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1 Towards an experimental approach for
2 measuring the removal of urban air pollutants by
3 green roofs

4 Yara Arbid, Claire Richard, Mohamad Sleiman*

5 University Clermont Auvergne, CNRS, Clermont Auvergne INP, Institut de Chimie de Clermont-Ferrand
6 F-63000 Clermont-Ferrand, France

7 Yara.arbid@etu.uca.fr

8 Claire.richard@uca.fr

9 Mohamad.sleiman@sigma-clermont.fr

10 *Corresponding author: Mohamad Sleiman – University Clermont Auvergne, CNRS, Clermont Auvergne
11 INP, Institut de Chimie de Clermont-Ferrand F63000 Clermont-Ferrand, France; orcid.org/0000-0002-
12 2273-1053; Email: Mohamad.sleiman@sigma-clermont.fr

13 **ABSTRACT**

14 Green roofs are a promising approach to mitigate air pollution in urban environments, but limited
15 experimental data is yet available. In this study, we developed a laboratory-scale setup to measure the
16 removal nitrogen dioxide (NO₂) and ozone (O₃) using a variety of common green roof species.
17 Experiments were conducted on detached leaves and whole plants using two chambers (0.6 L and 12 L),
18 visible lighting, NO_x/O₃ sources and online analyzers. Three species were the best performant (Thymus
19 vulgaris, Sedum sexangulare and Heuchera Americana L.) with deposition velocities (v_d) ranging from
20 1.6 to 4.82 m/h for NO₂, and 1.7 to 5.56 m/h for O₃. In both cases, thyme was the most effective plant
21 likely due to its higher stomatal area and the reactivity of its volatile metabolites with O₃ leading to
22 several oxidized by-products. Furthermore, NO₂ uptake was found to be enhanced by surface water
23 released by leaf transpiration leading to the production of nitrous acid (HONO). Similar values of (v_d)
24 were observed (3.84 – 4.65 m/h) when whole thyme plant was used. The soil was also found to be
25 competitive in removing O₃ but less performant in capturing NO₂. Using a dry deposition model, we
26 estimated that the three plant species can uptake up to 9 kg/ha/year of NO₂ and 13.6 kg/ha/year, which fall
27 in agreement with previously reported modeling data. Our experimental approach can be a rapid tool for
28 screening the depollution performances of green roof species enabling an effective prioritization for
29 deployment in urban environments.

30 Keywords: Green roofs, air pollution, NO_x, O₃.

31 **1. INTRODUCTION**

32 Outdoor air pollution causes up to 10 million deaths annually, and around 90 % of the world
33 population live in urban environments where air pollution exceeds the World Health Organization (WHO)
34 limits [1]. Air pollution mitigation strategies such as source reduction (electrical vehicles [2], fuel and
35 traffic regulations [3], renewable energy resources [4], etc.), and depollution technologies have been
36 increasingly adopted in the recent years. Among depollution methods, the use of highly reflective

37 photocatalytic roofs and walls [5] have been shown to be effective in reducing the urban heat island effect,
38 and in the removal of Volatile Organic Compounds (VOCs) and Nitrogen Oxides (NO_x) [6,7]. However,
39 photocatalytic oxidation process can lead to the formation of toxic intermediates and the VOC removal
40 performance can decrease over time [8]. Another promising alternative is the use of natural walls and
41 roofs such as vertical greening systems or green roofs which can be a replacement to conventional roofs
42 especially in crowded urbanized areas [9]. Green roofs have been receiving attention recently as effective
43 nature-based solution to eco-environmental problems arising from climate change and rapid urbanization
44 [10]. They can retain storm water via absorption into the substrate [11,12], reduce the building energy
45 demand by improving the thermal insulation [13], lower noise pollution [14], in addition to improving the
46 roof aesthetic values.

