Measurement of peroxy radical concentration in the atmosphere using Chemical Amplification / Laser Induced Fluorescence technique

Manabu Irie

Key Words: Peroxy radical. Ozone formation, ambient air measurement, PERCA, LIF

1.Introduction and objectives

Tropospheric Ozone is harmful for human body, vegetation and crops. And ozone has also the greenhouse effect. Therefore more detail information of tropospheric Ozone formation mechanism is required. Peroxy radical (ROx = OH + HO_2 + RO_2) are formed by reaction with OH and CO, or VOC (Volatile Organic Compound). NO_2 photolysis, which formed by reaction of NO with ROx, is an important source of tropospheric O_3 formation. And ROx also contribute to Secondary Organic Aerosol which change solar radiation .

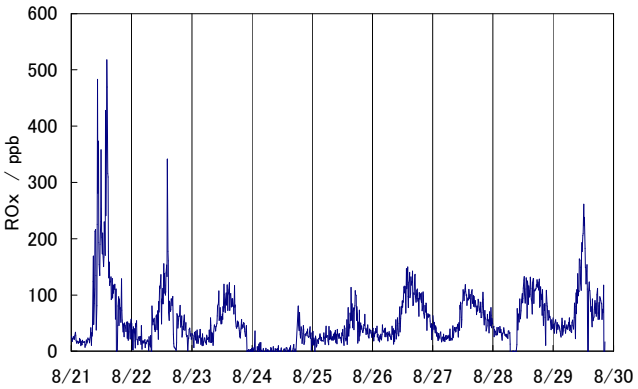
Since, ROx is key intermediate in atmosphere, studying reactive process is essential to understand the Oxidative capacity of atmosphere. However, ROx has very high reactivity, and present at low concentration, it is difficult to detect directly of ROx in atmosphere. Hence, despite ROx has very important role in photochemical reactions in the atmosphere, not so many reports are available on ROx measurement. Therefore, to increase our understanding of ROx is important, in terms of clarify O_3 formation capacity of atmosphere. For this reason, ROx concentration was measured by PERCA-LIF (PEroxy Radical Chemical Amplification - Laser Induced Fluorescence) to obtain knowledge about tropospheric Ozone formation mechanism in this research.

2. Experiment

In this research, ambient air was mixed to CO and NO before introduce to reaction tube, and amplified to 100-200 times amounts of NO_2 (PERCA mode). This amplified NO_2 was exited by 532.1nm wavelength laser and fluorescence was detected using photomultiplier tube as electric signal. Also to measure background siginal, CO addition point was changed to after reaction tube, not to amplification is occur (BG mode). Using magnet valve, the mode was changed every one minutes. Subtracting BG mode signal from the PERCA mode signal, and using previously measured amplification factor, ROx concentration was determined. Atmospheric measurement was performed during 21/08/13 – 30/08/13 in Kyoto university 3rd floor and measured ROx, O_3, NO, NO_2 and photolysis frequency simultaneously.

3.Results and discussion

Figure shows diurnal variation of ROx concentration. After sunrise, ROx concentration showed gradual increase, and had peak around noon. From this peak, ROx concentration was decreased gradually. It is related to going down of the sun and increasing of NOx concentration because of heavy traffic. ROx detected in nighttime because dark reaction of VOC contribute to ROx formation at night



Fig, Diurnal variation of ROx concentration.

And also ROx concentration by NOx photostationary state (PSS) was estimated . The ROx concentration estimated by PSS agree well with ROx concentration measured by PERCA-LIF. The benefit of estimate ROx concentration by PSS is simple determination. And this result of our work, suggests this technique is available

O_3 production rate P (O_3) was calculated by measured ROx concentration by PERCA-LIF . This P (O_3) showed correlation with ΔO_3.Where ΔO_3 is defined as O_3 concentration at 14:00 subtracting O_3, from O_3 concentration at 06:00. However, P(O_3) was exceeds ΔO_3 in all case. It is assumed that contribution of O_3 loss process, and dilution due to grow height of boundary layer. Because ΔO_3 is easily influenced by meteorological factors more reports and discussions are needed to clarify the O_3 formation mechanism including meteorological factors.