



Methodology for the quantification of the absorption potential of greenhouse - and pollutant gases by climbing plants used in façade greening; a case study on ivy (*Hedera helix*)

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ABSTRACT

How much do specific climbing plants contribute to the cleansing or absorption of harmful greenhouse and pollutant gases; often regarded as the main environmental threat in cities due to their adverse effects on human health? One of the main hurdles in the quantification of such ecosystem services is associated with the difficulty to obtain and design systems that provide detailed information on the interaction between various gases and the plant in question. To tackle these questions, two highly precise and accurate instruments, namely a mid-infrared laser absorption spectrometer (TDL) and a cavity-ring-down spectrometer (CRDS) were used to monitor the fate of gases when exposed to façade climbing plants like ivy. In a laboratory setting, a relaxation type of experiment was used consisting of a reaction chamber equipped with plant species and continuously flushed by synthetic air. This setup was used to determine the timescales of decay after short injections of the above-mentioned gases. After these injections, all gases followed simple exponential decay curves. N₂O, a non-reactive (inert) tropospheric gas, was used as a reference to which all other gases were compared and thereby quantified. This paper focuses on the detailed description of methods and processes to analyse the gas-absorptive behaviour of plants when exposed to gaseous pollutants. For demonstration purposes, quantified absorption features of nitrogen oxide (NO₂) are presented for ivy of the variety *Hedera helix* "Plattensee". Results of this method of quantification showed that - as compared to N₂O (control), - NO₂ had a reduced residence time (time scale) of 100 s, while N₂O resulted in a 600 s residence time (indicating no interference with the plant). This is equivalent to a 0.3 cm/s deposition velocity/ absorption rate of NO₂ under light conditions.

1. Introduction

Cities increasingly face some of the most challenging issues in contemporary times as a result of climate change. For example, cities have to deal with heat waves, frequent droughts, flooding, and urban heat islands, to name a few. The already stressed city environment faces an additional challenge from its air quality, which has additional detrimental impacts on the health of its inhabitants (Hernandez Carballo, et al., 2022; Juginović, et al., 2021; Mele, et al., 2021; WHO, 2019). The European Union attributes for 2019 40400 premature deaths per year in the 27 EU Member States to chronic nitrogen dioxide ("Health impacts of air pollution in Europe, 2021," 2021). Phytoremediation, the removal of toxic and harmful compounds by plants, can sustainably help to improve air quality. Along with an ever-increasing

incidence of soil sealing (Szumacher and Pabjanek, 2017), especially in inner cities, subsurface infrastructure, and the built environment have made the inclusion of trees in many urban sites difficult. Wall-bound climbers are increasingly being valued as a workable Nature-Based-Solution that can provide air phytoremediation.

There is ample evidence showing different absorption potentials of greenhouse- and pollutant gases in some woody plant species (Takahashi et al., 2005). However, information on the air phytoremediation potentials of commonly used climbers in façade greening is limited.

Given the heterogeneous distribution of air pollutants in the built environment (Zhang et al., 2017), a differentiated, scientific approach toward species-based air phytoremediation is required. This paper concentrates and presents the methodology used in the estimation of the

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greenhouse and pollutant gas absorption potential of a common climber species; namely *Hedera helix* “Plattensee”. In a follow-up paper we will compare two additional species (*Clematis montana*, *Lonicera henryi*).

2. Experiment

2.1. Experimental design

A graphical representation of the instrumental setup is shown below with the ivy subspecies “Plattensee” as an example. The plants were placed in a reaction chamber and subjected to a day-night cycle using an LED lamp. The illuminated phase (day) of the experiments ranged from 9 am to 6 pm, after which the lights were switched off for the dark phase (night). The operating temperature in the chamber has been monitored using a temperature sensor called “ibutton” (Hygrochron data logger) averaging $24^{\circ}\text{C} \pm 2^{\circ}\text{C}$.

The outflow of a gas mixing unit was directed into the fifty-three litre (53 L) rectangular glass chamber (later on called reaction chamber) in which the plant species were placed for the experiments. The reaction chamber was covered with a plexiglass lid and connected to the mass flow and injection controller box (regulating magnetic three-way-valves and mass flow controllers, see Fig. 1), delivering synthetic air spiked either with the contents of gas bottles or spiked with ambient air at an inflow rate of 5 L/min for the experiments discussed in this paper, respectively 10 L/min for subsequent experiments. Within the reaction chamber, there was a ventilator to ensure fast mixing of gases inside. To exclude any contamination from outside air during the experiment, the lid was sealed tightly. The outflow of the reaction chamber was fed towards the monitoring instruments (MIRO & PICARRO) through connecting tubes. These instruments took a total of 2 L/min from the outflow. The spill over of 3 L/min (at 5 L/min air flow) and the exhaust of the instruments was directed to a common exhaust line out of the laboratory.

2.2. Plant species

The plants used in the experiment were contributed by a plant breeder in the Cologne area (Containerbaumschule + Stauden Michael Kunz, Wusten 2, 42579 Heiligenhaus, Germany). All plants were transplanted into equal size pots with the same type of substrate to ensure uniformity.

Selected plants mentioned above were kept at their field capacity and covered with an expandable plastic film which was stretched to cover the substrate with the plant in the middle, and held around the plant to prevent direct loss of water from the substrate Fig. 2.

2.3. Light source

At the level of the lid of the reaction chamber, a constant illumination of approximately 25 klx (measured with a WinLab luxmeter) or PPFD (Photosynthetically Active Photon Flux Density) of $950 \mu\text{mol s}^{-1} \text{m}^{-2}$ (Photon System Instruments FluorPen FP110-LM/S) was provided by a photosynthetic LED lamp (Niello G 600) during the illuminated phase of the experiment. The transparency of the Plexiglas lid was determined to be about 92 % for the light source. The properties and spectrum of the light source are provided in Fig. 3 below.

2.4. Instrumentation

The main instrumentation consisted of a mid-infrared direct laser absorption spectrometer (MIRO Analytical AG, Wallisellen CH-8304, Switzerland; type MGA10 - GP+) and a cavity-ring-down spectrometer (Picarro Inc. Santa Clara, CA 95054, USA; type G2307). The MIRO instrument is a tunable-diode-laser system with five QCL-lasers observing absorption lines of 10 species. This gas analyser can simultaneously measure 10 greenhouse and pollutant gases, namely: carbon dioxide (CO_2), carbon monoxide (CO), nitrogen monoxide (NO), nitrogen dioxide (NO_2), nitrous oxide (N_2O), nitric acid (HONO), ozone (O_3), carbonyl sulfide (OCS), ammonia (NH_3), and water vapour ($\text{H}_2\text{O}_{(\text{g})}$). In

