Observation of the nighttime nitrate radical in Hefei, China

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Abstract

Observation of nighttime nitrate radical (NO_3) was performed by using long path differential optical absorption spectroscopy (LP-DOAS), on the outskirts of Hefei, China. The time series of NO_3 and supporting parameters were simultaneously measured for a week (31 May–7 June 2006). The results indicated that the average concentration of NO_3 was 15.6 pptv with an average lifetimes of 96 s, whereas, NO_3 production rates varied from $8 \times 10^5/(cm^3 \cdot s)$ to $2.98 \times 10^7/(cm^3 \cdot s)$. Furthermore, the calculated N_2O_5 concentration averaged at 380 pptv. Analysis of data indicated that direct sinks were probably dominating the NO_3 loss process during this campaign. The results were compared with other campaigns in the boundary layer.

Key words: nitrate radical; nighttime chemistry; differential optical absorption spectroscopy; sinks

Introduction

Nighttime chemistry plays a key role in determining the initial chemical conditions for photochemistry during the following morning, in the troposphere. And the nitrate radical (NO_3) is the main oxidant in nocturnal chemistry (Bey *et al.*, 2001; Geyer *et al.*. 1999, 2001; Heintz *et al.*, 1996; Smith *et al.*, 1995; Robert *et al.*, 2004). NO_3 reacts with a number of volatile organic compound (VOCs), which initiates their nighttime degradation. Furthermore, the nitrate radical has a strong influence on the levels of nitrogen compounds and it is responsible for the nonphotochemical conversion of nitrogen to nitric acid via N_2O_5 (Geyer *et al.* 1999, 2001; Wood *et al.*, 2005; Vrekoussis *et al.*, 2003, 2004).

In this article, the authors reported the recent results from a field campaign (31 May–7 June 2006) on the outskirts of Hefei (117°23′E, 31°86′N), China. The observation showed that the possibility of investigations of nighttime NO_3 concentration was obtained by long path differential optical absorption spectroscopy (LP-DOAS) (LI *et al.*, 2007). The authors also calculated N_2O_5 concentrations, the production rates of NO_3, and the lifetime of NO_3. In addition, the correlation studies yielded the probable sink processes for NO_3. Finally, the results were compared with other campaigns of NO_3 in the boundary layer.

1 NO₃ chemistry

By far the significant source of NO_3 is the oxidation of nitrogen dioxide (NO_2) by ozone (O_3) in the boundary layer:

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \tag{1}$$

The reaction rate is $k_1 = 1.4 \times 10^{-13}\exp(-2470/T)$ cm^3/s, then $k_{1(298\ K)} = 3.55 \times 10^{-17}$ cm^3/s (Vrekoussis *et al.*, 2004). The production rate P_{NO_3} of NO_3 can be calculated from the concentration of NO_2 and O_3 (Heintz *et al.*, 1996; Carslaw *et al.*, 1997; Geyer *et al.*, 2001):

$$P_{NO_3} = C_{NO_2} \times C_{O_3}k_1 \tag{2}$$

Assuming local steady state conditions for the nitrate radical, which is usually established in the order of a few minutes, the NO_3 lifetime can be calculated from the measured concentration and production rate (Heintz *et al.*, 1996; Carslaw *et al.*, 1997; Geyer *et al.*, 2001; Vrekoussis *et al.*, 2003, 2004):

$$\frac{d}{dt}C_{NO_3} = P_{NO_3} - C_{NO_3}/\tau_{NO_3} = 0 \tag{3}$$

$$\tau_{NO_3} = \frac{C_{NO_3}}{C_{NO_2}C_{O_3}k_2} = \frac{C_{NO_3}}{P_{NO_3}} \tag{4}$$

During the daytime, NO_3 has a very short lifetime (about 5 s) (Amekudzi *et al.*, 2005; Heintz *et al.*, 1996; Geyer *et al.*, 2001) because of its rapid photolysis. The photolysis frequency for solar zenith angles below 70° is about 0.3/s (Noxon, 1980; Geyer *et al.*, 2001; Platt *et al.*, 2002; Vrekoussis *et al.*, 2004):

$$NO_3 + h\nu \longrightarrow NO_2 + O(^3P) \tag{5}$$

$$NO_3 + h\nu \longrightarrow NO + O_2 \tag{6}$$
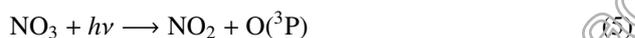
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A rapid loss mechanism is the gas phase reaction with NO:

$$NO_3 + NO \longrightarrow NO_2 + NO_2 \tag{7}$$

$k_{6\ (298\ K)} = 2.6 \times 10^{-11}$ (cm^3/s) (Vrekoussis *et al.*, 2004). However, NO is rapidly oxidized by the reaction with ozone.

