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Characteristics and influence factors of NO₂ exchange flux between the atmosphere and *P. nigra*

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ABSTRACT

Nitrogen dioxide (NO₂) is an important substance in atmospheric photochemical processes and can also be absorbed by plants. NO₂ fluxes between the atmosphere and *P. nigra* seedlings were investigated by a double dynamic chambers method in Beijing from June 15 to September 3, 2017. The range of NO₂ exchange fluxes between *P. nigra* seedlings and the atmosphere was from −14.6 to 0.8 nmol/(m²·sec) (the positive data represent NO₂ emission from trees, while the negative values indicate absorption). Under ambient concentrations, the mean NO₂ flux during the fast-growing stage (Jun. 15–Aug. 4) was −3.0 nmol/(m²·sec), greater than the flux of −1.5 nmol/(m²·sec) during the later growth stage (Aug. 8–Sept. 3). The daily exchange fluxes of NO₂ obviously fluctuated. The fluxes were largest in the morning and decreased gradually over time. Additionally, the NO₂ fluxes were larger under high light intensities than under low light intensities during the whole growth period. The effects of temperature on NO₂ fluxes were different under two growth periods. The NO₂ exchange fluxes were larger in a range of temperatures close to 44°C in the fast-growing stage, whereas there were no evident differences in NO₂ exchange fluxes under widely differing temperatures in the later growth stage. Under polluted conditions, the uptake ability of NO₂ was weakened. Additionally, the compensation point of NO₂ was 5.6 ppb in the fast-growing stage, whereas it was 1.4 ppb in the later growth stage. The deposition velocities of NO₂ were between 0.3 and 2.4 mm/sec.

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Introduction

Nitrogen compounds in the atmosphere mainly include nitrous oxide (N₂O), nitrogen oxide (NO), nitrogen dioxide (NO₂), ammonia (NH₃), nitrous acid (HNO₂), nitric acid (HNO₃), and a small amount of N_xO_y. NO and NO₂ are known as nitrogen

oxides (NO_x), which are the major high-activity nitrogen pollutants in the atmosphere. The most common anthropogenic source of NO_x is the combustion of fuel. The main biological sources include the oxidation of NO₃ by bacteria, the oxidation of biogenic N₂O and the oxidation of ammonia decomposed from amino acids by OH. The removal of NO_x

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mainly occurs via dry and wet deposition. As the chemical cycle between NO_x and O_3 is the basis of the atmospheric chemical process, which is involved in the formation of photochemical smog and haze, and therefore, NO_x plays an important role in pollution of the atmosphere.

Plants have been proven to be a sink of NO_2 for the atmosphere. By using the isotopic marker ^{15}N (Okano et al., 1990; Rogers et al., 1979a; Segschneider, 1995; Yoneyama et al., 2003), NO_x was determined to be absorbed by the leaves of plants. For the process of NO_2 entering through the stomata of the leaves, it is generally believed that NO_2 dissolves in the apoplast to form nitrous acid and nitric acid first and then dissociates into NO_2^- , NO_3^- and a proton (H^+). After NO_2 dissolves into NO_2^- and NO_3^- in the leaf apoplast, these two forms of nitrate nitrogen are then transported into the cell, and the NO_3^- is rapidly reduced to NO_2^- in the cell by nitrite reductase. After that, NO_2^- is transported to chloroplasts and reduced to NH_4^+ by nitrite reductase (Lea and Mifflin, 1974; Maeck, 1995; Sakakibara et al., 1996; Tischner, 2000), which is involved in protein synthesis. For some species of NO_3^- that cannot be transported in suitable amounts, the N in the atmosphere may be the only or the most important way for plants to obtain NO_2^- or NO_3^- from their leaves (Sparks, 2009).

The NO_2 exchange flux between plants and the atmosphere has been widely researched. The main factors that influence these fluxes are the ambient NO_2 concentration and the stomatal conductance of different plants (Johansson, 1987; Thoene et al., 1991, 1996). In addition, there are also ambient factors impacting the stomatal conductance such as temperature, photosynthetically active radiation (PAR) and relative humidity. In early research, determination of the NO_2 exchange flux was often done under controlled concentrations (0.10–0.55 ppm) which were higher than those in the real atmosphere (Bengtson et al., 1982; Pawloskisinn et al., 1984; Rogers et al., 1979b). It was considered that plants were mainly absorbing NO_2 . Based on suspicion of the veracity of these results, the NO_2 concentrations used to study the NO_2 exchange flux have gradually approached the true ambient values. Later research used lower NO_2 concentrations has found NO_2 emissions from the plant and put forth the idea of the NO_2 compensation point. The NO_2 compensation point is defined as the NO_2 concentration where the NO_2 exchange flux is 0. When the ambient concentration is higher than the compensation point, plants absorb NO_2 ; otherwise, plants release NO_2 . Many studies have reported NO_2 concentration points, and the range is basically between 0.1 and 3 ppb (Geßler et al., 2000; Hereid and Monson, 2001; Johansson, 1987; Rondón and Granat, 1994; Rondón et al., 1993; Sparks et al., 2001; Teklemariam and Sparks, 2006; Thoene et al., 1996; Thoene et al., 1991; Weber and Rennenberg, 1996). However, the compensation point is still being questioned (Lerdau, 2000). In recent years, the existence of compensation points has still been discussed. Chaparro-Suarez et al. (2011) investigated the compensation points of five common European tree species through laboratory experiments and determined that these five common European species could absorb NO_2 under any ambient NO_2 concentration. Breuninger et al. (2013) also considered that the NO_2 emitted from plants was negligible during field research.

Therefore, the compensation point of NO_2 between the atmosphere and the plant still needs to be studied.

NO_2 exchange fluxes with the atmosphere are usually investigated using conifers (Ammann et al., 1995; Geßler et al., 2002; Johansson, 1987; Slovik et al., 1996), broad-leaved forests (Horii et al., 2004) and oak species as the subjects. Broad-leaved trees are often used as an important part of researching the middle and low latitudinal urban environments. China is located in the North Temperate Zone, and thus there are many broad-leaved trees planted in the city, countryside and other zones. However, there are rare researches about NO_2 exchange fluxes between the atmosphere and broad-leaved trees in China. In this article, the exchange fluxes of NO_2 between the atmosphere and *P. nigra* under natural conditions (uncontrolled conditions) are investigated. The seasonal variation characteristics and the influence factors of NO_2 exchange fluxes between *P. nigra* and the atmosphere are discussed systematically.

1. Material and methods

1.1. Site and materials

The experimental site was selected in the Research Center of Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing (40°0′27.91″N, 116°20′11.15″E). The experimental site is located between the fourth and fifth ring roads. The surrounding area consists of highways, office buildings, urban greening belts and parks, so it is a typical urban area.