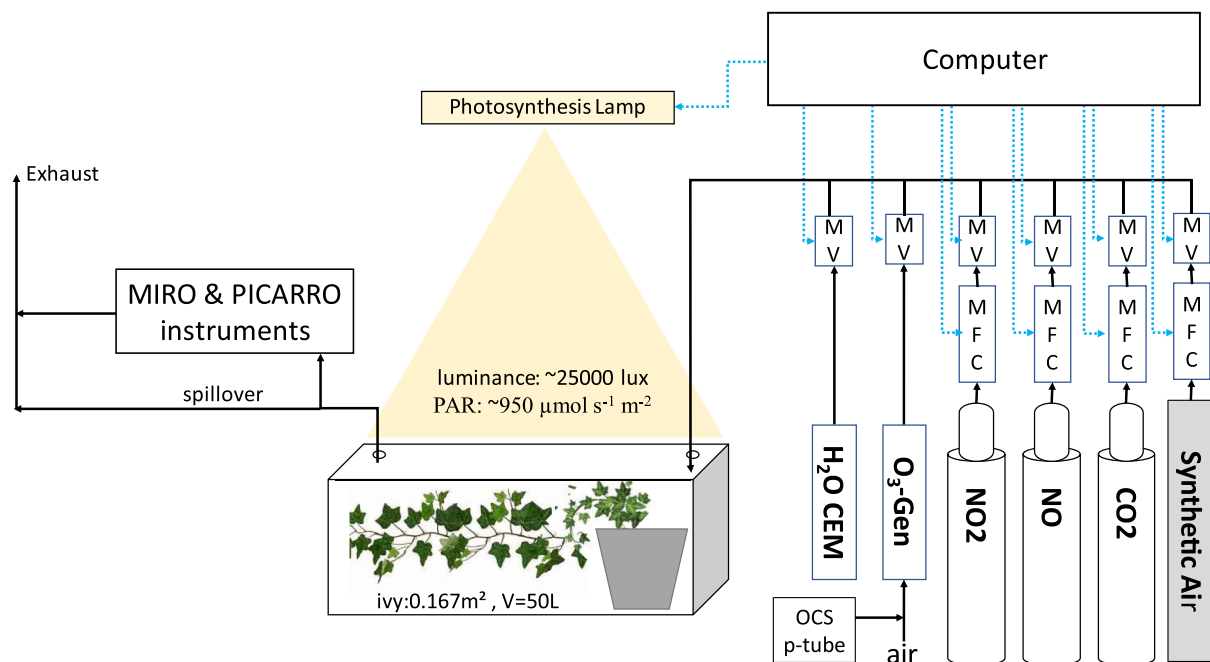


Fig. 1. Experimental setup (with an ivy plant) for the greenhouse and pollutant gas absorption experiment. The reaction chamber (outside dimensions 30 cm*30 cm*60 cm) incorporates a ventilator and a temperature sensor. The volume is 53 L without and 50 L with the deployed plant. The constant volume flow rates of synthetic air through the reaction chamber were 5 L/min in this example, and 10 L/min was used in other subsequent experiments to optimize the experimental outcome. The term “MFC” denotes mass flow controllers and “MV” magnetic three-way-valves. The leaf area of 0.167 m² given in this figure relates to a specimen of the ivy variety *Hedera helix* “Plattensee”.



Fig. 2. Plants used in the experiment were watered and after 2 days taken for measurements (at field capacity).

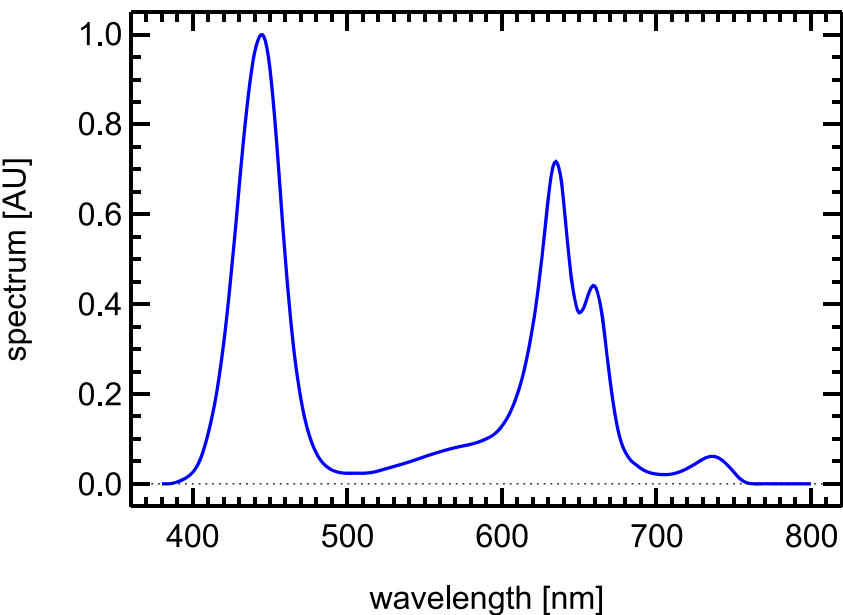


Fig. 3. Properties and spectrum of the photosynthetic 600W LED-lamp used for illumination, 41,1 × 26,7 × 6,5cm type Niello GS-600, Epileds Technologies Inc, No.7 Kanxi Road, Xinshi District, Tainan 744, Taiwan. The spectrum was traced using an illustration supplied by the manufacturer.

some experiments, a Picarro G2307spectrometer was additionally used to determine the concentrations of formaldehyde (HCHO) and methane (CH₄). The principal time resolution of the instruments is 1 s both for the MIRO and for the PICARRO. The detection limits for the different species are given in Table 1.

2.5. The mass flow control unit

This unit controls a constant addition of 5 L/min synthetic air into the reaction chamber and the spiking of intended species following a

repeated time schedule. Spiking was done at each full hour XX:00 (XX = any hour of the day) for 3 min with NO, NO₂, CO₂ from gas bottles (containing 10 ppm NO in N₂ from Air Liquid, 500 ppm NO₂ in N₂ from Praxair, 100 % CO₂ from Air Products)

- at each half hour XX:30 for ten minutes with ambient air (containing H₂O, N₂O, CH₄, NO₂, HCHO, CO, CO₂, and OCS) with added O₃ from an ozone generator and extra OCS from a permeation tube.

The synthetic air was produced by mixing evaporated N₂ and O₂ from liquid N₂ and O₂ reservoirs by the gas supply unit of the SAPHIR chamber (Simulation of Atmospheric Photochemistry In a large Reaction

Table 1
Detection limits (2 sigma) at 60s integration time and legally permitted limit values in the European Union.

MIRO (for O ₃ and NO ₂ :1 ppb ≈ 2 µg/m ³)							PICARRO		
CO	CO ₂	H ₂ O	O ₃	NO	NO ₂	OCS	HCHO	CH ₄	H ₂ O
ppb	Ppm	%abs	ppb	ppb	ppb	ppb	ppb	ppm	%abs
0.03	0.05	0.0005	0.25	0.1	0.03	0.004	0.25	0.005	0.001
global tropospheric concentrations									
100	424	varies	20-60	0-500	0-500	0.5	5-30	1.875	varies
urban concentration limits (European Union - 2010)									
Maximum daily 8-h mean: 120 µg/m ³					Yearly mean: 40 µg/m ³				

chamber) of the Research Centre Jülich. The synthetic air flow could be enriched with several gases each from gas bottles with the help of flow-controllers (MFC) and magnetic three-way valves (MV, Fluoroware Inc.). Other gases like N_2O were added by using their presence in ambient air which was pushed into the synthetic air flow by an ozone generator with an attached permeation tube for OCS. The used three-way magnetic valves each had two directions, one into a common exhaust line, and the other into the synthetic air flow. The flow controllers were purchased from Bronkhorst Deutschland Nord GmbH, 59174 Kamen, GERMANY, and were of type EL-FLOW. They provided in each case a constant predetermined mass flow of gas in accordance to a temperature of 0°C and a pressure of 1013 mbar. Also, gaseous H_2O could be provided by evaporating purified liquid water by a humidification system from Bronkhorst model "CEM Evaporator W-102A". The Ozone generator labelled "O3-Gen" in Fig. 1 was obtained from 2 B Technologies, Broomfield, CO 80020, USA, model 306 "Ozone Calibration Source". This ozone generator pushed ambient air through a quartz tube adding a selectable amount of ozone by illumination with UV light provided by a Pen-Ray Mercury lamp. The very same air also was enriched with OCS from a permeation tube (Fine Metrology S.r.l.s., 98048 Spadafora, Italy).