47 Plants used in such green roofs are able to mitigate air pollution [15] by absorbing the pollutants
48 through their stomata via dry deposition on the surfaces of leaves [16]. Urban trees and shrubs are known
49 to remove efficiently air pollutants [17]. Reactive pollutants (O₃, NO_x, SO₂) can be removed by
50 absorption via stomata or by surface uptake via potential chemical reactions with volatile metabolites such
51 as terpenes. On the other hand, the formed particulate matter (PM) can be removed via deposition on the
52 leaf surface. The performance depends on various factors such as the proximity of the vegetation to the
53 road and its height [18]. Although trees are a very effective strategy in controlling pollution, planting trees
54 in crowded cities with high percentages of impervious areas is challenging. Thus, in metropolitan cities,
55 green roofs can be an alternative solution to make use of rooftops [19]. Several modelling studies showed
56 that green roofs can be efficient in removing various prevalent air pollutants. According to Yang et al.,
57 22.8 kg/ha/year of NO₂ and around 44 kg/ha/year of O₃ can be eliminated using green roofs [16]. Grass
58 was found effective in removing O₃ (5.2 kg/ha/year) whereas, shrubs have the potential to eliminate 18
59 kg/ha/year of PM₁₀ [20]. Speak et.al [21] showed that sedum, a widely used plant species on extensive
60 green roofs, could remove 4.2 kg/ha/year of PM₁₀. However, most aforementioned studies were based

61 solely on modelling using estimated deposition velocities (v_d) which can vary significantly depending on
62 the plant species, seasonality, climate, etc.

63 To the best of our knowledge, the air depollution performance of green roofs species has been
64 very little investigated, and only limited recent data exist on their efficiency in the laboratory and in the
65 field [22,23]. Performance-based laboratory screening measurements –in combination with field
66 campaigns- are thus needed to improve the precision of models and to provide a valuable tool for
67 implementing the best performant species as a function of target pollutants. In this study, we developed an
68 experimental setup to measure the NO_x/O₃ uptakes of 13 plants commonly used on green roofs. After
69 initial screening, 3 species were selected (*Sedum sexangulare*, *Thymus vulgaris*, and *Heuchera micrantha*
70 *palace purple*). The removal rates of these plants were investigated using detached leaves as well as full
71 size plants. This work aimed to guide in the choice of plants to be used on green roofs according to the
72 need of targeting a specific pollutant in an urbanized area, and to get insight into the mechanisms taking
73 place.

74 **2. MATERIALS AND METHODS**

75 **2.1. Chemicals and materials**

76 Imidacloprid (IMD) was purchased from Sigma Aldrich, Switzerland (Pestanal™, analytical standard,
77 ≥98.0% purity HPLC area %). Sodium carbonate anhydrous was purchased from Fluka, Germany
78 (≥99.5% purity ACS). Both were used without further purification. Water was produced using a reverse
79 osmosis RIOS 5 and Synergy (Millipore) device (resistivity 18 MΩ cm, DOC<0.1 mg L⁻¹). Acetonitrile
80 (ACN) was purchased from Carlo Erba Reagents (HPLC Plus Gradient grade-ACS-Reag.

81 Process of plant selection: Green roofs vary from intensive to extensive roofs differing in the maintenance
82 needs, substrate depth, plants implemented, etc. Contrarily to intensive ones where shrubs or even trees
83 may be implemented, extensive green roofs use shallow root plants and thus are more commonly used due
84 to their low maintenance needs and lightweight. Hence, in this study, we solely focused on extensive
85 green roof species which are drought tolerant such as grasses, perennials, and succulents. Based on

86 literature review, and after careful consideration of weather conditions in central France, 13 species were
87 selected for screening: *Achillée millefeuille paprika*, *Achillea umbellata à feuillage gris*, *Alchemille jaune*,
88 *Aster des alpes rose*, *Heuchera americana L.*, *Joubarbe calcareum*, *Joubarbe rubin*, *Thymus nummularius*,
89 *Sedum floriferum jaune*, *Sedum reflexum jaune*, *Sedum sexangulare*, *Sedum spurium*, and *Thymus*
90 *vulgaris*. After pre-screening, three species were chosen to further investigate their performance for the
91 removal of O₃ and NO₂: *Sedum sexangulare*, *Thymus vulgaris*, *Heuchera americana L.*

92 Conditions for plant storage and care: Plants were stored in an indoor greenhouse exposed to outdoor
93 sunlight through a large window and were watered every two days. Temperature was between 20-25 ° C
94 in the greenhouse during storage and around 23°±2 C when used in the laboratory. Relative humidity (RH)
95 was ranged between 30-55%.

