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Temperature Dependence of Atmospheric NO$_3$ Loss Frequency

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A new indicator with temperature dependence of the NO$_3$ loss frequency, was developed to study the contribution of NO$_3$ to the oxidation of monoterpenes and NO$_x$ removal in the atmosphere. The new indicator arises from the temperature dependence of kinetic constant. The new indicator was applied to data of observation based on differential optical absorption spectroscopy system on the outskirts of Hefei, China. According to the findings, the contribution of monoterpenes to the loss of NO$_3$ was 70%−80%.

Key words: NO$_3$, Differential optical absorption spectroscopy, Indicator, Loss frequency, Oxidation capacity

I. INTRODUCTION

The quality of environment has a close relationship with its self-cleaning capacity. NO$_3$ serves as the cleaners of the nighttime atmosphere. NO$_3$ is not only the primary oxidizing agent for volatile organic compounds (VOCs), but also plays a vital role in transforming the NO$_x$ to HNO$_3$ and forming nitrate particulate [1−3]. The oxidizing capacity of NO$_3$ on VOCs and removal of NO$_x$ in that NO$_3$ can change the ratio of VOC/NO$_x$, which has a direct role on producing the ozone of the day [2].

Since the first measurement of NO$_3$ in tropospheric layer in 1980 by Noxon *et al.* and Platt *et al.* [4, 5], environmental scientists have begun to measure NO$_3$ under different atmosphere modes (in polluted and clean atmosphere, land and seaside atmosphere) to have a better understanding on the role of NO$_3$ to forming ozone and to photochemical reaction. The findings show that in polluted districts the NO$_3$ is removed mostly through the reaction with NO, and that in suburbs and countryside the loss of NO$_3$ is mainly through the reaction with VOCs and N$_2$O$_5$ [8−14].

The current approaches to studying the NO$_3$ sinks can be mainly classified into three parts: (i) using models to investigate the oxidation of NO$_3$ on VOC and NO$_x$. (ii) through correlation analysis to predict the oxidation of NO$_3$ on VOCs and removal of NO$_x$. (iii) measuring not only the concentration of NO$_3$, but also all the VOCs components related to reaction [6, 7].

In this work, we use a new method to calculate the contribution of NO$_3$ to VOCs and NO$_x$ in the atmosphere by analysis of the relationship between loss rate of NO$_3$ and temperature. The new indicator is used to investigate the loss process of NO$_3$ through analyzing the relationship of dynamics constants and the relationship of monoterpene emission rate and temperature. This method is simple, the concentration of NO$_3$, NO$_2$, O$_3$ and temperature in the atmosphere are only needed. Then, this indicator was applied to investigate the contribution of NO$_3$ to VOCs and removal of NO$_x$ in the field campaign of Hefei.

## II. RELATIONSHIP BETWEEN NO$_3$ LOSS FREQUENCY AND TEMPERATURE

NO$_3$ concentration is very low for the rapid photolysis and the reaction with NO during the day, whereas NO$_3$ is accumulated quickly after the sunset and becomes the essential oxidizing agent in the nighttime. In the boundary layer, the primary source of NO$_3$ is from the oxidizing reaction of NO$_2$ and O$_3$.

$$NO_2 + O_3 \xrightarrow{k_1} NO_3 + O_2 \qquad (1)$$
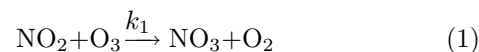
The primary chemical rate constant of NO$_3$ is listed in Table I. The productivity of NO$_3$ is calculated with the concentrations of NO$_2$ and O$_3$:

$$P_{NO_3} = [NO_2][O_3]k_1 \qquad (2)$$

Another source of NO$_3$ is the thermal analysis of N$_2$O$_5$:

$$NO_2 + NO_3 + M \xleftarrow{K_{eq}} N_2O_5 + M \qquad (3)$$
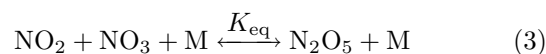
Because the Eq.(3) reaches dynamic balance in a few minutes, thermal analysis of N$_2$O$_5$ is not the major

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TABLE I kinetic data of the reactions in NO_3 chemistry $k(T) = A\exp(B/T)$ [2, 5, 16].