2.6. Determination of gas exchange parameters of the plants

2.6.1. Mathematical background

The described experimental setup with a glass chamber, stirred by a ventilator, flushed with a fixed inflow and adequate air outflow represents a so-called "continuously stirred tank reactor". This means that

- there will be no concentration gradients inside the chamber since the ventilator is mixing all gaseous compounds within seconds, and
- the concentration of a gas inside the chamber outflow line will be equal to its concentration inside the chamber.

For such an ideal reactor one can set-up the budget for input and output terms of the chamber as follows:

$$\frac{\partial X(t)}{\partial t} = (P_{Inj} + P_{plant}) - (D_{plants} + D_{surface} + D_{DIL}) \cdot X(t) \quad (1)$$

X :	compound of interest
t :	time
P_{Inj} :	production rate by dedicated injection of X
P_{plant} :	production rate of X by the plants
D_{plants} :	loss rate coefficient due to removal by the plants
D_{surf} :	loss rate coefficient for removal at the surfaces of the chamber
D_{DIL} :	loss rate coefficient for dilution inside the chamber due to inflow of synthetic air

$\partial X(t)/\partial t$ denotes the concentration change of a compound X at time t in the reactor which is reflected in the outflow monitored by the instruments. The loss processes inside the chamber are treated here as first order in X . The loss rate coefficients themselves will depend on boundary conditions, namely the internal surface area of the 6 walls of the reaction chamber, the leaf area, the inflow rate of synthetic air, and the volume of the chamber. For a given experiment they can be treated as a constant with unit " s^{-1} ". These loss rate coefficients are often called "reactivity". The reciprocal of a loss rate coefficient is called a timescale with the unit "seconds" and denotes the residence time of a substance with respect to a certain process. A timescale is often abbreviated with the letter τ . The above Eq. 1 can be simplified to

$$\frac{\partial X(t)}{\partial t} = P - D \cdot X(t) \quad (2)$$

by adding up the individual production and loss terms: $P = P_{Inj} + P_{plant}$ and $D = D_{plants} + D_{surface} + D_{DIL}$. The general solution of this first-order partial differential Eq. 2 is

$$X(t) = \left(X(t=0) - \frac{P}{D} \right) \cdot e^{-D \cdot t} + \frac{P}{D} \quad (3)$$

$X(t=0)$ denotes here the starting concentration at time $t=0$. In the special case that P_{Inj} is zero, for example taking the only the time interval just after the injection is finished, Eq. 3 simplifies to

$$X(t) = \left(X(t=0) - \frac{P_{plant}}{D} \right) \cdot e^{-D \cdot t} + \frac{P_{plant}}{D} \quad (4)$$

In the long term limit $t \rightarrow \infty$, $X(t)$ simplifies to a stable value $X(t \rightarrow \infty) = P_{plant}/D$. This means that after an injection is over, the concentration of X approaches a steady state in the long term if the boundary conditions are kept constant. For the practical issue of fitting the experimental results Eq. 4 can be taken as a three-parameter function of the form

$$A(t) = A0 \cdot e^{-t/\tau} + offset \quad (5)$$

with $A0 = (X(t=0) - P_{plant}/D)$, $\tau = 1/D$, and $offset = P_{plant}/D$ as defined in Eq. 4. The parameter τ can be understood as the residence time of a molecule inside the reaction chamber. The determination of the parameters $A0$, τ , and $offset$ has been done iteratively using a Levenberg-Marquardt algorithm. After each injection of substances, either at the full hour or at the half-hour, the observations of the different species were taken for time intervals of 20 min and were fitted to Eq. 5. The visual inspection of all these observations showed that the decay of the species after injection followed closely the form given in Eq. 5 most of the time except for a few cases when the illumination was switched on or off within the analysed time intervals of 20 min. Then, the observed time series of some of the species were more complex since the parameter D_{plant} was not constant in that time frame due to the opening or closure of the stomata of the leaves. These few time points were excluded from analysis since the fitting procedure could not resolve these more complicated decays.

The concept of residence time describes how fast a gas molecule remains in a given setting or system before being eliminated or changed. To show the performance of the described algorithm, one of the species examined (*Hedera helix* "Plattensee") was used for the analysis of NO_2 absorption.

2.6.2. Determination of residence time and time scale

The theoretical residence time of a species inside the empty chamber with a constant inflow rate of 5 L/min is given by dividing the volume of the rectangular chamber with the flow rate. The residence time is thus 53 (L)/5 (L/min) = 10.6 min or 636 seconds for the empty reaction chamber. However, the air volume within the rectangular glass chamber is subject to change after the introduction of a plant, thus the volume would be the actual air volume (53 L minus the volume of the plant and flowerpot). A smaller volume after the plants are introduced will reduce the residence time of the gases inside the chamber, which in this example with the ivy plant was determined to be about 3 L. This implies a residence time of about 50 (L)/5 (L/min) = 10 min = 600 s. To take any change in the exact flow rates, temperature, and plant/flowerpot volume into account, we looked at the observed decay of gases which seems to react neither with the chamber surface nor with the plant/flowerpot. Such a gas can serve as a reference for the residence time. Nitrous Oxide (N_2O) is a fairly stable greenhouse gas with an atmospheric lifetime of 123 years (Prather et al., 2015). In the troposphere, N_2O can be treated as an inert noble gas. Thus, N_2O will not be absorbed by plants and will pass through the reaction chamber unchanged. N_2O can be used to correct the effect of the plant/flowerpot on the effective volume of the reaction chamber and also to account for any effect of a temperature change on the gas density during the experiments.

The experiments involved the injection of NO , NO_2 , and CO_2 from gas cylinders, OCS from a permeation tube, and O_3 from an Ozone

generator using a pen-ray UV lamp. N_2O , H_2O , CH_4 , and CO were either introduced into the reaction chamber by flushing-in ambient air or, in the case of H_2O , as a result of transpiration of the plants. For this study, the quantitative determination of the absorption of NO_2 by façade climbing plants is the main intent. NO_2 is one of the major pollutants with major emissions from vehicular traffic (Ehlers et al., 2016). Since traffic emissions are often released in close proximity to humans and often lead to hot spots of local pollution in inner city districts (Ehlers et al., 2016), they are contributing to health problems and loss of life on a global scale. Façade greening at least has the potential to improve air quality exactly at these pollution hot spots.

2.7. Leaf area

At the end of the series of experiments, all leaves were removed from a plant. The total weight of all the leaves was then determined and related to the area of five individual leaves by cutting out and weighing equivalent pieces of paper of known grammage. The mean ratio of mass/area of one of the leaves was then used to extrapolate the total area of the leaves of the investigated plant.

3. Results

Fig. 4 and Fig. 5 present the observed concentration time series of N_2O and NO_2 for repeated injections of N_2O at XX:30 and NO_2 at XX:00 hours for a full day. In Fig. 4, N_2O shows very homogeneous injection peaks in width and height for the illuminated and the dark interval since the plant does not interact with N_2O . NO_2 in Fig. 5, on the other hand, behaves differently. During the illuminated interval, the peaks are less high and narrower, which is due to the instantaneous absorption of NO_2 by the plant.

For comparison, Figs. 6 and Fig. 7 show simulated concentration profiles for N_2O and NO_2 using Eq. 4 with a fixed injection rate ($P_{\text{inj}} > 0$) during the time interval of injection and a fixed degradation rate for

N_2O . For a realistic simulation, two fixed degradation rates for NO_2 were required, one for the illuminated and the other for the dark phase of the experiment. The peak heights and widths in both observed and simulated results show the effect of the plant on the degradation of both, NO_2 and N_2O . Due to faster degradation during the illuminated time periods, the peak heights and widths for NO_2 are smaller compared to the dark periods. In the N_2O observations, there is a small variability of the peak heights caused by changes in the N_2O content of ambient air over the day which was used for the N_2O injection at each XX:30 h. The similarity between observed and simulated concentration profiles is striking especially if one considers that besides the exact injection times, only two fixed parameters were used for N_2O ($P_{\text{inj}}(\text{N}_2\text{O})$, $D(\text{N}_2\text{O})$) and three fixed parameters for NO_2 ($P_{\text{inj}}(\text{NO}_2)$, $D(\text{NO}_2, \text{dark})$, and $D(\text{NO}_2, \text{illuminated})$).

