Development a technique to measure OH reactivity of unidentified VOCs using GC-FID

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1. Background and objectives

The role of trace species such as VOCs (Volatile organic compounds), nitrogen oxides (NOx) and carbon monoxide (CO), ozone, radical species in the atmosphere is noted to study about photochemical oxidants and global warming, acid rain and so on. Especially, OH radical plays important role. Most of trace species are removed by the reaction with OH radical; this reaction determines the lifetime of the trace species in the atmosphere. OH radical is also related to formation of photochemical oxidants. Therefore, revealing the behavior of OH radical in the atmosphere is important to know the mechanism of atmospheric reactions. Previously developed instrument to measure the OH reactivity directly in the atmosphere using a laser-induced pump and probe technique was used to observe OH reactivity in the ambient air. The OH reactivity measured using laser-induced pump and probe technique was compared with that the calculated OH calculated defined as the sum of the products of the observed concentrations and reaction rate coefficients for each species. The observed and the calculated OH reactivities should ideally be equal if the all species are taken account. However, an underestimation of the calculated OH reactivity was occasionally observed. The reason for the difference has not been revealed, however a possibility could be unmeasured VOCs. In this study, a technique to measure OH reactivity comes from unidentified VOCs by GC-FID is developed to evaluate the contribution of unidentified VOCs to the total OH reactivity measured by laser-induced pump and probe technique.

2. Development of OH exposing system and observational campaign

In this study, OH reactivity of unidentified VOCs which detected by GC-FID is calculated using concentration change to expose OH radical and OH reaction rate coefficient measured by GC-FID. To expose OH radical to the sample gases, OH generating system was developed. OH radical was generated in the photolysis of water vapor. Reaction rate coefficient was calculated using OH exposing system to make sure the system work accurately. The reaction rate coefficients calculated by using GC-FID exposing system were almost the similar values of literature. The measurement campaign was conducted from 13:30 to 14:00 on December 11th, 12th and 13th. In this campaign, GC-FID with OH exposing system and CO, NOx and O_3 analyzer were used to measure trace gas in ambient air.

3. Results and disccuccion

10.7% (11th), 11.0% (12th) and 62.3% (13th) of unknown OH reactivity were discovered that the contribution of unidentified VOCs. The figure shows the percentages of groups of chemical species in December 12th. Total OH reactivity was measured by laser-induced pump and probe technique. The concentration of NO is so high on December 13th that OH reactivity cannot be measured by laser-induced pump and probe technique. Therefore, the results of the measurement on 13th have possibility to underestimate the actual total OH reactivity. In this study, the OH reactivity of unidentified VOCs is revealed. Therefore, OH reactivity can be measured with more precision. The carbon number and reaction rate coefficients of unidentified VOCs are estimated, however the high reactive unidentified VOCs are needed to identify. It is our future task to identify high reactive unidentified VOCs using standard sample.

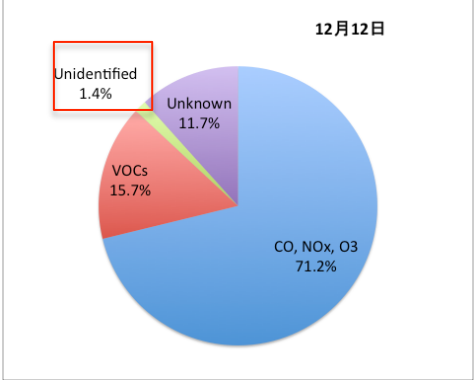

Fig. The percentages of the OH reactivities of the trace gas groups.