$$O_3 + NO \longrightarrow NO_2 + O_2 \tag{8}$$

Rate constant is $k_8 = 1.8 \times 10^{-14}$ (cm^3/s), resulting in a typical lifetime of NO of the order 1 min at 30 ppbv ozone. At night, as there is no photolysis of NO_2 (providing an NO source during the day) and the rapid reaction of NO and ozone (Reaction 8), NO levels are generally very low except in the vicinity of the NO source or in the absence of ozone. The NO_3 lifetime and its concentrations are expected to become much larger at nighttime.

In the continental boundary layer, NO_3 can rapidly react with several volatile organic compounds, in particular, with alkenes such as monoterpene and isoprene (Carslaw *et al.*, 1997; Smith *et al.*, 1995; Mihelcic *et al.*, 1993; Geyer *et al.*, 2001). NO_3 can noticeably contribute to the degradation of several hydrocarbons in nighttime atmosphere (Geyer *et al.*, 2001; Heintz *et al.*, 1996).

Another major scavenging process besides the direct NO_3 sinks is based on the combination of NO_3 and NO_2 to yield N_2O_5:

$$NO_3 + NO_2 + M \rightleftharpoons N_2O_5 + M \tag{9}$$
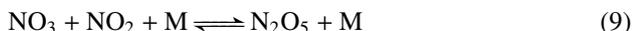
Owing to the thermal decay of N_2O_5, a temperature dependent equilibrium between the three species is established favoring N_2O_5 at typical boundary layer temperatures and moderate NO_2-levels of more than 1 ppbv:

$$C_{N_2O_5} = K_{eq\ (T)} C_{NO_2} C_{NO_3} \tag{10}$$

The strong temperature-dependent equilibrium constant is $K_{eq\ (T)} = 9.7 \times 10^{14}\ (T/300)^{0.01} \times \exp(-11080/T)$ (cm^3/s) (Vrekoussis *et al.*, 2003, 2004). Loss processes for N_2O_5 are indirect sinks of NO_3. A possible sink of N_2O_5 is its homogeneous reaction with water vapor, producing HNO_3, and the rate constant is in the range $(3–9) \times 10^{-22}$ cm^3/s.

$$N_2O_5 + H_2O \longrightarrow HNO_3 + HNO_3 \tag{11}$$

Reaction of N_2O_5 on aerosol surfaces is another possible sink of N_2O_5. Finally, N_2O_5 can be removed by dry deposition to the ground (Geyer *et al.*, 1999, 2001).

In the marine atmosphere, reaction with DMS is of importance (Noxon, 1983; Allan *et al.*, 1999; Vrekoussis *et al.*, 2003, 2004). Here the discussion is restricted to the continent boundary layer, Hefei, China.

2 Experimental

2.1 Location

The measurement was performed by LP-DOAS on the outskirts of Hefei (117°23′E, 31°86′N). The LP-DOAS setup was deployed on the fifth floor of the Anhui Institute of Optics and Fine Mechanics building. There was little traffic and few industries, and the main pollution came from urban Hefei, which is situated at a distance of about 18 km (center).

2.2 Experimental system

The concentrations of NO_3, NO_2, and O_3 were averaged along the optical path of 3 km (NO_3) and 0.7 km (NO_2 and O_3) by LP-DOAS. The meteorological data of temperature, wind speed, wind direction, and relative humidity were provided by a meteorological station nearby.

Figure 1 shows the important part of the DOAS system. A Cassegrain telescope was used to transmit and receive light. The reflecting system consisted of an array of 13 retro-reflectors. A 610-nm long-pass red filter, to reduce stray light effects below 610 nm, was placed in the fiber optic coupler. A diameter fiber bundle, 7×0.1 mm, which was regulated by a mode mixer to reduce the unwanted structures, carried light to the spectrometer. The CCD detector, cooled to –45°C, was mounted in the focal plane of the spectrograph. Finally the optical signal was stored and analyzed in the computer (Li *et al.*, 2007).