Fig. 8 shows a closer, high temporal resolution look at one of the $\frac{1}{2}$ h intervals. Within the injection period, the concentration of the species is climbing until the injection is stopped. After this culmination point, the decay is starting. The time between the peak concentration until the beginning of the next injection is used for the analysis fitting the observed data points to Eq. 5.

For every injection period the above explained methods and processes are repeated for each decay curve under both the light and dark phases of the experiment. Results of this fitting procedure for *Hedera helix* “Plattensee” are presented in Fig. 9 and Fig. 10 below. The observed removal of gases after each injection interval followed single exponential decay curves as expressed in Eq. 5. This is expressed in Fig. 10 with logarithmic Y-axis, where the data points appear to lie on a straight line.

The above-described methodology is repeated for each injection over a 24 h period to obtain the sequence of the parameter “timescale” (see Fig. 11). It is important to note that the change in the parameter timescale of NO_2 due to illumination is not directly related to the gas phase reaction $\text{NO}_2 + \text{O}_2 \xrightarrow{\text{UV-light}} \text{NO} + \text{O}_3$, the well-known photolysis of NO_2 producing NO and O_3 . The amount of UV-light emitted by the LED-

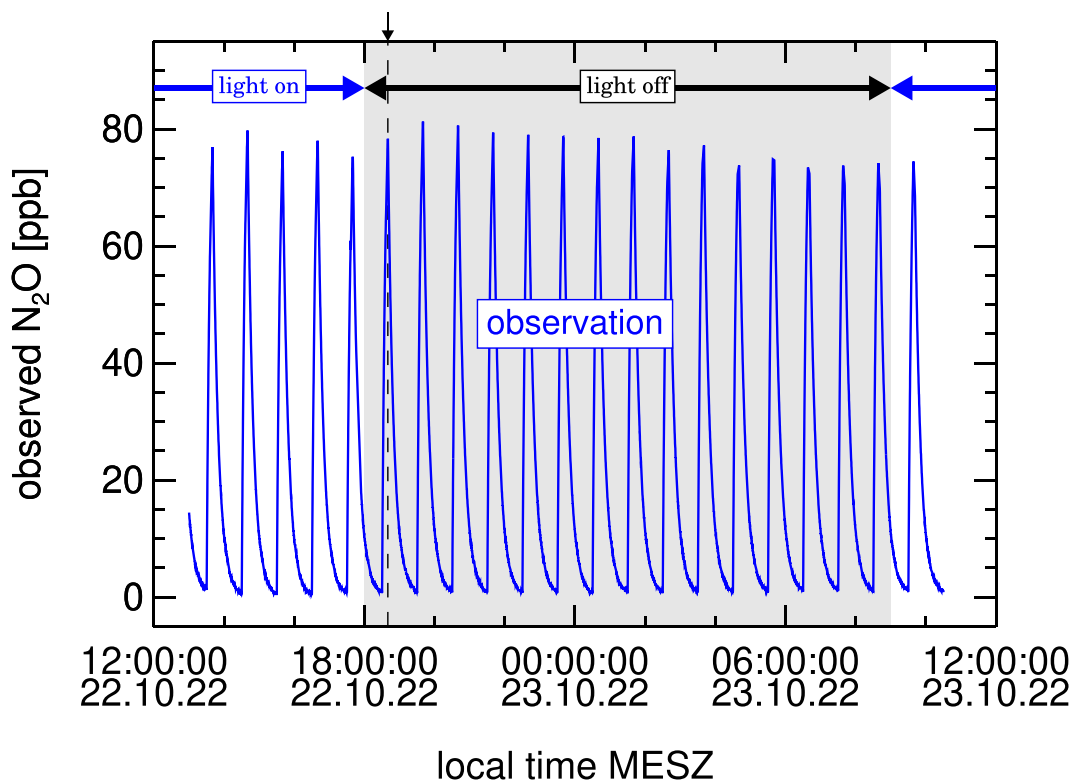


Fig. 4. Observed time series of N_2O showing repeated injections and the almost constant decays with equal peaks heights and widths over 24 h for a *Hedera Helix* “Plattensee” specimen. The vertical dashed line and the vertical arrow denote the position of the time period shown in Fig. 9 and Fig. 10.

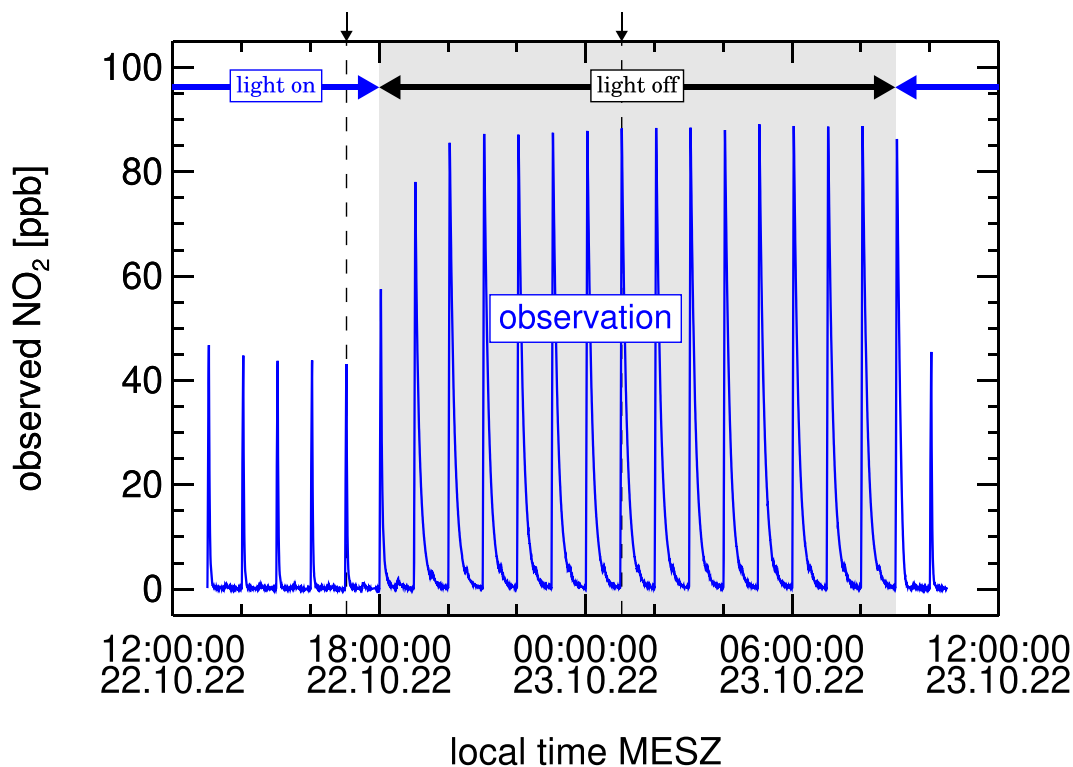


Fig. 5. The decay of NO_2 showing a repeated decay trend with more pronounced absorption with smaller peaks heights and narrower widths at identical injection amounts during the illuminated phase for a Hedera Helix “Plattensee” specimen. The vertical dashed lines and the vertical arrows denote the positions of the time periods shown in Figs. 9 and Fig. 10.