96 *Sedum sexangulare*, *Thymus vulgaris*, and *Heuchera micrantha palace purple* were purchased from a
97 plant nursery (Botanic®, Beaumont, France) and watered every two days. These species are used on green
98 roofs and different studies report their performance towards different air pollutants [24–26].

99 *Sedum sexangulare* (sedum): Sedum species are considered as appropriate plants to be applied on
100 extensive green roofs. They are drought tolerant and can survive in harsh climate conditions. In the
101 literature, *Sedum sexangulare* showed a good performance under severe climate conditions and that it is
102 suitable to be implemented in a Mediterranean climate [24].

103 *Thymus vulgaris* (thyme): Thyme is an odorous perennial plant used on green roofs. It emits different
104 VOCs (**Fig.SI-1.**) which can react with air pollutants [25].

105 *Heuchera Americana L.* (heuchera): Heuchera species are used in vertical greenery systems and green
106 roofs because their colorful glossy leaves give them important aesthetics values. Heuchera retains
107 different elements and particulate matter (PM) due to its hairy undersides [26].

108 Plants were stored in an indoor greenhouse with direct solar light. They were either used directly as a full-
109 size plant (pot size: 9-15 cm) or their leaves cut using scissors into pieces of 0.9-1.2 g prior to the
110 experiment.

111 To avoid changes induced by diurnal cycles, all experiments using plants were performed during the day
112 from 10 am to 3 pm. The planting soil was a universal soil with a water retention capacity of 75%,
113 pH=6.5, and N, P, K values of 5.5, 2.5, and 1.5 for 2 kg/m³ respectively.



114
115 **Fig.1.** Pictures of the 3 studied plants: *Sedum sexangulare*, *Thymus vulgaris*, and *Heuchera Americana L.*
116 (left to right).

117 2.2. Experimental setup

118 A new experimental setup was designed to measure the uptakes of leaves and the full-size plant
119 under irradiation with NO_x and O₃ configurations.