P. nigra seedling was selected as the experimental object, which is a common greening species in Beijing. The one-year-old *P. nigra* seedling was cultivated by cuttage in a flowerpot with volumes of 16 L in March 2017 and watered with 1 L of tap water per day. The exchange fluxes of NO_2 between *P. nigra* and atmosphere were investigated by using a double dynamic chambers method from Jun. 15 to Sept. 3, 2017.

1.2. Measurement method of NO_2 exchange fluxes between *P. nigra* and the atmosphere

The exchange fluxes of gases have been always determined by the chamber method, including the static and dynamic chamber methods. Generally, the exchange fluxes of some greenhouse gases, such as carbon dioxide (CO_2) and methane (CH_4), have historically been measured by the static chamber method (Fang and Mu, 2006; Geng and Mu, 2006; Jones et al., 2011; Li and Wang, 2007), while more active gases, such as NO_2 and O_3 , were investigated by the dynamic chamber method due to the activity of the gases and the adsorption of the chamber wall (Breuninger et al., 2013; Chaparro-Suarez et al., 2011). Hence, in this study, the exchange fluxes of NO_2 between the atmosphere and *P. nigra* seedling were measured by the dynamic chamber method.

The structure of our chambers is as follows. Two air inlets are arranged at symmetrical positions on the bottom of the

chamber, and the inlet air flow was approximately 40 L/min in total throughout the chamber so that the chamber can exchange air completely within 197 sec. The chamber is coated by PTFE film and composed of a stainless steel bracket (inner diameter 52 cm, height 62 cm, volume approximately 131.6 L). Six holes with a diameter of 1.5 cm each are distributed evenly on the top of the chamber to be used for air leaving. Micro fans inside the chamber are used to provide a continuous turbulent mixing of the gas to minimize turbulent and boundary layer resistance. The sampling port is placed in the middle of the chamber body. It is 15 cm from the top of the chamber, and it's about 26 cm from the chamber wall.

To eliminate the influence of the chamber on measurements, one chamber acted as a sample chamber with *P. nigra* seedling, and an identical but empty chamber served as the reference chamber. The chambers were placed at a height of 1.3 m (above the ground) and replenished with ambient air simultaneously. To reduce the error between different instruments, the measurements of the blank chambers and sample chambers alternated every 15 min. Temperature, humidity, light intensity and photosynthetic activity radiation (PAR) data were recorded in the blank chamber.

Before measuring the NO₂ exchange flux, we compared two chambers without plants. The average ratio of temperature, relative humidity and photosynthetic effective radiation between the two chambers was 1.01, 1.02 and 0.91 (*n* = 722), so the two chambers were determined to be parallel. Hence, the dual dynamic chambers eliminated the influences of the wall, reactive gas reactions and the external environment.

In the process of determination, the potted *P. nigra* seedling (part of a trunk with leaves) were put into the chambers from the bottom. A PTFE film was tightly connected to the trunk, and the soil remained outside the chamber. The exchange fluxes between the atmosphere and the leaves of *P. nigra* were measured. At the end of each experiment, we took the potted *P. nigra* seedling out carefully and measured the leaf area, and then put it into the chamber again.

Calculation of NO, NO₂ and NO_x exchange fluxes is done as follows (Chaparro-Suarez et al., 2011):

$$F_{ex,NO_2} = -\frac{Q}{A_{leaf}}(m_{a,NO_2} - m_{s,NO_2}) \quad (1)$$

$$F_{ex,NO} = -\frac{Q}{A_{leaf}}(m_{a,NO} - m_{s,NO}) \quad (2)$$

$$F_{ex,NO_x} = -\frac{Q}{A_{leaf}}(m_{a,NO_x} - m_{s,NO_x}) \quad (3)$$

where F_{ex,NO_2} (nmol/(m²·sec)) is the exchange flux of trace gas NO₂, $F_{ex,NO}$ (nmol/(m²·sec)) is the exchange flux of trace gas NO, F_{ex,NO_x} (nmol/(m²·sec)) is the exchange flux of trace gas NO_x, Q (m³/sec) is the purging rate, A_{leaf} (m²) is the leaf area, m_{a,NO_2} (μg/m³) is the volume concentration of NO₂ in ambient air, m_{s,NO_2} (μg/m³) is the volume concentration of NO₂ within the plant chamber, $m_{a,NO}$ (μg/m³) is the volume concentration of NO in ambient air, $m_{s,NO}$ (μg/m³) is the volume concentration of nitrogen oxide within the plant chamber, m_{a,NO_x} (μg/m³) is the volume concentration of NO_x in ambient air, and m_{s,NO_x} (μg/m³) is the volume concentration of NO_x within the plant chamber.

Calculation of the deposition velocities of NO₂ is done as follows (Chaparro-Suarez et al., 2011)

$$V_{NO_2} = \frac{F_{ex,NO_2}}{m_{s,NO_2}} \quad (4)$$

where V_{NO_2} (m/sec) is deposition velocity of NO₂.

The concentrations of NO, NO₂, and NO_x were measured by a nitrogen oxide analyzer (Model 42i-D1MSNAA, Thermo Fisher Scientific, USA), while the concentration of O₃ was determined using an ozone analyzer (Model 49i-D1NAA, Thermo Fisher Scientific, USA). Temperature, photosynthetically active radiation, and humidity were recorded by an Air Temperature Humidity Photosynthetically active radiation Light intensity Recorder (YM-28, Yi Meng Electronic recorder, Co., Ltd., China).

Data assurance methods included correction for the inlet air flow and measurement of leaf areas. The inlet flow was corrected for by the foam flowmeter (SENSIDYNE, USA). The leaf area was measured using the LAM living leaf area (Shiya Technology Co., Ltd.) instrument.

2. Results and discussion

2.1. Characteristics of NO₂ exchange fluxes between *P. nigra* seedlings and the atmosphere

The changes in environmental parameters and ambient concentrations of NO, NO₂, and O₃ during the experiment are shown in Fig. 1. During the experiment, the range of temperatures was between 19.1 and 57.2°C (mean value of 34.1°C), while the relative humidity ranged from 13.4% to 100% (mean value of 49.7%), and the light intensity ranged from 0 to 1712.2 μmol/(m²·sec) (mean value of 310.5 μmol/(m²·sec)). The environmental concentration of O₃ was continuously measured during the day and night with a range of 0–143.1 ppb (mean value of 29.0 ppb). The concentrations of NO and NO₂ were used to investigate the ambient concentrations during the experiment. The environmental concentration of NO was from 0 to 40.0 ppb (mean value of 2.2 ppb), and the NO₂ environmental concentration varied from 3.9 to 63.8 ppb (mean value of 16.4 ppb).

The NO_x (NO, NO₂, NO_x) exchange fluxes are shown in Fig. 2. The NO exchange flux was between –2.8 and 0.3 nmol/(m²·sec) (mean value of –0.1 nmol/(m²·sec)). The exchange flux of NO was not obvious during the experimental period. The exchange fluxes of NO have always been small because the concentrations of NO are always near the detection limit, but the uptake of NO can still be observed (Breuninger et al., 2013; Hereid and Monson, 2001).