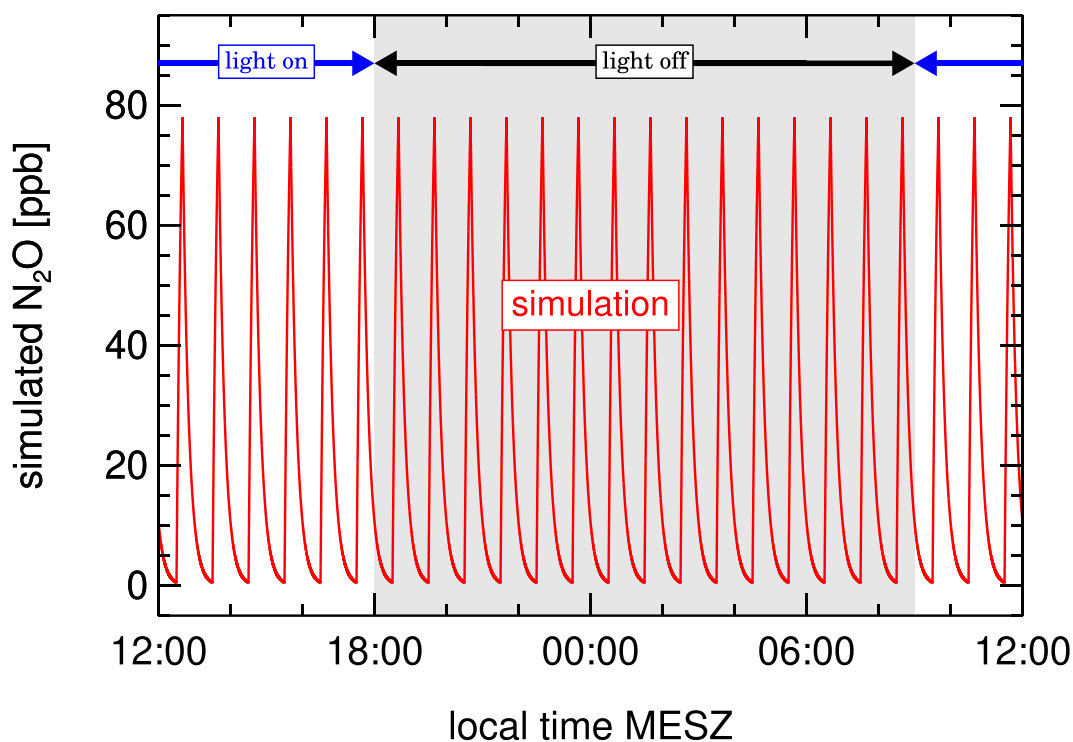


Fig. 6. Simulated (following Eq. 5) time series of N_2O obtained for repeated identical injections and constant decay with $\tau=600$ s. A constant N_2O injection rate $P_{\text{inj}}=46.8$ ppb/min was selected for all injection intervals to be consistent to the observed average N_2O -value in Fig. 4. P_{plant} was kept to zero at all times.

lamp is not large enough to activate this photolysis process. Rather, the observed effect depends on an interaction between the plant inside the reaction chamber and the gas phase containing NO_2 . This is

demonstrated by a separate experiment shown in Figure S1 showing the illumination of a NO_2 -containing air mixture in the empty reaction chamber. No effect of light from the LED-lamp could be detected for this

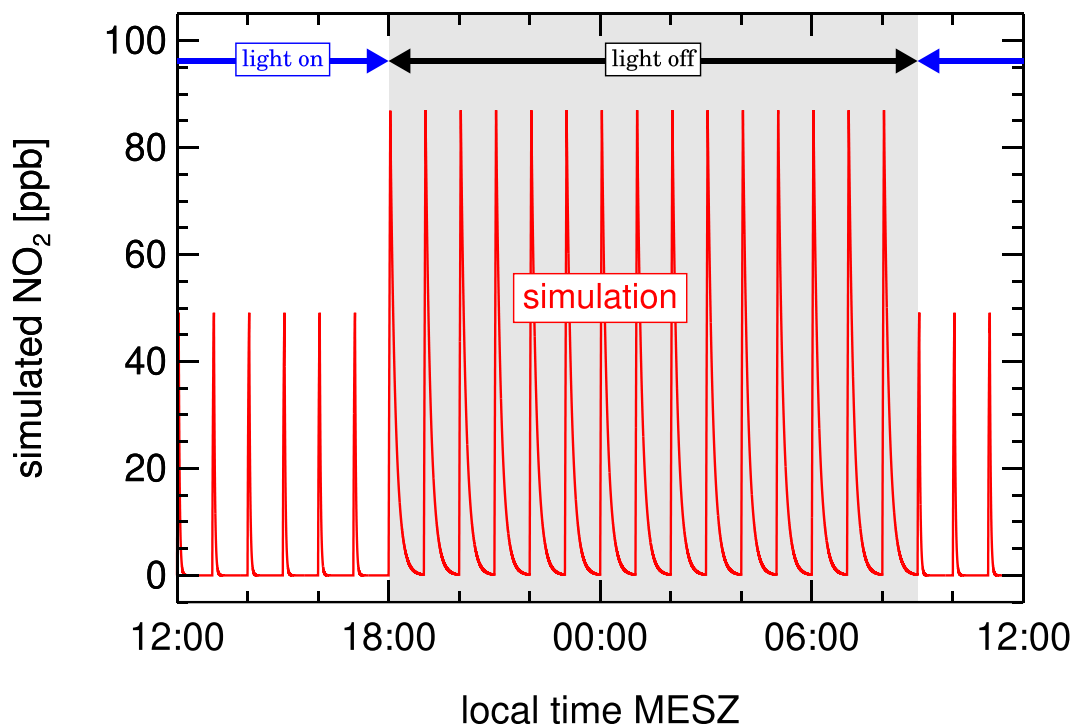


Fig. 7. Simulated (following Eq. 5) time series of NO_2 obtained for repeated identical injections and constant decay with $\tau=520$ s for dark and $\tau=100$ s for illuminated periods. A constant NO_2 injection rate $P_{\text{inj}}=52.5$ ppb/min was selected for all injection intervals to be consistent to the observed NO_2 -values in the dark period in Fig. 5. P_{plant} was kept to zero at all times.

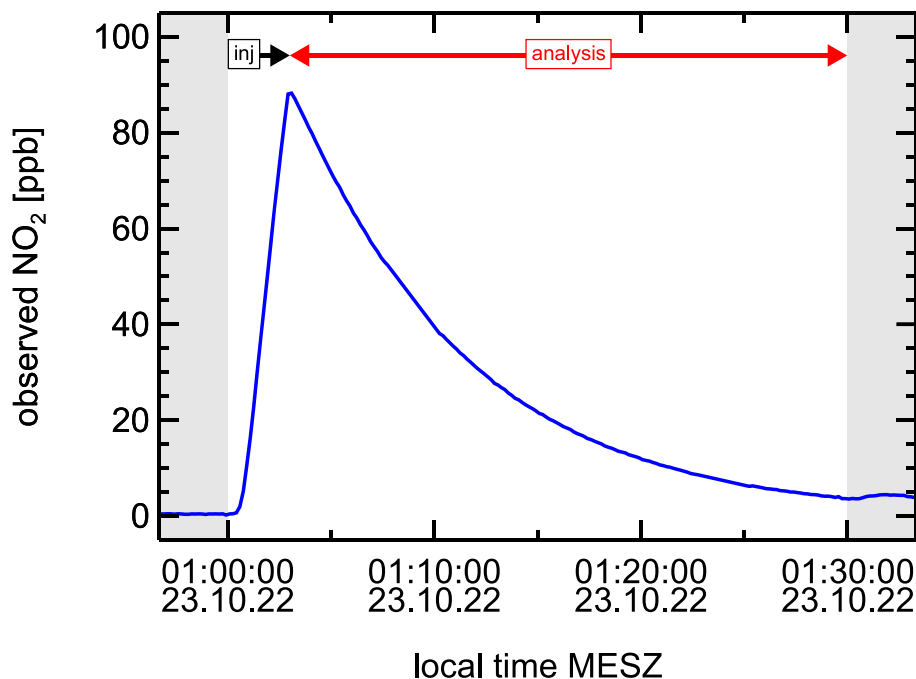


Fig. 8. Zoomed $\frac{1}{2}$ h time interval from Fig. 5 showing the injection period (labeled “inj”) and the time frame used for the determination of the exponential decay parameters (labeled “analysis”) for the injection of NO_2 starting at 01:00 23.10.2022 MESZ.

condition without the presence of the ivy plant.

