h\nu\ (\lambda < 420mm) \rightarrow NO + O \qquad (R2)$$

$$NO + HO_2 \rightarrow NO_2 + OH \qquad (R3)$$

$$NO + RO_2 \rightarrow NO_2 + RO \qquad (R4)$$

where, RO_2 is any organic peroxy radicas including CH_3O_2. The NO_2/NO ratio can be formulated in the form of equation (1):

$$\frac{[NO_2]}{[NO]} = \frac{(k_1[O_3]+k_3[HO_2]+k_4[RO_2])}{J_2} \qquad (1)$$

The previous studies testing the NO-NO_2 cyclic system were conducted in urban and remote areas using O_3(R1) and/or peroxy radicals(R3-R4) (Crawford et al., 1996). Since the MIRAGE-Mex campaign measured the peroxy radicals, the photostationary state(PSS) of NO-NO_2 system can be assessed in this study.

2. Method

The intensive field campaign of MIRAGE-Mex was carried out during nearly 1-month period of 4 Mar to 29 Mar 2006, which involved NSF/NCAR C-130 aircraft, ground-based measurements, and satellite observations. This campaign made several physic-chemical measurements such as reactive nitrogen species, oxidized sulfur species, oxygenated VOCs, aerosols, peroxy radicals, and so on. It also includes the measurements of actinic flux and atmospheric photolysis frequencies such as J(O_3), J(NO_2), J(HNO_2), etc. In this study, we focused on the data of chemical measurements of reactive nitrogen species(NO, NO_2, HNO_3, PANs, organic nitrates, particulate nitrate, NO_y) and other trace gases such as O_3, which were made in NSF/NCAR C-130 aircraft. Part of reactive nitrogen species (such as NO, NO_2, and NO_y) and O_3 were measured at one second interval with a chemiluminescence technique, while HNO_3, PANs, and organic nitrates were measured with four-channel chemical ionization mass spectrometer(CIMS), CIMS, whole air sampler(WAS), respectively. As one of key measurements for the analysis of NO-NO_2 PSS(Eq. 1) in this study, peroxy radicals(HO_2+RO_2) was measured by four-channel CIMS.

3. Results and Discussion

In order to analyze the NO-NO_2 cyclic system in the light of chemical regimes/air masses, the air masses were categorized into 5 groups such as boundary layer(labeled as "BL"), free troposphere (continental, "FTCO" and marine, "FTMA"), biomass burning("BB"), and Tula oil refinery plume

("TORP"). The air mass characterization was determined based on geographical location, meteorological parameters(temperature and relative humidity, etc.), model(weather research and forecasting, WRF), and observations of trace gases.

The PSS of NO-NO_2 system was analyzed in Figure 1 with different air mass categories. The ratios(ϕ) of {$k_1[O_3]+k_3[HO_2]+k_4[RO_2]$}/$J(NO_2)$ to NO_2/NO ranged from 0.84(FTMA) to 2.60(BB) with 1.18 for all data. In general, NO_2/NO ratios seem to be in PSS with strong correlation(r^2=0.74) between two parameters. There was large deviation from the PSS for the BB air mass and the NO_2/NO ratio in BB (5.18) was higher than those (2.35-4.20) in other air masses. It appears that there is no distinct trend in the PSS paramemter, in terms of altitude, when deduced from results for BL, FTCO, and FTMA plots (Figure 1b, 1d, and 1e).

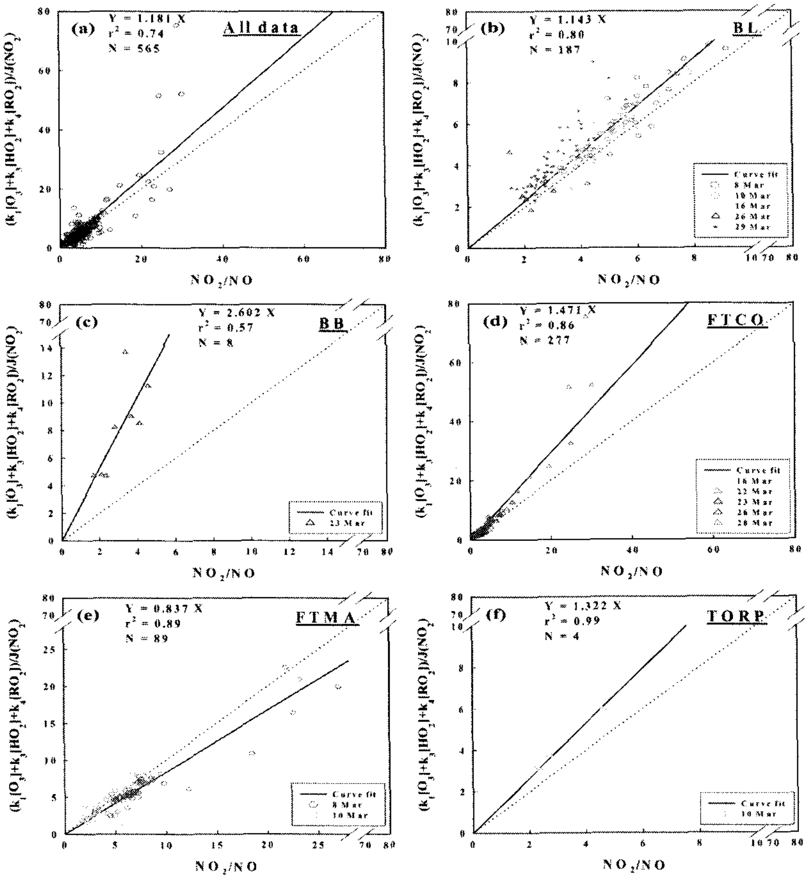

Fig. 1. Photostationary state analysis for NO-NO_2 system during MIRAGE-Mex field campaign(4 Mar. to 29 Mar. 2006) for 5 air mass categories (all (a), BL (b), BB (c), FTCO (d), FTMA (e), and TORP (f)).

References

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