The NO₂ exchange flux was between –14.6 and 0.8 nmol/(m²·sec) (mean value of –2.3 nmol/(m²·sec)) during the whole experimental period. Some studies of NO₂ exchange flux via the chamber method are listed in Table 1. Thoene et al. (1996) reported that the NO₂ exchange flux of pine trees was –1.88 to –0.03 nmol/(m²·sec) while Sparks et al. (2001) reported that the NO₂ exchange flux of tropical tree species was –1.55 to –0.15 nmol/(m²·sec). Berugine (2011) determined the NO₂ exchange flux of Norway pine trees to be between –0.08 and –0.01 nmol/(m²·sec). The variation trend of NO_x is consistent

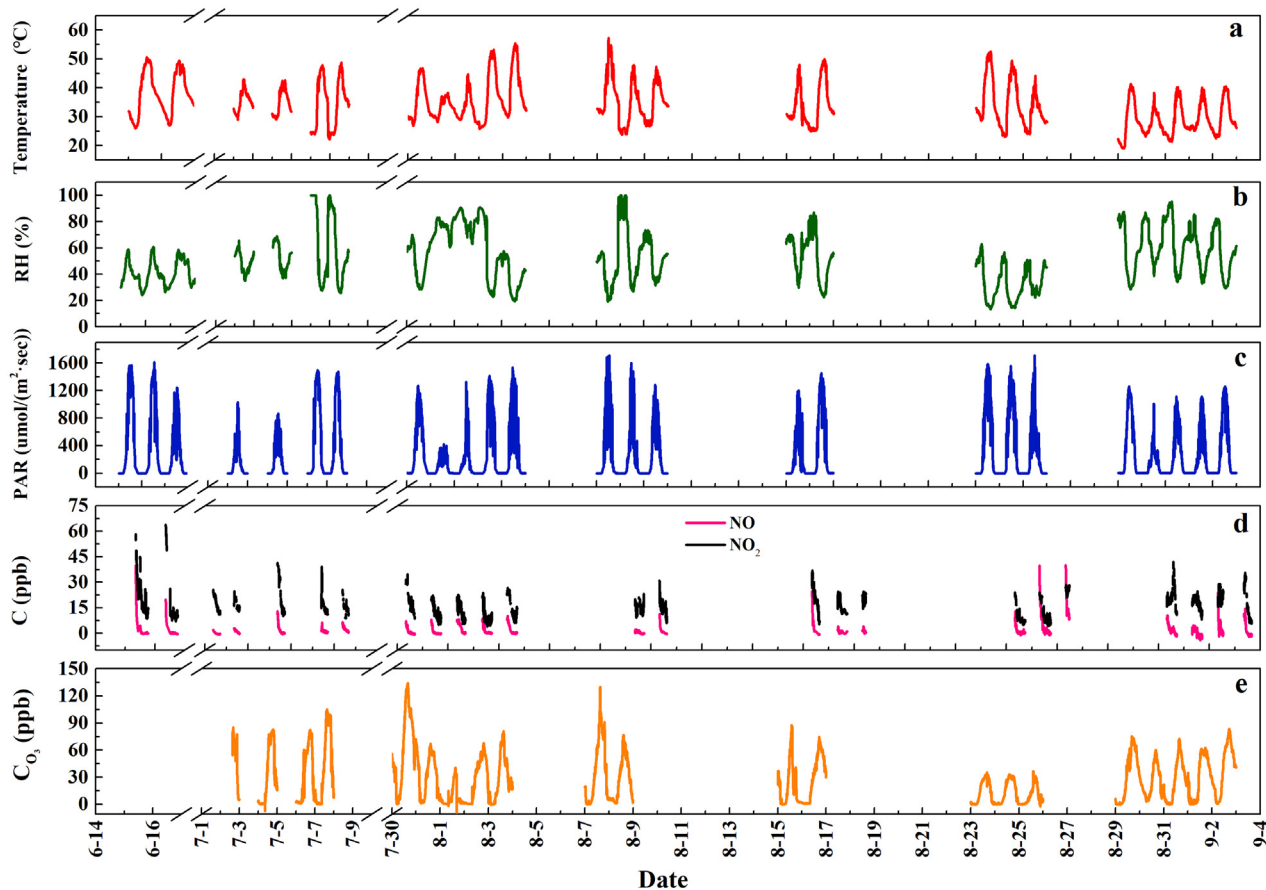


Fig. 1 – Environmental conditions and gas exchange fluxes during the whole measurement period. (a) the temperature ($^{\circ}\text{C}$) of the blank chamber (red); (b) the relative humidity (%) of the blank chamber (green); (c) the photosynthetic effective radiation ($\mu\text{mol}/(\text{m}^2\cdot\text{sec})$) of the blank chamber (blue); (d) NO environmental concentration (ppb) (pink) and NO_2 environmental concentration (ppb) (black). (e) O_3 environmental concentration (ppb) (orange).

with that of NO_2 . The NO_x exchange flux is between -17.4 and $1.0 \text{ nmol}/(\text{m}^2\cdot\text{sec})$ (mean value of $-2.4 \text{ nmol}/(\text{m}^2\cdot\text{sec})$).

In 2017, the rainy season in Beijing was mainly concentrated from the middle of August to the middle of September. In August, there were 18 days of rain, with 15 of those days occurring after August 8. It is obvious that the temperature

began to decrease significantly after Aug. 9 (Fig. 1a). Therefore, Jun. 15–Aug. 4 is considered the fast-growing stage of *P. nigra*, and Aug. 9–Sept. 2 is considered the later growth stage of *P. nigra*. After mid-August, the growth of the subsurface and upper parts of *P. nigra* was obviously slowed (Liu, 2016; Qin and Jiang, 2004). This finding indicated that the transition

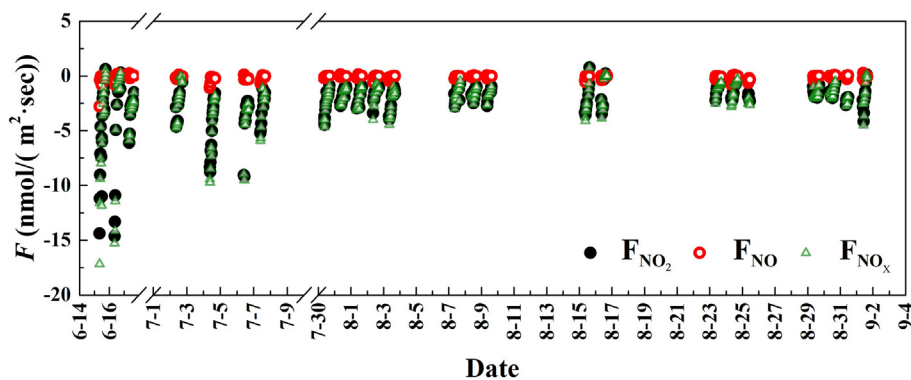


Fig. 2 – Exchange fluxes of NO, NO_2 and NO_x during the experimental period. $F_{\text{ex,NO}}$ is the exchange flux of NO ($\text{nmol}/(\text{m}^2\cdot\text{sec})$) (hollow red circle); $F_{\text{ex,NO}_2}$ is the NO_2 exchange flux ($\text{nmol}/(\text{m}^2\cdot\text{sec})$) (solid black rectangle); $F_{\text{ex,NO}_x}$ is representative of NO_x fluxes ($\text{nmol}/(\text{m}^2\cdot\text{sec})$) (hollow green triangle).