3.1. Reactivity and deposition velocity

The reactivity, given here as $D=1/\tau$ (where τ = timescale, see Fig. 11–y-axis, and Eqs. 1–5), is a measure of the overall degree to which the plants absorbed or altered a particular greenhouse- or pollutant gas.

From the definition $D=D_{\text{plant}}+D_{\text{surface}}+D_{\text{DIL}}$ follows

$$\frac{1}{\tau_{\text{observed}}} = \frac{1}{\tau_{\text{plant}}} + \frac{1}{\tau_{\text{surface}}} + \frac{1}{\tau_{\text{DIL}}} \quad (6)$$

This implies that the reactivity of the plant versus a species like NO_2 can be calculated from the observations of this species and N_2O :

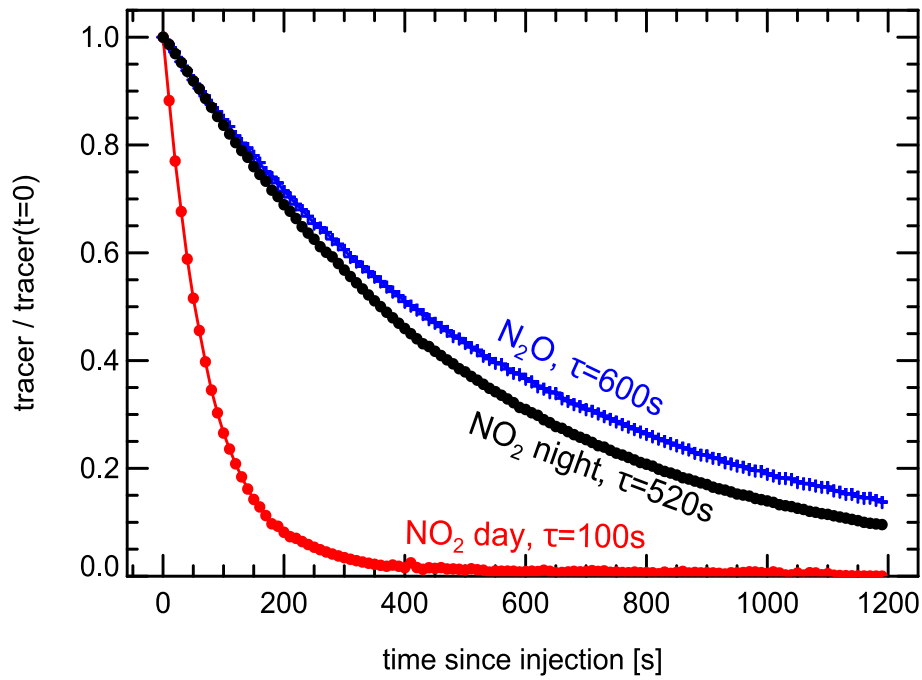


Fig. 9. Time scale decay of observed N_2O (18:40:00 22.10.2022) and NO_2 during illuminated (17:03 22.10.2022) and dark (01:03 23.10.2022) phases of the experiment. The tracer concentrations are scaled to the concentrations at the end of the respective injection intervals and are shown here on a linear Y-axis.

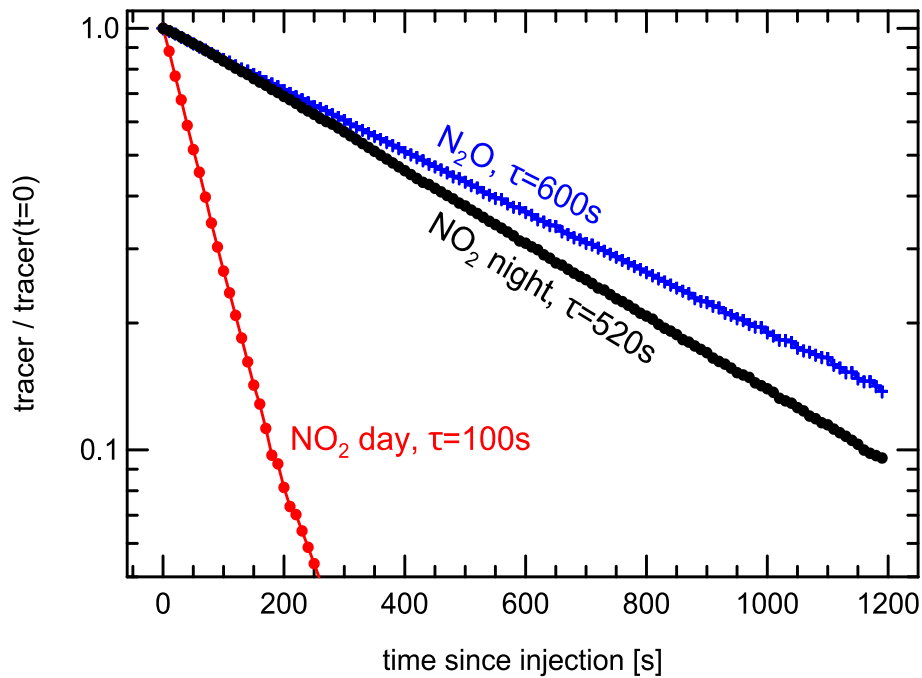


Fig. 10. Logarithmic time scale decay of observed N_2O (18:40:00 22.10.2022) and NO_2 during illuminated (17:03 22.10.2022) and dark (01:03 23.10.2022) phases of the experiment. The tracer concentrations are scaled to the concentrations at the end of the respective injection intervals.

$$D_{plant,NO_2} = \frac{1}{\tau_{observed,NO_2}} - \left(\frac{1}{\tau_{surface,NO_2}} + \frac{1}{\tau_{DIL,NO_2}} \right) \quad (7)$$

$$= \frac{1}{\tau_{observed,NO_2}} - \frac{1}{\tau_{observed,N_2O}}$$

Eq. 7 uses N_2O as a reference to which the observed timescales of NO_2 and NO are compared to account for the effect of dilution, temperature variations, and the exact volume of the reaction chamber equipped with flowerpot and plant. In a separate experiment without a

plant, NO_2 showed the same residence time as N_2O , so $\tau_{surface,NO_2} = 0$ and $\tau_{DIL,NO_2} = \tau_{DIL,N_2O}$. The obtained reactivities of the plant, D_{plant,NO_2} and $D_{plant,NO}$, then can be scaled by the leaf area LA and the effective volume of the reaction chamber VOL_{RC} to produce the deposition velocity (Seinfeld, 1986) v_{dep} of the plant for NO_2 and NO which describes the flux density F at a certain concentration c_{gas} of the gas of interest Fig. 12:

$$F = v_{dep} \cdot c_{gas} = \frac{D_{plant} \cdot VOL_{RC}}{LA} \cdot c_{gas} \quad (8)$$