3 Results

The data presented here covered a week from 31 May to 7 June 2006. The following analysis of the NO_3 budget was restricted to the nighttime, exceeded the detection limits (3.8 pptv) of the DOAS system, and photolysis of NO_3 could be neglected.

3.1 Time series of O_3, NO_2, NO_3, and N_2O_5

The time series of O_3 concentrations are shown in Fig.2a. The change of ozone showed a typical diurnal variation. During the measuring period the average values ranged closer to 50 ppbv, but typically, the minimum was around 20 ppbv with a maximum of 80 ppbv. The NO_2 concentrations (Fig.2b) averaged at 8.2 ppbv. NO_2 values were typically varied between 1 and 51.9 ppbv, and maximum of 51.9 ppbv appeared on June 2, 2006.

Nighttime measurement of NO_3 was performed for a week. The maximum value of 43.7 pptv appeared on June 2, 2006, and NO_2 also reached a maximum value at this time. Fig.2c shows the time series NO_3 concentrations with an average concentration of 15.6 pptv.
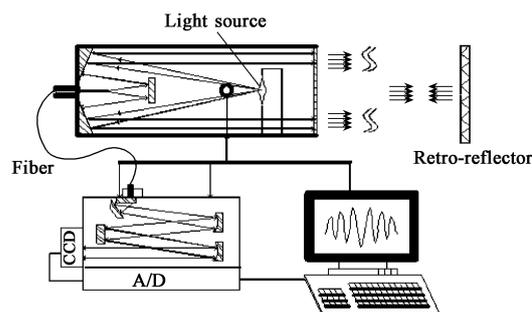

Fig. 1 Schematic view of a DOAS instrument.
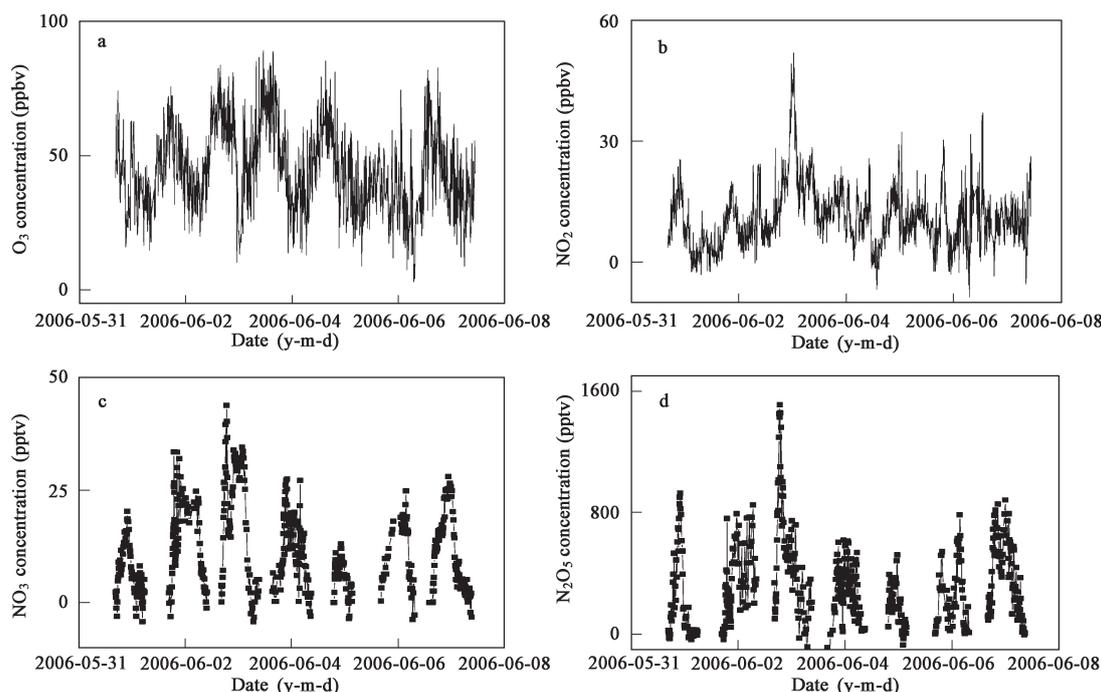
Fig. 2   Time series of O_3 (a), NO_2 (b), NO_3 (c), and N_2O_5 (d) concentration.