Table 1 – Researches of NO₂ exchange fluxes between the atmosphere and trees.

	Species	Flux (N mol/ (m ² -sec))	Concentration point (ppb)	Method
Johansson (1987)	Pine forests		0.1~5	Fumigation chambers
Rowland-bamford and Drew (1988)	<i>Hordeum vulgare</i> cv. Patty	-13.5 ± 1.8		
Thoene et al. (1991)	<i>Picea abies</i> L. Karst.		1.6~2.6	
Hereid and Monson (2001)	<i>Zea mays</i> L.	-0.643	0.1~0.3	
Sparks et al. (2001)			0.53~1.60	Leaf chamber measurements
Geßler et al. (2002)	<i>Picea abies</i>	0.05~0.02	1.7	Dynamic chamber
Ganguly et al. (2009)	<i>Avicennia officinalis</i> , <i>Avicennia alba</i> , <i>Avicennia marina</i> , and <i>Aegiceros</i> sp.,	0.06~0.12	4.68 ± 1.34	
Geßler et al. (2000)	<i>Fagus sylvatica</i>		1.8~1.9	Dynamic chamber
Breuninger et al. (2013)	<i>Picea abies</i> L.	-0.341~0.045	0.05~0.65	Dynamic chamber
Our study	<i>P. nigra</i>	-14.64~0.77		Dynamic chamber

period of the rapid growth period and the later growth stage occurred in mid-August. The exchange fluxes of NO₂ between *P. nigra* and the atmosphere changed violently during the fast-growing stage while remaining stable during the later growth stage.

The exchange fluxes obtained in this experiment are larger than those reported in the past. Differences in tree species could be considered the main factors causing these differences. It demonstrates the ability of NO₂ absorption by *P. nigra*. The other impacting factors will be discussed in the following chapters.

During the experiment, the emission of NO₂ was observed under the real NO₂ concentration. Surprisingly, there are two days that it was emitted continuously. However, since the causes of emission were not able to be found, this issue still needs further studies in the future.

To depict the changes in daily NO₂ exchange fluxes, the NO₂ exchange flux from 7:12 a.m. to 21:36 p.m. of one day is shown in Fig. 3. The exchange flux of NO₂ gradually decreased over time. The most important reason for this is that the NO₂ concentrations are the highest in the morning and decrease over the course of the day. After sunset, because the plant stomata gradually close in the dark, the NO₂ exchange fluxes undergo minor fluctuations.

2.2. Effect of ambient parameters on NO₂ flux

2.2.1. Effect of ambient NO₂ concentration on NO₂ exchange flux between *P. nigra* and the atmosphere

The flux of NO₂ between plants and the atmosphere is positively correlated with environmental NO₂ concentrations (Johansson, 1987; Rondón et al., 1993; Rondón and Granat, 1994;

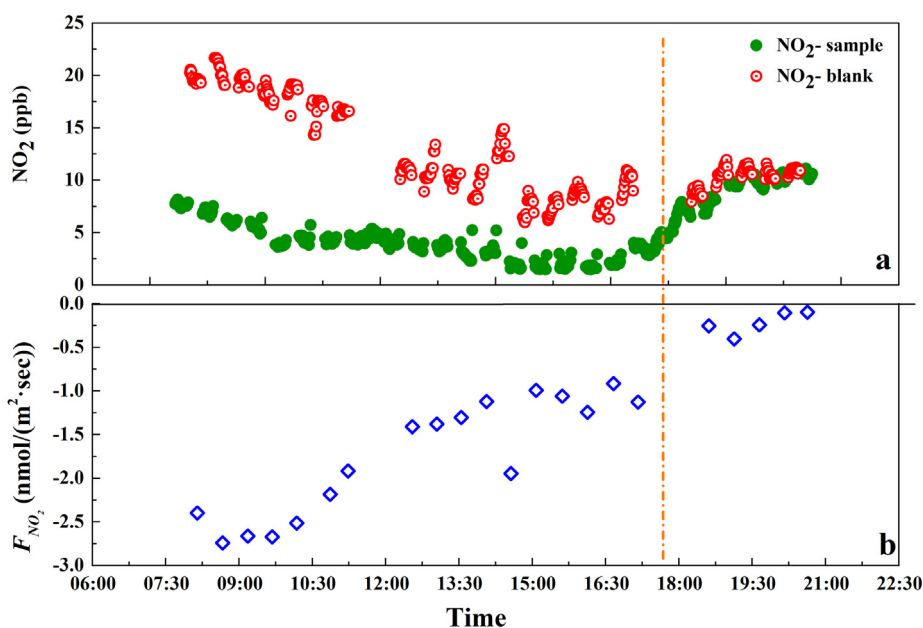


Fig. 3 – The diurnal variations of NO₂ exchange fluxes between the atmosphere and *P. nigra*. NO₂ concentration in the blank chamber and the sample chamber (a), NO₂ exchange fluxes between the atmosphere and *P. nigra* (b). The broken line denotes the sunset time.

Weber and Rennenberg, 1996; Thoene et al., 1991; Gefßler et al., 2000; Sparks et al., 2001; Teklemariam and Sparks, 2006).

The relationship between the ambient NO_2 concentration on one day and the exchange flux of NO_2 is shown in Fig. 4a. From the diagram, it can be seen that the exchange flux of NO_2 has a strong linear relationship with the environmental NO_2 concentration when the plant stomata are open ($R^2 = 0.97$) during the daytime. However, at night, almost no gas exchange happened after stomatal closure, and NO_2 exchange flux had no correlation with environmental NO_2 concentration ($R^2 = 0.021$).

The relationship between the exchange flux of NO_2 during different growth stages and the environmental NO_2 concentration is shown in Fig. 4b. It can be seen that there is a strong linear correlation in the NO_2 exchange fluxes between *P. nigra* and the atmosphere at different growth stages ($R^2 = 0.88$ in the fast-growing stage while 0.62 in later growth stage). The concentration of ambient NO_2 is the most important factor that impacts the NO_2 exchange flux.