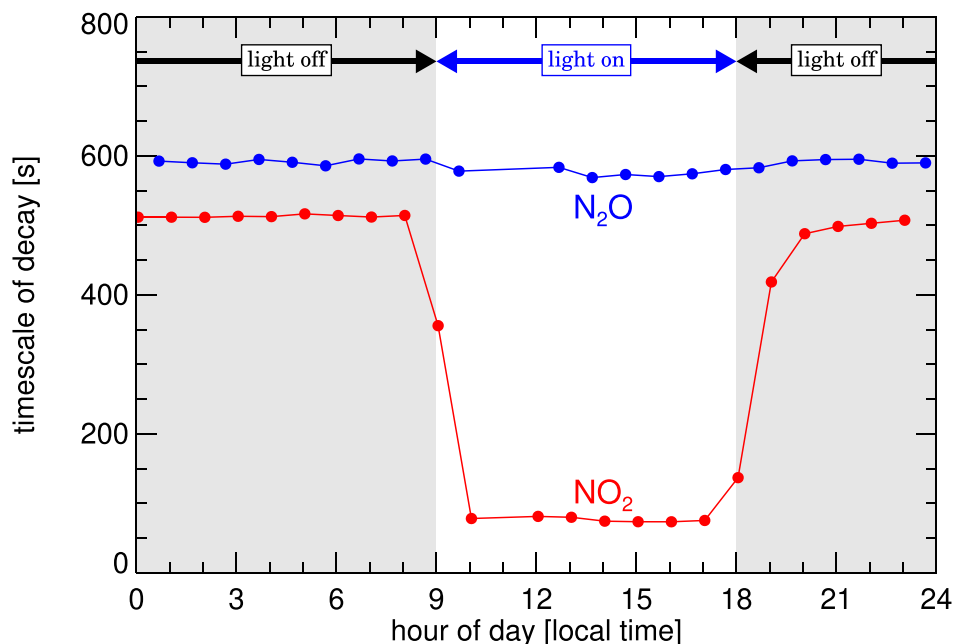


Fig. 11. Diurnal variations of the timescale-of-decay for N_2O and NO_2 using the ivy variety *Hedera helix* "Plattensee"

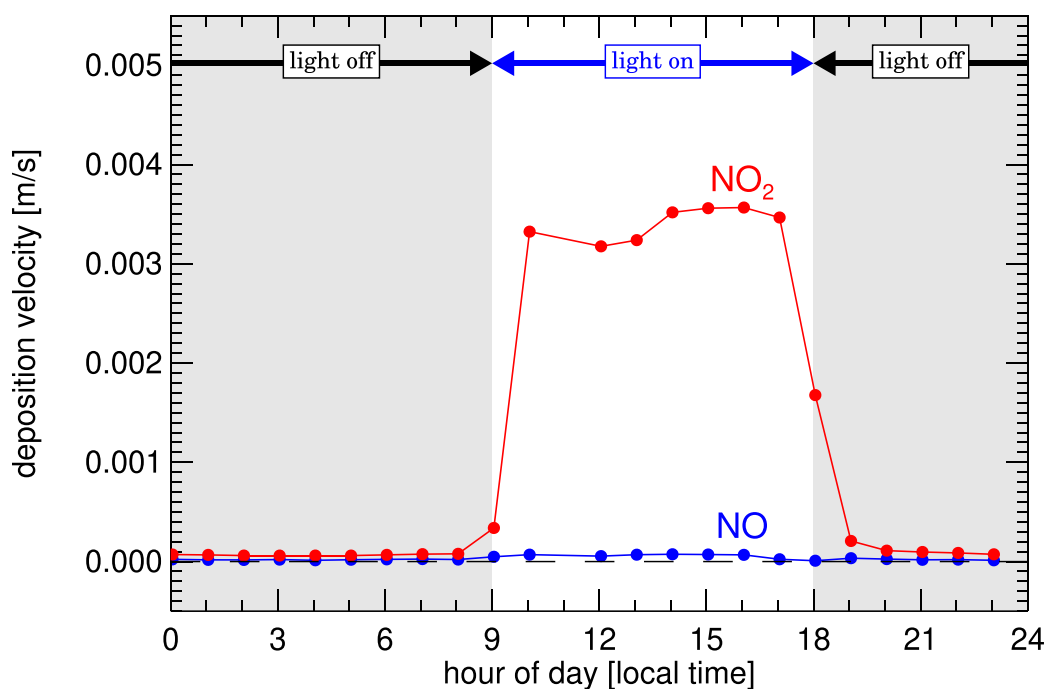


Fig. 12. Deposition velocity (relating reactivity ($1/\text{s}$) to leaf area (m^2) and chamber volume (m^3), see Eq. 8) of NO and NO_2 showing a strong absorption of NO_2 during the illuminated time period but none for NO during an experiment with the ivy variety *Hedera helix* "Plattensee."

The parameter "deposition velocity" can be used to describe the absorption behaviour of the plants also in different environments like inner-city districts. The derived values of NO and NO_2 on a specimen of the ivy variety *Hedera helix* "Plattensee" are within the range of observed values for other plants (see Table 2). Our results do not show the existence of a compensation point for NO_2 . Such a compensation point would work out as a significant concentration of NO_2 applying synthetic air without NO_2 . It should be visible at the end of each decay curve as an offset. See for example Fig. 9, where NO_2 is going straight to zero in the illuminated phase. The cited v_{dep} studies use a dynamic branch or leaf enclosure system comparing the NO_2 concentration within two cuvettes,

one plant and one empty reference cuvette. In contrast, our study is using a relaxation type of experiment directly observing the flux of a gaseous compound towards a plant.

The observed deposition velocities for NO_2 are directly related to the transpiration of $\text{H}_2\text{O}_{\text{gas}}$ (see Fig. 13). The observations show the humidification of the dry synthetic air entering the reaction chamber by transpiration of the plant. The flowerpot and the surface of the soils within the reaction chamber were covered by a foil so the dominant part of the water can be attributed to evaporation of the leaves and the stem of the plant. It cannot be ruled out that the surface of the soil had some humidification effect but this is expected to be minor.

Table 2

Overview of published data on deposition rates for NO₂ and NO from plants. The values for PAR are given in $\mu\text{mol s}^{-1} \text{m}^{-2}$.

Species	$v_{\text{dep}}(\text{NO}_2)$ [cm/s]	condition	Reference
Grass	NO ₂ : 0.38 NO: 0.02	literature search	(Jonas and Heinemann, 1985)
Corn <i>Zea mays</i>	NO ₂ : 0.14	difference between two cuvettes, PAR 1600	(Hereid and Monson, 2001)
Wheat	NO ₂ : 0.20	difference between two cuvettes, PAR 1000	(Teklemariam and Sparks, 2006)
Periwinkle	NO ₂ : 0.12		
Sunflower	NO ₂ : 0.14		
Corn	NO ₂ : 0.08		
Norway spruce	NO ₂ : 0.15 ± 1.3	difference between inlet and outlet of a cuvette PAR 500 $\pm$ 400	(Rondón, et al., 1993)
Scots pine	NO ₂ : 0.14 ± 1.1		
Norway spruce <i>Picea abies</i>	NO ₂ : 0.09	difference between two cuvettes, PAR 600	(Thoene, et al., 1996)
<i>Fagus sylvatica</i>	NO ₂ : 0.1	difference between two cuvettes, PAR 170	(Gessler, et al., 2000)
25 tropical tree species	NO ₂ : 0.17-0.68	difference between two cuvettes, PAR 1000	(Sparks, et al., 2001)
five European tree species	NO ₂ : 0.2-0.3	difference between two cuvettes, PAR 450, 900	(Chaparro-Suarez, et al., 2011)
<i>Hedera helix</i> "Plattensee"	NO ₂ : 0.3 NO: 0.01	PAR 950	this study