Although N_2O_5 could not be directly measured by the DOAS technique, its equilibrium concentration was calculated from the measured levels of NO_2, NO_3, and temperature (11). N_2O_5 concentrations varied from 5 pptv to 1578 pptv. As shown in Fig. 2d, the mean N_2O_5 concentration was about 380 pptv.

3.2 Meteorological data

Temperature (T), relative humidity (RH), wind speed (WS), and wind direction (WD) are shown in Fig.3. Usually, low wind speeds prevailed over the measurement period, wind speed ranged up to 4 m/s at an average of 1.4 m/s. The dominant wind direction was east and northwest appearing during more than 80% of the nighttime cases. Thus the measurement site was hardly affected by urban pollution from southeast Hefei. The relatively unpolluted air masses from ambient agricultural areas should have reached the measurement site. The temperature and relative humidity showed a typical diurnal variation, with mean values of 298 K and 82%, respectively. Both quantities showed high relative humidity and low temperatures during nighttime.

3.3 NO$_3$ production rate and lifetime

The production rate P_{NO_3} was calculated from reaction (1) using the measured levels of NO_2 and O_3. The production rate varied from $8 \times 10^5/(cm^3 \cdot s)$ to $2.98 \times 10^7/(cm^3 \cdot s)$ (Fig.4a). Maybe there was some direct correlation between the production rates of nitrate radicals and their concentrations, which will be discussed in the following.

To obtain a measure of the depletion of NO_3 radicals, it was interesting to inspect its lifetime, which is shown in Fig.4b. Generally, the NO_3 lifetime ranged between several seconds and a maximum value of about 698 s, which
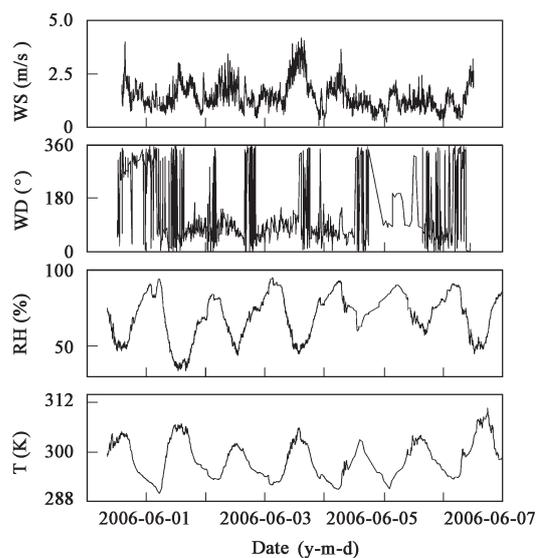

Fig. 3   Time series of the meteorological parameters.

appeared on June 4, 2006. The mean NO_3 lifetime was observed at about 96 s.

3.4 Nature of the NO$_3$ possible sinks during this campaign

Nature of the NO_3 possible sink during this campaign was obtained by analyzing the correlation between NO_3 concentrations and its production rate and that between the NO_3 lifetime and NO_2 concentrations, respectively (Allen *et al.*, 1999; Heintz *et al.*, 1996; Geyer *et al.*, 2001; Vrekoussis *et al.*, 2003). Correlation studies were a powerful tool to get qualitative information, whether NO_3 was depleted directly or indirectly (via N_2O_5) during this campaign. Considering a simple reaction scheme with
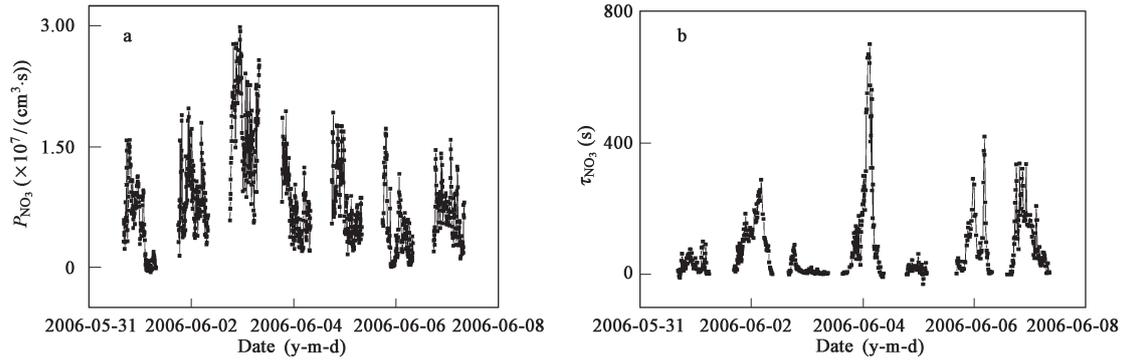
Fig. 4 Time series of NO_3 production (a) and τ_{NO_3} lifetime (b).