Comparing two growth periods of *P. nigra*, the emission fluxes of NO_2 during the fast-growing stage are greater than those during later growth stage when the ambient NO_2 concentration is between 0 and 64 ppb. During the fast-growing stage, the ambient concentration of NO_2 was between 5.5 and 60.4 ppb, while the mean NO_2 exchange flux was $-3.0 \text{ nmol}/(\text{m}^2\cdot\text{sec})$, and during later growth the environment, NO_2 was between 5.1 and 38.3 ppb, while the mean NO_2 exchange flux was $-1.5 \text{ nmol}/(\text{m}^2\cdot\text{sec})$. Some figures are listed in Table 2. Under the corresponding ambient NO_2 concentrations, the NO_2 exchange fluxes during the fast-growing stage were higher than those during the later growth stage.

2.2.2. Effects of light intensity on NO_2 exchange flux between *P. nigra* and the atmosphere

The effects of different light intensities on NO_2 exchange flux between *P. nigra* and the atmosphere were determined by comparing NO_2 fluxes and the ambient NO_2 concentrations under different PARs (Table 3) and similar temperature and

Table 2 – Range and mean of NO_2 exchange flux between the atmosphere and *P. nigra* in different growth periods.

	$F_{(\text{NO}_2)}$ in fast-growing stage	$F_{(\text{NO}_2)}$ in later growth stage
Range (nmol/ $(\text{m}^2\cdot\text{sec})$)	-14.6~0.6	-4.2-0.2
Mean (nmol/ $(\text{m}^2\cdot\text{sec})$)	-3.0	-1.5

relative humidity, as listed in Table 3. The ranges of light intensity were divided into two groups. One group ranged from 358.4 to 646.5 and 659.8 to 976.8 $\mu\text{mol}/(\text{m}^2\cdot\text{sec})$, and the other ranged from 800.4 to 1225.7 and 1259.3 to 1397.4 $\mu\text{mol}/(\text{m}^2\cdot\text{sec})$ in the fast-growing stage. In the later growth period, the ranges of light intensity were 217.0 to 362.4 /502.9 to 793.1 $\mu\text{mol}/(\text{m}^2\cdot\text{sec})$ and 742.9 to 877.2 /1035.7 to 1324.1 $\mu\text{mol}/(\text{m}^2\cdot\text{sec})$.

The effects of light intensity are shown in Fig. 5. During the fast-growing stage and the later growth stage, the effects of light intensity on the exchange flux of NO_2 between the *P. nigra* and the atmosphere were consistent. Under high light intensity, the NO_2 absorptive capacity of *P. nigra* is stronger. In a certain range, stomatal conductance increased with the increase of light intensity. Therefore, under high light conditions, NO_2 absorption of *P. nigra* is higher than it is under low light conditions. The increase in stomatal conductance is considered to be the leading factor. Teklemariam and Sparks (2006) and Chaparro-Suarez et al. (2011) report similar conclusions that the NO_2 exchange flux under high light intensity was higher than that under low light intensity.

2.2.3. Effect of temperature on NO_2 exchange flux between *P. nigra* and the atmosphere

To determine the effect of temperature on NO_2 exchange fluxes between *P. nigra* and the atmosphere, similar PARs and relative humidities were chosen under different

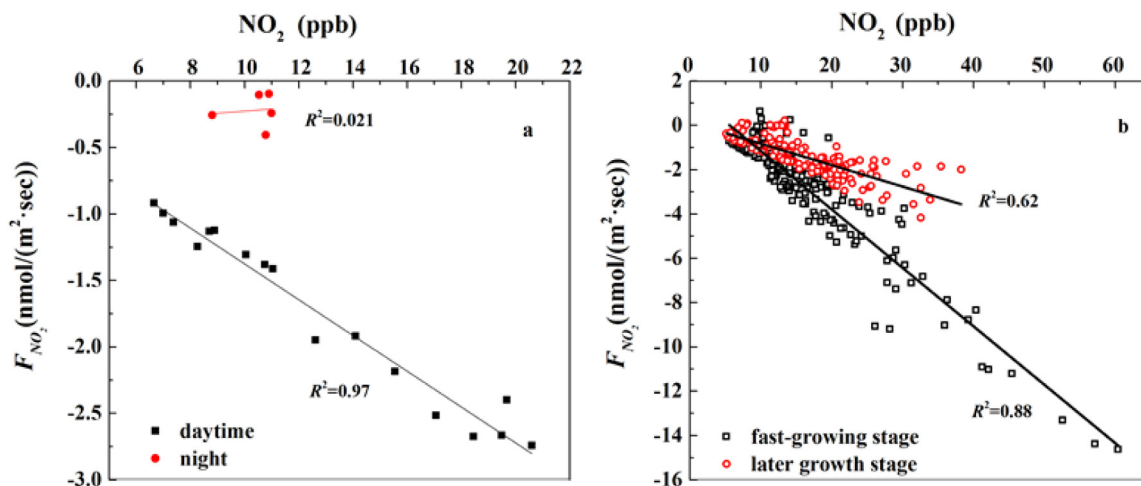


Fig. 4 – The correlation between NO_2 flux and ambient NO_2 concentration during one day (a) and during different growth periods (b).

Table 3 – Ambient parameters under different light intensities in different growth periods of *P. nigra*.

Growth period		PAR ($\mu\text{mol}/(\text{m}^2\cdot\text{sec})$)	Temperature ($^{\circ}\text{C}$)	RH (%)
Fast-growing stage	First group	512.8 (358.4~646.5)	42.0 (40.4~44.4)	37.6 (28.5~53.1)
		921.9 (659.8~976.8)	42.7 (40.2~44.9)	42.4 (29.6~52.8)
	Second group	1111.8 (800.4~1225.7)	47.1 (45.2~49.9)	30.7 (24.4~37.7)
		1323.4 (1259.3~1397.4)	47.6 (45.2~49.8)	32.8 (26.6~45.3)
Later growth stage	First group	276.0 (217.0~362.4)	32.0 (30.8~34.3)	51.8 (47.4~56.2)
		646.1 (502.9~793.1)	32.9 (30.7~34.8)	43.5 (27.3~50.6)
	Second group	804.6 (742.9~877.2)	41.8 (40.1~43.0)	36.9 (31.9~42.6)
		1166.1 (1035.7~1324.1)	43.7 (42.2~45.0)	26.5 (18.3~33.7)

temperature levels. The temperature ranges were divided into two groups. One was 34.2–39.8°C and 40.4–44.4°C, while the other was 40.9–47.0°C and 48.0–54.4°C in the fast-growing stage. In addition, in the later growth period, temperature ranges were 30.7–36.8°C/40.1–45.7°C and 41.4–45.0°C/45.2–49.3°C. The ambient parameters have been shown in Table 4.