4. Discussion

To analyse the potential of plants for cleaning air polluted with greenhouse- and other harmful gases, very accurate and sophisticated measurements of plant gas metabolism are required. For this purpose, high-resolution measurement methods were used in the present study, which can yield very precise absorption parameters resolved in time. These detailed temporary measurements allow to detect instant and direct causal impacts and interactions of the surrounding air with the gas metabolism of the plant, as a function of the changes in the proportions

of gas components within the supplied air. An important advantage of the experimental design shown in Fig. 1 is the modulation capability giving the possibility of regulating light quantity and adding constant background concentrations for example for CO₂ and H₂O_{gas}, as envisaged in ongoing further pending investigations. The supply of the measuring chamber with defined N₂O injections, which can be seen in Fig. 4 was carried out at half-hour cycles. This gas, being a strong climate gas (Prather et al., 2015) with a long atmospheric lifetime, can be used as a reference for the undisturbed passage of a gas mixture through a reaction chamber, illustrating a decay (i.e. its decrease in the concentration of the outflow) as to be expected when no interaction with the plant occurs. Thus, its decay remained equal during both illuminated and dark phases of the experiments with and without a plant present in the chamber. This finding can be interpreted as an indication that this gas is not absorbed by the plant, regardless of the state (open or closed) of the stomata. In contrast to this, NO₂ is quickly absorbed at such a rate, that the peak height during the injection interval only develops to approximately half the height observed during the dark phase, as well as a strongly faster decay rate. NO₂ shows— in contrast to N₂O - a pronounced light-dependent absorption capacity, which reveals during the dark phase a similar decay as observed for N₂O. In contrast to NO₂, NO shows no absorption by the plant, neither during the dark nor the illuminated phase. The low absorption of NO₂ in the dark is a hint that it is not interacting with the cuticula or other surfaces of the plant. During the illuminated phase, the stomata open and release water into the gas phase, enabling gas transport to the inner surfaces of the stomata. This allows NO, NO₂, and N₂O to reach the membranes, facilitating the transport of gas into the liquid phase inside the cells. In principle, this gas-liquid exchange should follow Henry's law which describes the solubility of a gas in liquid water. Astonishingly, the Henry coefficient of N₂O is the largest of the three gases (see Table 3), larger than NO₂, but still in both cases the budget between gas and liquid phase is in favour of the gas phase. Since NO₂ is observed to be removed from the gas phase fast, that means, that NO₂ entering the liquid phase inside the stomata is absorbed and metabolised there quite fast. Since the concentration of

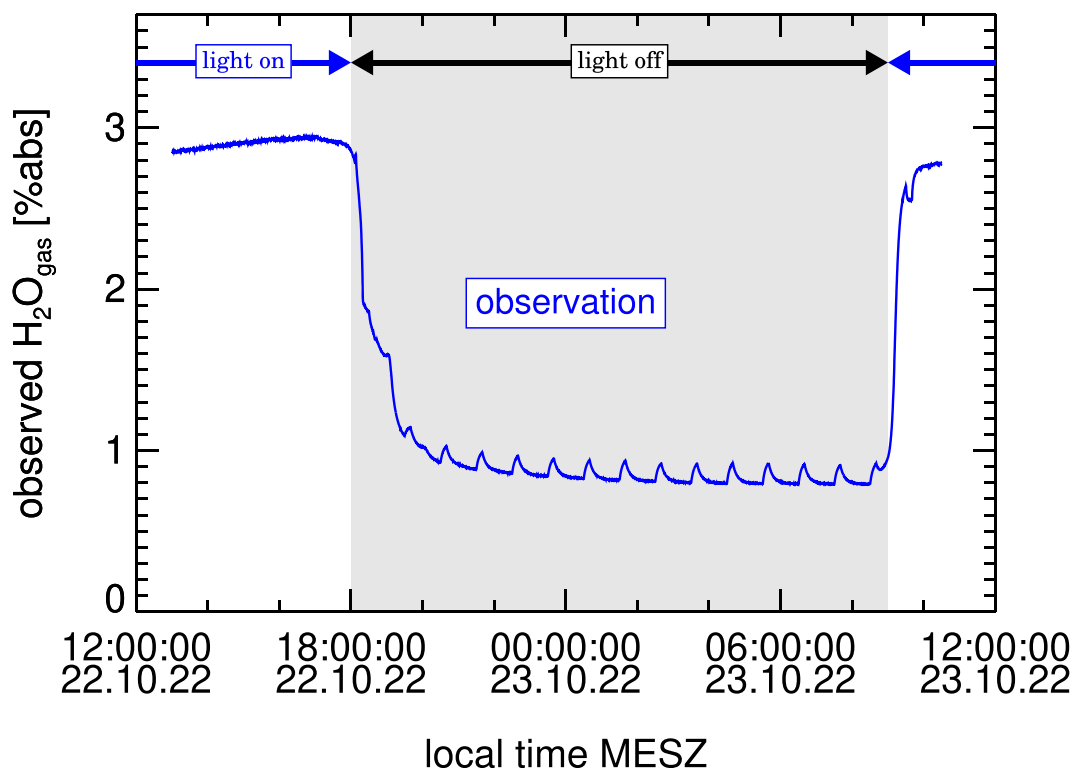


Fig. 13. Observed H₂O_{gas} mixing ratios indicating the opening of stomata during the illuminated phase for the ivy variety *Hedera helix* "Plattensee".

Table 3

Henry’s law constants (Sander, 2015) ($k_{H,i}^*$) at 298K describing the solubility of a gaseous compound in water. It is specifying the ratio of the concentration in the liquid phase relative to the pressure of the compound in the gas phase. The unit is mol/(m³*Pa).

NO	NO ₂	N ₂ O	O ₃	CO	CO ₂	OCS	CH ₄	HONO
1.9e-5	1.2e-4	2.4e-4	1.0e-4	9.7e-6	3.3e-4	2.0e-4	1.4e-5	4.7e-1

NO₂ in the liquid phase is going towards zero due to this efficient metabolising process, NO₂ can be transported from the gas phase into the liquid phase constantly over time since the balance described by Henry’s law is never reached.

The potential of a range of different climbing plants on the improvement of the air quality with respect to environmentally relevant air compounds will be presented in a following paper. The findings will provide a precise differentiated assessment of the properties and characteristics of the various façade plants, and thus emphasise the relevance of these plants for planting with regard to the challenges expected due to climate change.

5. Conclusion

The results obtained show that the plant specimens tested in this analysis actively reduced the NO₂ concentration under light conditions. This absorption can be attributed to a stomata-controlled activity. Contrary to expectation of Henry’s law which describes the solubility of the used gases in water, the observed results strengthen the notion that specific pathways exist in the plant for the removal of NO₂. These removal pathways are clearly lacking for gases like NO and N₂O. Compared to other methods used to determine absorption of greenhouse and pollutant gases, the method described in this study offers a great range of flexibility and repeatability; while given the opportunity to observe quantitatively the changes in plant reaction towards different parameters such as light intensity, water stress, background gas concentrations (CO₂, NO₂, N₂O, O₃ etc.)

CRediT authorship contribution statement

Minka Aduse-Poku: Investigation, Data curation. **Franz Rohrer:** Methodology, Formal analysis. **Benjamin Winter:** Validation, Resources, Methodology. **Hans G. Edelmann:** Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Supplementary materials

Supplementary material associated with this article can be found, in

the online version, at [doi:10.1016/j.envadv.2024.100568](https://doi.org/10.1016/j.envadv.2024.100568).

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