the NO_3 production Reaction (1), the equilibrium between NO_3 and N_2O_5, and two different removal paths of NO_3, (a) direct and (b) indirect loss, with corresponding NO_3 degradation frequencies f_{dir} and f_{indir}, the NO_3 and N_2O_5 concentrations were given by the following equations (Allen *et al.*, 1999; Heintz *et al.*, 1996; Geyer *et al.*, 2001; Vrekoussis *et al.*, 2003):

$$k_1 C_{NO_2} C_{O_3} + k_{-9} C_{N_2O_5} = f_{dir} C_{NO_3} + k_{+9} C_{NO_2} C_{NO_3} \quad (12)$$

$$k_{+9} C_{NO_2} C_{NO_3} = f_{indir} C_{N_2O_5} + k_{-9} C_{N_2O_5} \quad (13)$$

Eq.(13) indicated that the "effective" equilibrium constant K_{eq} (9) slightly decreased in the presence of N_2O_5 sinks. Both Eqs.(12) and (13) could easily be combined, yielding:

$$C_{NO_3} = C_{NO_2} C_{O_3} k_1 \times (f_{dir} + C_{NO_2} k_9 \frac{f_{indir}}{k_{-9} + f_{indir}})^{-1} \approx \quad (14)$$
$$P_{NO_3} \times (f_{dir} + C_{NO_2} K_{eq} f_{indir})^{-1}$$

For conditions where the loss of NO_3 proceeded only via direct sink ($f_{indir} = 0$), Eq.(14) is reduced to:

$$C_{NO_3} = P_{NO_3} \times f_{dir}^{-1} \quad (15)$$

In the case of negligible direct sinks of the nitrate radical ($f_{dir} = 0$), an indirect dependency of the concentrations of NO_3 and NO_2 was obtained from Eq.(13) yielding an inverse correlation of NO_2 and NO_3:

$$C_{NO_3} = P_{NO_3} \times (C_{NO_2} K_{eq} f_{indir})^{-1} \quad (16)$$

$$\tau_{NO_3}^{-1} = C_{NO_2} \times K_{eq} \times f_{indir} \quad (17)$$

3.4.1 Reaction with NO

The reaction of NO_3 with NO was very unlikely to be an NO_3 sink on the outskirts of Hefei because of the expected low values of NO during nighttime. This is assumed for two reasons, because of the absence of direct NO sources near the measurement site and the rapid reaction of NO with ozone at typical O_3 levels (50 ppbv), as the measurement was on the outskirts of Hefei, which converts NO to NO_2 in an order of minutes. Thus, the impact of NO-polluted air, contributing to NO_3 loss could probably be neglected.
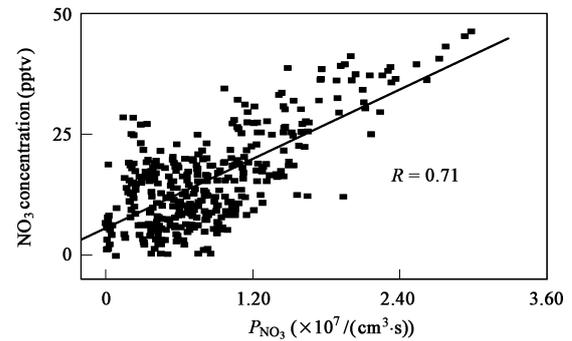

Fig. 5 Correlation of NO_3 production rate and NO_3 concentrations.