The effects of different temperatures on the exchange flux of NO₂ between *P. nigra* and the atmosphere are shown in Fig. 6. During the fast-growing stage, under similar PARs and

relative humidities, the NO₂ exchange flux at an average temperature of 38.1°C (34.2–39.8°C) was less than that under an average temperature of 41.9°C (40.4–44.4°C), and the NO₂ exchange flux at an average temperature of 50.65°C (48.0–54.4°C) was less than that under an average temperature of 44.70°C (40.9–47.0°C).

In a certain range, with an increase in temperature, the stomatal conductance first increases but then decreases under excessively high temperatures because excessive transpiration rates could lead to the loss of guard cells and

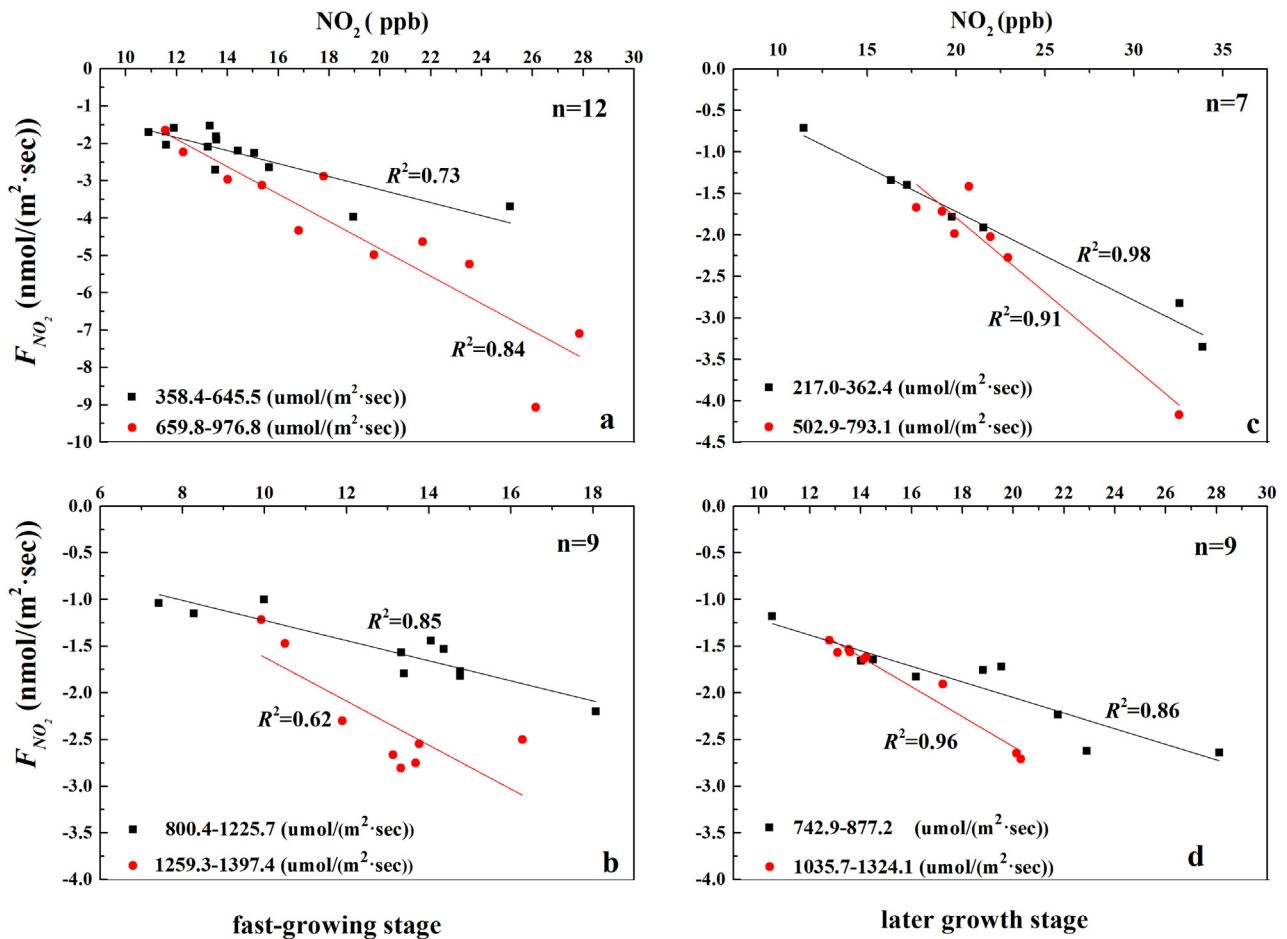


Fig. 5 – The effect of light on NO₂ fluxes in the fast-growing (a, b) and later growth periods (c, d). The solid squares (black) represent the exchange fluxes of NO₂ under low light intensities and the solid dots (red) represent the exchange fluxes of NO₂ under high light intensities.

Table 4 – Ambient parameters under different temperatures in different growth periods of *P. nigra*.

Growth period		Temperature (°C)	RH%	PAR ($\mu\text{mol}/(\text{m}^2\cdot\text{sec})$)
Fast-growing stage	First group	38.1 (34.2–39.8)	45.6 (39.0–53.8)	556.2 (408.8–693.5)
		41.9 (40.4–44.4)	41.81 (36.0–53.1)	528.5 (403.2–667.6)
	Second group	44.7 (40.9–47.0)	35.9 (26.6–47.4)	1348.9 (1220.1–1491.7)
		50.7 (48.0–54.4)	30.8 (22.0–39.3)	1325.6 (1226.0–1490.6)
Later growth stage	First group	34.4 (30.7–36.8)	38.9 (27.8–45.8)	579.5 (433.4–793.1)
		43.0 (40.1–45.7)	35.0 (28.1–42.6)	660.9 (436.3–783.6)
	second group	43.1 (41.4–45.0)	27.9 (18.4–36.0)	964.6 (809.7–1079.7)
		46.5 (45.2–49.3)	25.3 (15.0–29.4)	1023.2 (828.4–1152.0)

closure of the stomata (Gao et al., 2016). The increase in stomatal conductance with increased temperature (30–40°C) was found in *P. deltoides* × *nigra* by Josef Urban (Urban et al., 2017). Weston and Bauerle (2007) reported that stomatal conductance (of *Acer rubrum*) changed very little across a temperature range of 35–48°C. So we inferred that this range of temperature didn't change the common physiological metabolism apparently. But some of the temperature was much higher than ambient temperature, we supposed it would change the common physiological metabolism and affected the NO₂ exchange flux. Therefore, in this experiment, high temperatures could be the reason that the

absorption of NO₂ was weaker under an average temperature of 50.7°C.

During the later growth stage, the effect of temperature was not obvious, as shown in Fig. 6c and Fig. 6d. It can be inferred that over a temperature range of 30–50°C, the temperature has little effect on the NO₂ exchange flux during the later growth period.