Reaction	$A/(\text{cm}^3/\text{s}^{-1})$	B/K^{-1}	$k(298\text{ K})/(\text{cm}^3/\text{s})$
$NO_2+O_3 \to NO_3+O_2$	1.4×10^{-13}	-2470 ± 150	3.5×10^{-17}
$NO_3+NO \to 2NO_2$	1.8×10^{-11}	-110 ± 100	2.6×10^{-11}
$O_3+NO \to NO_2+O_2$	1.4×10^{-12}	-1310 ± 200	1.8×10^{-14}
$NO_3+\alpha\text{-pinene} \to \text{pinon aldehyde}$	1.19×10^{-12}	490	6.2×10^{-12}
$NO_2+NO_3+M \leftrightarrow N_2O_5+M$	5.5×10^{-27}	10724 ± 75	2.3×10^{-11}

source of NO_3. Therefore, the contribution of N_2O_5 to the productivity of NO_3 is negligible [1, 2].

Suppose the local stabilization of NO_3, the production and loss of NO_3 reach dynamic balance. Then its loss frequency f_{NO_3} could be reached through the measured concentration of NO_3 and its production P_{NO_3} [5−11]:
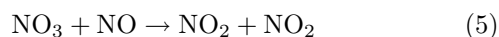
$$\frac{d}{dt}[NO_3] = P_{NO_3} - [NO_3]f_{NO_3} = 0$$
$$f_{NO_3} = \frac{[NO_2][O_3]k_1}{[NO_3]}$$
$$= \frac{1}{\tau_{NO_3}} \tag{4}$$

here, τ_{NO_3} is lifetimes of NO_3.

A. NO_3 direct sinks

1. Reaction of NO_3 with NO

A rapid loss mechanism is gas phase reactions of NO_3 and NO:

$$NO_3 + NO \to NO_2 + NO_2 \tag{5}$$

When NO reaches 0.5−2.5 µmol/L, the typical loss frequency of NO_3 is 0.5−0.1 s^{-1}. The reaction rate is 5% higher at 298 K than that at 273 K (Table I), which indicates that the temperature has minor influence on the gas phase reactions of NO_3 and NO [1, 2]. In nighttime, due to missing photolysis NO_2 and the rapid reaction of NO with O_3, with typical lifetimes of NO of the order 1 min (298 K, O_3 at 40 µmol/L), this loss mechanism can be neglected, except in the vicinity of NO sources.

$$O_3 + NO \to NO_2 + O_2 \tag{6}$$
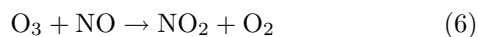
No prominent temperature dependence of anthropogenic NO emission is known. Compared with NO_3 loss caused by other reactions, Eq.(5) has a loose connection with temperature. When the loss of NO_3 is mainly through the reaction with NO, the influence of surrounding temperature on the loss frequency of NO_3 can be neglected.

2. Reaction of NO_3 with VOCs

In land boundary layer, NO_3 reacts rapidly with VOCs released by organic compounds, in particular with monoterpenes released by biosphere. A recent comparison of reaction rates of NO_3 with hydrocarbons at Pabstthum, yielded a partitioning of 90%, 5%, and 5% for monoterpenes, isoprene, and anthropogenic VOCs, respectively [5].

The reaction of NO_3 with α-pinene will decrease by 13% when the temperature varies from 273 K to 298 K. Whereas the emission flux F of monoterpenes increases with the temperature [14, 15]:

$$F \sim \exp[\beta(T - T_s)] \tag{7}$$

β is an empirical constant in the range of 0.06−0.14 K^{-1}, which is related to plants type. The maximum of monoterpene emission is observed at temperatures T_s around from 310 K to 320 K [5, 16]. Supposing when $\beta=0.09$ K^{-1}, $T_s=315$ K, and the variation of temperature is 273−298 K, the total emission of monoterpenes is increased by 8.6 times. In fact, it is the monoterpenes in the environment that controls the loss frequency $f_{NO_3MT}(T)$ of NO_3. When the primary removal path is through reaction with monoterpenes, the loss frequency of NO_3 increases with temperature index:

$$f_{NO_3MT}(T) \sim \exp(0.09T) \tag{8}$$

Eq.(8) indicates that the reaction of NO_3 and monoterpenes is of great importance in hot season. Based on Eq.(8), we can research the whole loss contribution of the reaction of NO_3 and monoterpenes on NO_3 at any temperature. In the rural areas, even the temperature is 285 K, NO_3 mainly reacts with monoterpenes. In the city, anthropogenic discharge of VOCs influences the emission of NO_3, while, in the presence of NO, it is not the natural or man-made VOCs that plays a great role but NO that is the foremost capture [6, 9, 14].

B. NO_3 indirect sinks

N_2O_5 is generated in the reaction of NO_3 and NO_2. In a few minutes the Eq.(3) reaches a dynamic balance. The loss process of N_2O_5 is also the indirect removal

process, in which $f_{N_2O_5}$ denotes the total loss of N_2O_5 and f_{NO_3indir} denotes the indirect loss:

$$f_{NO_3indir} = K_{eq}(T)\,[NO_2]\,f_{N_2O_5} \qquad (9)$$

K_{eq} is strongly temperature dependant, and the value of K_{eq} exponentially decreases with increasing temperature. Because of a higher factor of 24 at 273 K compared with 298 K, indirect sinks play an important role in winter [5]:

$$f_{NO_3indir} \sim \exp\left(\frac{10724}{T}\right) \qquad (10)$$

The possible sinks of N_2O_5 are homogeneous reaction with moisture or inhomogeneous reaction in aerosols surface to generate nitrate:

$$N_2O_5 + 2H_2O \rightarrow 2HNO_3 \qquad (11)$$

With auxiliary meteorological data, calculation of the loss frequency of N_2O_5 caused by the homogeneous reaction of N_2O_5 and moisture is a minor reaction in atmosphere. Though the relation of temperature with this reaction is still under question, Eq.(11) indicates that the hydrolysis of N_2O_5 should has a positive temperature coefficient.

In the liquid layer of aerosols surface, N_2O_5 can make a rapid hydrolysis reaction. The absorption coefficient $\gamma_{N_2O_5}$ on N_2O_5 varies with different aerosols components and particle diameters [1, 6, 16], which would affect the indirect NO$_3$ sinks. According to the findings, absorption coefficient decreases with temperature rise, but the variation is slight. For example, absorption coefficient is 13.9% at 247 K while it is 10% at 293 K [5]. Therefore, the variation of attrition rate of N_2O_5 in aerosols surface with temperature can be disregard.

C. The temperature dependence of NO$_3$ loss frequency

In land boundary layer, without the discharge of NO, the losses of NO$_3$ are mainly through two paths: one is the direct reaction with monoterpenes, the other is inhomogeneous hydrolysis of N_2O_5. The temperature dependence of the NO$_3$ loss frequency is consequently given by:

$$\begin{aligned} f_{NO_3} &= f_{NO_3MT}(T) + f_{NO_3indir}(T) \\ &= A_0 \exp(0.09T) + B_0 \exp\frac{10724}{T} \end{aligned} \qquad (12)$$

So far, the parameters related to temperature are primarily the emission rate of monoterpenes and the dynamic equilibrium factor of N_2O_5. Coefficients of A_0 and B_0 in Eq.(12) have no connection with temperature. The contributions of monoterpenes reaction to the total NO$_3$ sinks (TC) is given by:

$$TC = \frac{100 f_{NO_3MT}(298K)}{f_{NO_3MT}(298K) + f_{NO_3indir}(298K)} \times 100\% \quad (13)$$
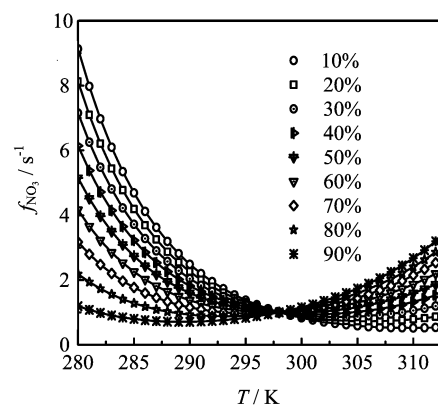
FIG. 1 Calculated temperature dependence of the NO$_3$ loss frequency at different TC (all frequency are calibrated to unity at 298 K).
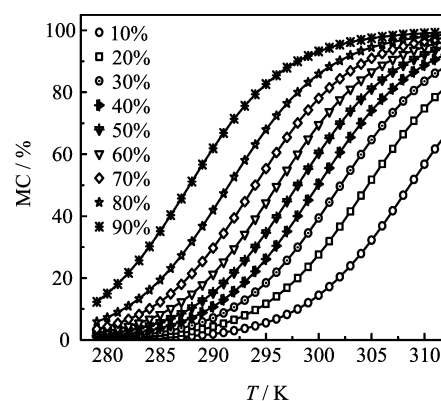

FIG. 2 Variation of the contribution of NO$_3$-monoterpene reaction to the total NO$_3$ removal (MC) with temperatures at different TC.

To correlational study, the absolute value of f_{NO_3} is not important, so the loss frequency of NO$_3$ is normalized at 298 K as $f_{NO_3}(298\,K) \approx 1$. The relationship between f_{NO_3} and temperature variation is simulated in Fig.1, in which the loss contribution of monoterpenes on NO$_3$ known as TC ranges from 10% to 90%. Figure 2 shows the influence of monoterpenes obviously increases at higher temperature.

Figure 3 is the calculated contribution of NO$_3$ and momoterpene reactions to the total NO$_3$ removal as a function of the derivative of $f_{NO_3}(T)$. The clear linear dependence indicates that temperature dependence of the NO$_3$ loss frequency can be used as a new indicator for NO$_3$ sinks. TC is obviously linear as function of:

$$TC = 57.3 + 474.5 \frac{1}{f_{NO_3}} \frac{df_{NO_3}}{dT} \times 100\% \qquad (14)$$

Based on the acquired connection between f_{NO_3} and temperature above, NO$_3$ loss under different temperatures can be calculated through Eq.(14). When
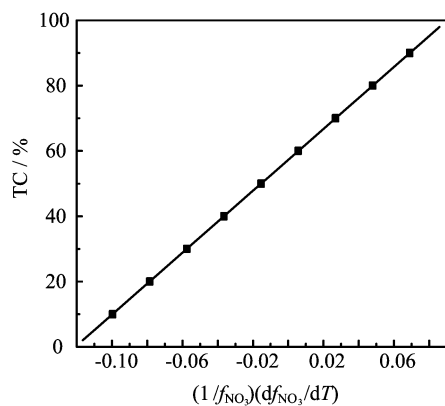
FIG. 3 The calculated contribution (TC) of NO_3-momoterpene reactions to the total NO_3 removal at 298 K as a function of the derivative of f_{NO_3} toward temperature.
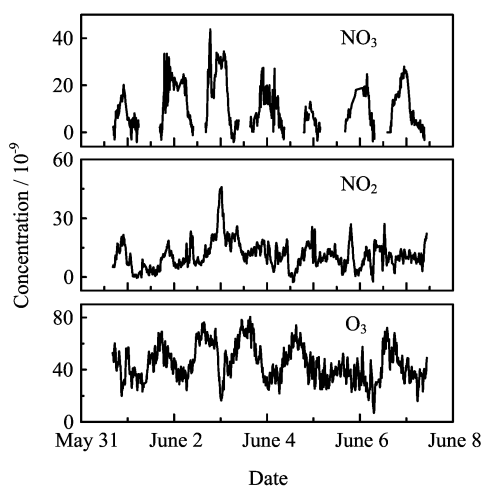

FIG. 4 Time series of NO_3, NO_2, and O_3 by DOAS system.

$\dfrac{1}{f_{NO_3}}\dfrac{\mathrm{d}f_{NO_3}}{\mathrm{d}T}$ at 298 K is zero, the reaction contribution of monoterpenes is 57%. Uncertainty of monoterpenes emission factor β in Eq.(7) causes error of 30% about NO_3 loss contribution in the reaction of NO_3 with monoterpenes.