3.4.2 Reaction with VOCs

To one's knowledge only reactions with biogenic VOCs have played the important role of direct scavengers of NO_3 in the continental boundary layer during earlier measurement campaigns (Heintz *et al.*, 1996; Geyer *et al.*, 2001), especially in summer. Unfortunately, VOCs were not measured during this campaign. However, the probable sink could be drawn from the supporting parameters.

Following expression (15) of a direct correlation between NO_3 concentrations and its production rate predicted direct sinks. Fig.9 shows the correlation of NO_3 concentration and P_{NO_3}. A clear positive correlation was found. The coefficient R of the correlation was 0.71. This analysis pointed out that the contribution of direct sinks (e.g., NO_3–VOCs reactions) might be dominant during this campaign.

3.4.3 Indirect loss of NO_3 via N_2O_5

In the case of negligible direct sinks of the nitrate radical, an indirect dependency of the concentrations of NO_3 and NO_2 was obtained from Eq.(17), yielding an inverse correlation of NO_2 and the lifetime of NO_3. Fig.6 shows the lifetime of NO_3 as a function of the concentration of NO_2. The analysis was restricted to data with NO_3 and NO_2 above the detection limits. A linear fit was performed for this data yielding an indirect dependency at a correlation coefficient $R = -0.31$.

The correlation coefficient R of nitrate radical concentration and P_{NO_3} was 0.71, whereas, R of the radical lifetime versus NO_2 concentration was –0.31. This analysis pointed out that the contribution of indirect sinks was less
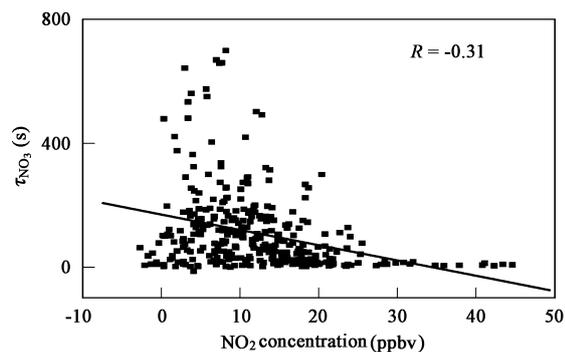
Fig. 6   Correlation of the NO_3 lifetime and NO_2 concentrations.

important, although direct sinks were predominant during this campaign.

3.5 Comparison with other observations in the boundary layer

The results of this campaign were compared with observations in Lindenberg (14°07′E, 52°13′N), Germany (Geyer *et al.*, 2001). Similar removal processes for NO_3 were found in Table 1, which were direct sinks in June, for they were in a similar condition. Levels of NO_2 and O_3 were higher during this study, perhaps lending support to the enhanced values of NO_3 and a shorter lifetime during this campaign (Table 2).

Table 1   Comparison of the NO_3 in the boundary layer

Average values	Continental Hefei (June)	Continental Lindenberg (May–Sep.)
NO_3 (pptv)	15.6	5.7
τ(s)	96	130
Major removal path	Direct	Direct (by monoterpenes)
Reference		Geyer *et al.*, 2001

Table 2   Comparison of the NO_2, O_3, and NO_3 in the continental boundary layer

Site of observation	Coordinates	Average levels		
		NO_2 (ppbv)	O_3 (ppbv)	NO_3 (pptv)
Lindenberg	14°07′E, 52°13′N	3.9	32	5.7
Hefei	117°23′E, 31°86′N	8.2	50	15.6

4 Conclusions

The concentrations of NO_3, NO_2, and O_3 were simultaneously measured by LP-DOAS for a week on the outskirts of Hefei, China. The average concentration of NO_3 was 15.6 pptv with an average lifetime of 96 s, whereas, NO_3 production rates varied from 8×10^5/(cm^3·s) to 2.98×10^7/(cm^3·s). Moreover, the calculated N_2O_5 concentration was about 380 pptv. The correlation coefficient R of NO_3 concentration and P_{NO_3} was 0.71, whereas, the correlation

coefficient of the radical lifetimes versus NO_2 concentrations was $R = -0.31$. This analysis pointed out that the contributions of indirect sinks were less important, whereas, those of the direct sinks were predominant, during this campaign.

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