2.2.4. The effects of relative humidity on the NO₂ exchange flux between the atmosphere and *P. nigra*

For comparing the effects of different humidities on the NO₂ exchange flux between the atmosphere and *P. nigra*, data with

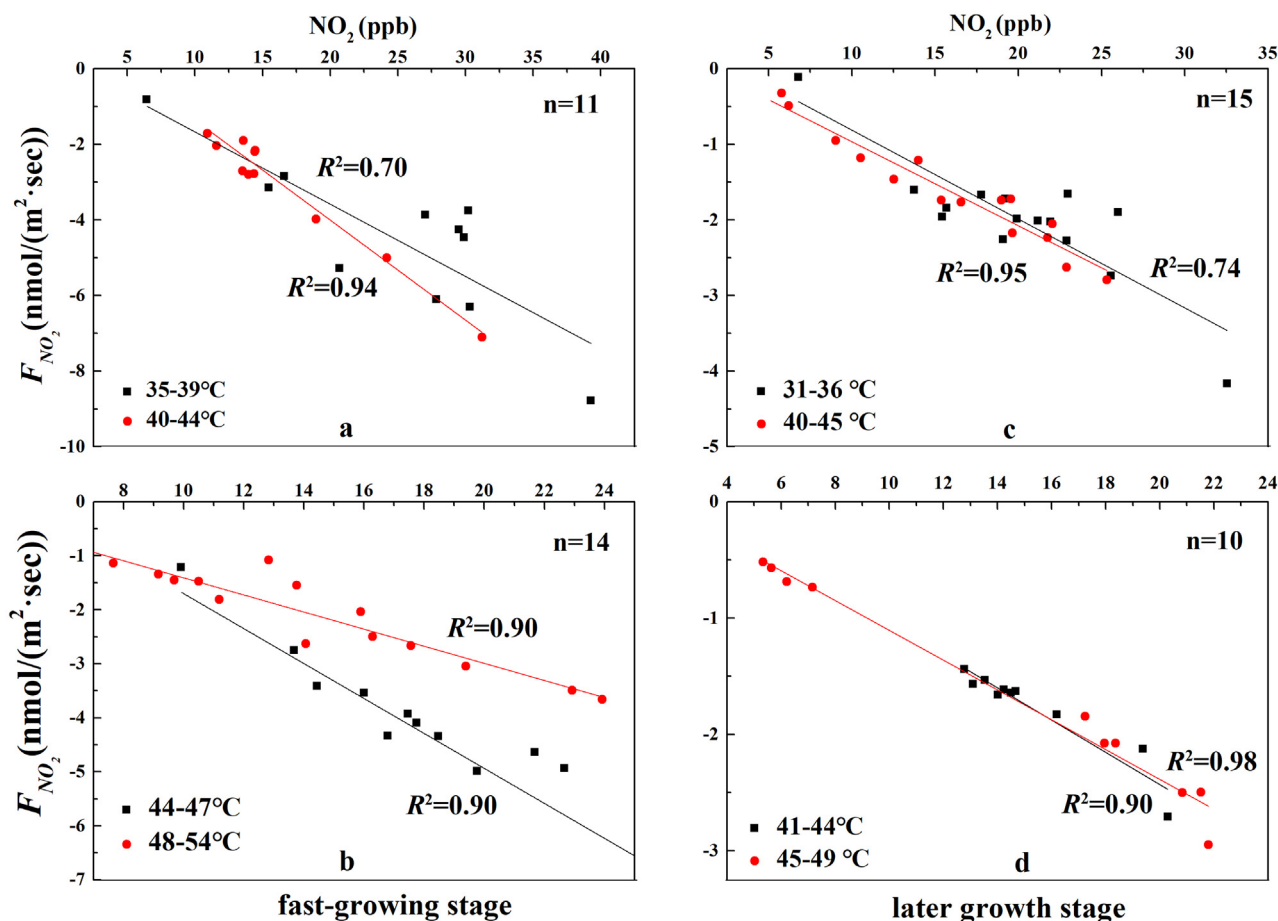


Fig. 6 – The effect of temperature on NO₂ exchange flux in the fast-growing stage (a, b) and in the later growth stage (c, d). The solid squares represent the exchange fluxes of NO₂ under low temperatures and the solid dots represent the exchange fluxes of NO₂ under high temperatures.

Table 5 – Relevant environment parameters under different relative humidity conditions in different growth periods of *P. nigra*.

	RH (%)		PAR ($\mu\text{mol}/(\text{m}^2\cdot\text{sec})$)		Temperature ($^{\circ}\text{C}$)	
	Range	Mean	Range	Mean	Range	Mean
Low RH	30.6–44.5	38.9	109.7–237.6	171.1	36.3–42.9	38.9
High RH	74.6–86.7	79.2	116.8–249.8	176.3	31.5–37.6	35.2

similar PARs and temperatures were chosen under different humidities in the fast-growing stage. As Table 5 shown, the PARs of samples with low humidity and high humidity are almost unanimous, and the error of temperature is 9.5%. Because there are minor differences in relative humidity in the later stage, the effect of relative humidity on the NO₂ exchange flux during the later growth stage was not considered.

The effects of different relative humidities on the NO₂ exchange flux between *P. nigra* and the atmosphere are shown in Fig. 7. At the same environmental NO₂ concentrations, when the relative humidity is high, the absorption of NO₂ is more obvious in plants. The main factor concerning this result is the effect of relative humidity on stomatal conductance. The influence of relative humidity on stomatal conductance is that stomatal conductance increases with increasing humidity. However, after a certain range, stomatal conductance will oscillate and then decrease.

2.2.5. Effects of pollution weather on NO₂ exchange flux between *P. nigra* and the atmosphere

Beijing is a typical urban area with frequent pollution, with heavy haze. However, during summer it is not easy to occur. To explore the influence of bad weather on NO₂ exchange fluxes between *P. nigra* and the atmosphere, the NO₂ exchange fluxes in polluted conditions and in non-polluted conditions have been compared. Two days with different polluted conditions had similar values of light intensity, temperature and relative humidity. According to the air quality index (AQI), the weather condition can be divided into polluted condition (AQI > 100) and non-polluted condition (AQI < 100). The relevant environmental parameters are shown in Table 6.

The NO₂ exchange fluxes between the atmosphere and *P. nigra* were compared in two days during the later growth period (Table 6). The average temperatures have little effect on the fluxes when the average values of light intensity and relative humidity were close. Additionally, under polluted conditions, the average exchange fluxes of NO₂ were greater than the average NO₂ exchange fluxes in non-polluted weather, but it can be seen from Fig. 8 that under similar environmental NO₂ concentrations, the absorbability of *P. nigra* to NO₂ under polluted weather was weaker than that under non-polluted weather conditions. The O₃ concentration may also be an essential factor. It was found that stomatal conductance decreased with ozone concentration increases under open exposure to different O₃ concentrations (Hoshika et al., 2009), while Matyssek et al. (2010) indicated that despite the possible reaction mechanisms having some differences, both adult and young trees of different species showed similar sensitivities to O₃. The concentration of ozone under pollution conditions was higher than that under non-polluted weather conditions. Therefore, we believe that the increase in O₃ in pollution also

leads to decreasing stomatal conductance of poplars, which affects the exchange flux of NO₂ between the atmosphere and *P. nigra*. Additionally, fine particulate matter will plug plant stomata and also decrease stomatal conductance.