III. APPLICATION IN FIELD CAMPAIGN

Observation of nighttime NO_3, NO_2, and O_3 have been performed using long path-differential optical absorption spectroscopy (LP-DOAS) on the outskirts of Hefei (117°23′E, 31°86′N), China. The time series of NO_3 and supporting parameters were simultaneously measured for 31 May−8 June. Figure 4 is time series of NO_3, NO_2, and O_3 concentrations. Correlation analysis shows that NO_3 loss path is removed directly through the reaction with monoterpenes. For a detailed system
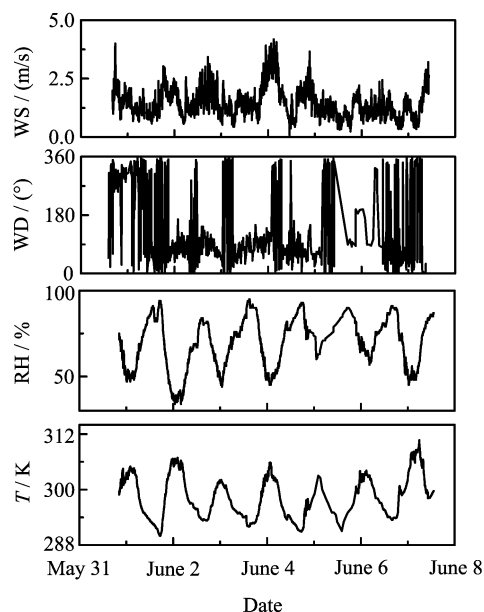

FIG. 5 Time series of the meteorological parameters. RH: relative humidity, WD: wind direction, and WS: wind speed.
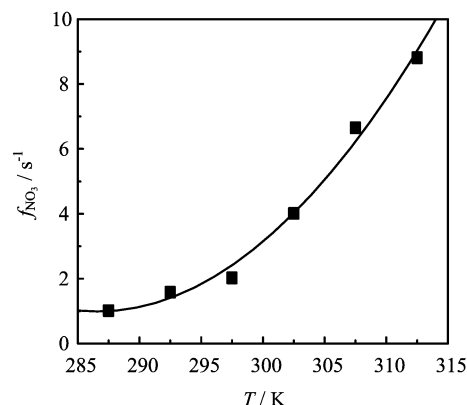

FIG. 6 Temperature dependence of the NO_3 loss frequency during the field campaign of NO_3 in Hefei.

analysis and calculation, see Ref.[3].

The new indicator is applied to analyze observed data, combined with the concentrations of NO_3, NO_2 and O_3 measured by DOAS (Fig.4). Figure 5 shows time series of the meteorological parameters with the temperature dependence of the NO_3 loss frequency at interval of 5 K, showing that f_{NO_3} increases with temperature obviously. The loss frequency at 310 K is about 4 times higher than at 298 K. Quadratic polynomial fitting is adopted in Fig.6, in which the correlation coefficient is 0.99. At 298 K, f_{NO_3} about temperature derivative is 0.037±0.011 (with 30% error factor). The contribution of the reaction of NO_3 and monoterpenes on the temperature loss is 70%−80%. The function curves are identical in Fig.6 and Fig.1, in which the

contributions of monoterpenes are both 80%.

In the same observation time, the conclusion is identical with Geyer's, in which the settlement of NO$_3$ is through the reaction with monoterpenes [5]. The analysis on the correlation of NO$_2$ and the life of NO$_3$ only show the qualitative result, while the quantitative information on settlement distribution can be obtained through temperature indicator.

IV. CONCLUSION

A new indicator for the sink distributions of NO$_3$, which is achieved from the relationship between dynamics constant and release rate of monoterpenes and temperature, is presented in this work. The new indicator can show the oxidation of NO$_3$ on VOCs and the contribution rate of the removal of NO$_x$ quantitatively. The contribution NO$_3$ on the removal of NO$_x$ and monoterpenes oxidization can be obtained directly through the temperature derivative in f_{NO_3}. This work also analyzes the field data on the outskirts of Hefei. The findings show that the loss path of NO$_3$ is mainly through monoterpenes reaction of plants, the contribution rate is 70%−80%.

V. ACKNOWLEDGMENTS

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