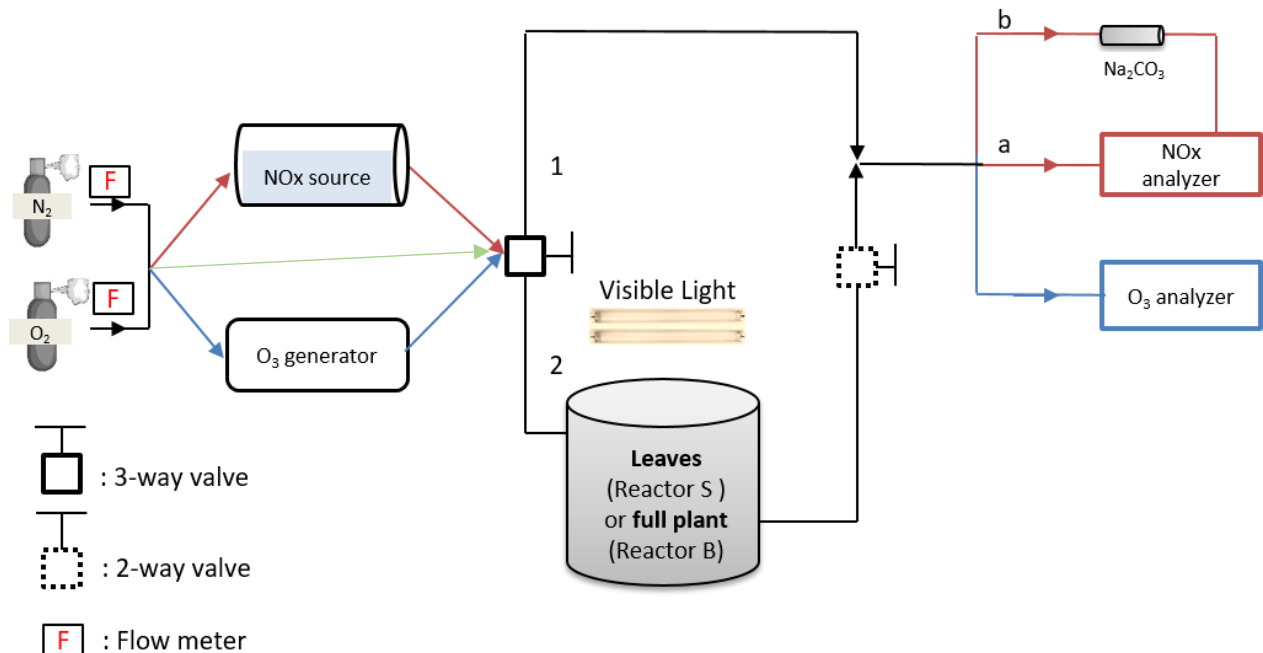


Fig.2. Experimental setup used for measuring the uptake of NO₂ (red) and O₃ (blue).

120 NO_x/O₃ setup The setup includes:

- 121 1. Two flow meters (Brooks 4800 series/ 50-500 ml/min) to regulate the flow of O₂ and N₂
 122 simultaneously mimicking the ratio of these gases in ambient air.
 123 2. An NO_x source via a 200 ml solution of IMD (10⁻⁵ M) producing 40-50 ppbv of NO₂ and 0.1-0.5
 124 ppbv of NO contained in a cylindrical Pyrex glass flow-reactor (0.65 L, length 27 cm and internal
 125 diameter 5.7 cm). This was based on our previous study showing that irradiating a solution of
 126 IMD with a polychromatic light (λ_{\max} = 365 nm) leads to the production of NO_x (NO + NO₂) with
 127 NO₂ being the major product [27].

128 A UVP ozone generator equipped with a UV pen-ray lamp that uses the photochemical reaction of
 129 O₂ under UVC (185 nm) to produce the continuous flow of O₃.

- 130 3. Two air-tight stainless-steel reactors (see **Fig.SI-2.**) that are cylindrical with a Pyrex glass top
 131 window for irradiation. A small one (Reactor S- 0.6 L) for leaves and a big reactor (Reactor B- 12
 132 L) for the full-size plant.

- 133 4. 2x55W Starlite tubes ($\lambda= 400-800$ nm) that were placed at a distance of ≈ 30 cm above the reactors
 134 for irradiation. Absolute Irradiance at this distance was $6-7 \mu\text{W}/\text{cm}^2/\text{nm}$ @ 610 nm. This lamp is
 135 commonly used for growing plants indoors where it covers the light range needed for
 136 photosynthesis (see spectrum **Fig.SI-3**).
- 137 5. A NO_x Thermo scientific 42i model-NO NO₂ NO_x analyzer (chemiluminescence analyzer). To
 138 measure the nitrous acid (HONO) and estimate its contribution to the NO₂ measured levels, a
 139 Na₂CO₃-impregnated quartz filter was installed upstream of the NO_x monitor, to trap HONO. Its
 140 concentration was then calculated by measuring the difference between measured NO₂ values with
 141 and without the HONO scrubber.
- 142 An O342e ozone analyzer O₃ (Environnement S.A). Both analyzers were online real-time
 143 analyzers with a 10 s temporal resolution.

144 The tubes used were PTFE (Teflon) to minimize secondary reactions, the fitting and valves were stainless
 145 steel from Swagelok (Lyon-France), and the temperature was regulated to 23 °C by an air conditioner.