2.3. Compensation point of NO₂

During the whole experimental period, the compensation point of NO₂ in the fast-growing stage is 5.6 ppb, while the compensation point of NO₂ at the later stage of growth was 1.4 ppb.

Many studies have reported NO₂ concentration compensation points of conifers (Table 1). Thoene et al. (1996) determined that the NO₂ concentration compensation point of the spruce is 1.64 ppb while Gefßler et al. (2002) determined it to be 1.7 ppb. To study the compensation points of broad-leaved trees, Horii et al. (2004) considered the compensation point to be 1.5 ppb, with subjects including maples, oaks and a few cedar trees. For the range of compensation points, Sparks (2009) summarized it as 0.5–3 ppb. Chaparro-Suarez et al. (2011) corrected it to a range of 0.1–3.2 ppb, and the specific value depends on different tree species.

The compensation points of *P. nigra* measured in the later growth stage are close to the reported values but are higher during the fast-growing stage than the values reported in the past. The main reason may be ascribed to the different tree species. Therefore, the influence of growth period on

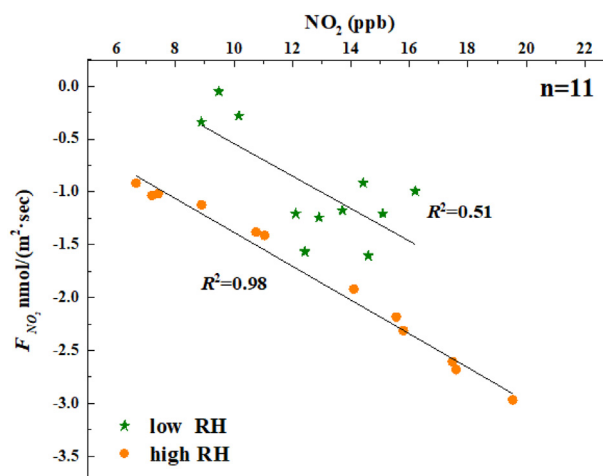


Fig. 7 – Correlation of the NO₂ exchange flux and the ambient NO₂ concentration under different relative humidity. The solid dots means the NO₂ flux investigated under the relative humidity of 70%–90% (orange) while the solid stars stand for the NO₂ flux investigated under the relative humidity of 30%–50% (green).

Table 6 – Relative ambient parameters under polluted weather conditions and non-polluted weather conditions.

	Non-polluted weather	Polluted weather
AQI	52	110
PM _{2.5}	57	125
F _{NO₂} (nmol/(m ² ·sec))	Range: -0.7 ~ -3.4 Mean: -1.5	Range: -0.9 ~ -4.5 Mean: -2.4
O ₃ (ppb)	Range: 0.1 ~ 40.6 Mean: 16	Range: 5.5 ~ 134.4 Mean: 82.4
PAR (μmol/(m ² ·sec))	Range: 317 ~ 1369 Mean: 941.0	Range: 472 ~ 1175 Mean: 806.7
Temperature (°C)	Range: 31.9 ~ 55.1 Mean: 50.	Range: 34.2 ~ 46.6 Mean: 43.15
RH (%)	Range: 20.0 ~ 31.9 Mean: 25.1	Range: 28.7 ~ 50.2 Mean: 34.1

compensation point should be considered when discussing compensation points.

2.4. Deposition velocities of NO₂

The deposition velocities of NO₂ were between 0.3 and 2.4 mm/sec during the whole growth period. The range of deposition velocities were from 0.03 to 2.4 mm/sec (average value of 0.5 mm/sec) during the fast-growing stage while they ranged from 0.01 to 0.6 mm/sec (average value of 0.3 mm/sec) during the later growth period.

Regarding the range of NO₂ deposition velocities of conifers, Thoene et al. (Thoene et al., 1991; Thoene et al., 1996) determined it to be 0.4 to 0.9 mm/sec, Rondón et al. (1993) reported it as 1.8 to 2.1 mm/sec and Breuninger et al. (2013) described it as 0.07 to 0.42 mm/sec. Referring to broad-leaved trees, Puxbaum and Gregori (1998) measured the monthly average range deposition velocities of oak trees (January–October) to be 0.2–6.4 mm/sec. Horii et al. (2004)

reported that the deposition velocity of broad-leaved forest was approximately 2 mm/sec.

The deposition velocities of *P. nigra* are similar to that of previous reports, but the reasons accounting for these differences may mainly be tree species.

3. Conclusions

The NO₂ exchange flux between the atmosphere and *P. nigra* was between -14.6 and 0.8 nmol/(m²·sec), which decreased over time during the whole growth period. The daily fluxes were larger in the morning and decreased gradually. There is a strong relationship between the NO₂ exchange fluxes of *P. nigra* and the ambient NO₂ concentration. The NO₂ emission fluxes during the fast-growing stage are higher than those of the later growth stage. In addition, under high PAR conditions, the NO₂ emission fluxes were larger than those under low PAR conditions. However, the effect of temperature on NO₂ exchange fluxes was inconsistent under different growth periods. Under polluted conditions, the uptake ability of *P. nigra* for NO₂ was obviously weakened. In addition, the compensation points were discrepant under different growth periods. Therefore, the growth period should be considered when the compensation is investigated.

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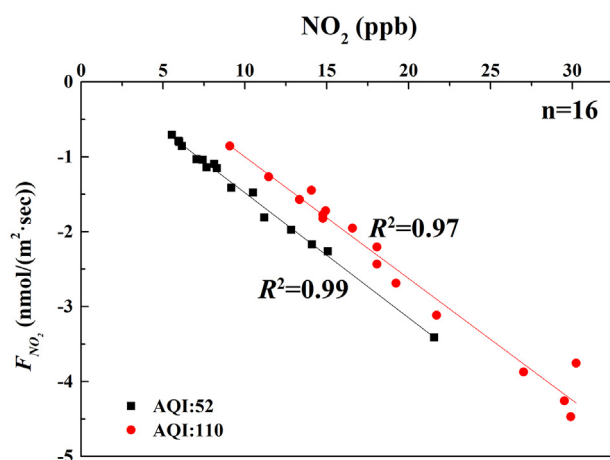


Fig. 8 – The relationship of between NO₂ exchange flux and environmental NO₂ concentration under different air quality indices over two days in close proximity. The solid squares (black) show low AQI indices while solid dots (red) indicate high AQI indices.

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