146 2.3. Calculation of deposition velocities and plant uptake coefficients

147 For the plants tested in this study, transient deposition velocities (v_d) for NO₂ and O₃ were calculated,
 148 similar to Poppendieck et al. [28] and Abbass et al.[29], based on a mass balance that is shown in equation
 149 (1):

$$150 \quad \frac{dC_{out}}{dt} = \lambda(C_{in} - C_{out}) - v_{d(p)}C_{out} \frac{A_{(p)}}{V} - v_{d(c)}C_{out} \frac{A_{(c)}}{V} \quad (1)$$

151 Where $\frac{dC_{out}}{dt}$ represents the change in the outlet O₃ or NO₂ concentration (ppb h⁻¹), C_{in} and C_{out}
 152 are the outlet concentration of NO₂ or O₃, in the inlet and the outlet of the exposure chamber
 153 (ppbv), respectively, λ is the air exchange rate for the chamber (h⁻¹), $v_{d(p)}$ and $v_{d(c)}$ are the
 154 deposition velocities for a plant and chamber (m/h), respectively, $A_{(p)}$ and $A_{(c)}$ are the exposed

155 area of the plant and chamber walls (m^2), respectively. Eq. (1) was solved for the transient deposition
156 velocity shown in equation (2):

$$157 \quad v_{d(p)}^t = \frac{V}{A_{(p)}} \frac{1}{C_{out}^t} \left[\lambda (C_{in}^t - C_{out}^t) - v_{d(c)} C_{out} \frac{A_{(c)}}{V} - \frac{C_{out}^t - C_{out}^{t+1}}{\Delta t} \right] \quad (2)$$

158 Where $v_{d(p)}^t$ is the time varying deposition velocity for a plant, t and t indicate consecutive data
159 points (h), V is the volume of the test chamber. The deposition velocity associated with chamber
160 walls $v_{d(c)}$ was observed to be negligible for all experiments. To facilitate comparison across
161 plants, the near steady-state deposition velocity was calculated when the rate of change in exit
162 concentration was less than 2 ppb over 15 min. The uptake coefficients U_p^t were then calculated
163 by multiplying the deposition velocity $v_{d(p)}^t$ by the inlet concentration of NO_2 or O_3 (C_{in}^t) after
164 its conversion from ppbv to $\mu g/m^3$ (eq. 3).

$$165 \quad U_p^t = v_{d(p)}^t (C_{in}^t) \quad (3)$$

166 2.4. Analytical methods

167 *VOC analysis.* The composition of VOC produced by the three plant species was determined using
168 headspace gas chromatography coupled with mass spectrometry detection (HS-GC/MS; Shimadzu HS-20
169 coupled with QP2010SE). 1 g of leaves from each species was transferred into a 20 mL headspace glass
170 vial and incubated for 10 min at 80 °C. The analytical column (Mega 5-MS 30 m \times 0.25 mm) was
171 operated initially at 60°C for 1 min, followed by an 8°C min^{-1} ramp to reach 240°C and held for 4 min.
172 The mass spectrometer source was heated to 200°C, and signals were detected between mass to charge
173 ratios (m/z) of 50 and 350. Identification of the major constituents was carried out using the NIST 17
174 database and when necessary, using authentic standards.

175 *ATD-GC-MS*. After the ozonation of thyme leaves, the reactor gas phase was sampled for 3 min at a
176 sampling rate of 100 mL min⁻¹ into the Tenax sorbent tubes. After sampling, the tubes were thermally
177 desorbed using TurboMatrix thermal desorption unit (ATD 150, Perkin Elmer) equipped with a cold trap
178 (Carbotrap 300) and coupled to an Agilent 6890 gas chromatograph and an Agilent 5973 mass
179 spectrometry detector. The separation of desorbed volatiles was carried out using a HP-5 μ s column (25 m
180 \times 0.25 mm \times 0.25 μ m) operated initially at 50 °C for 1 min, followed by a 10°C/min ramp to reach 230°C.
181 Mass spectra were scanned between m/z 35 and m/z 350 with the source temperature set at 20°C.

182 *HPLC-DAD*. HPLC analyses were performed using a NEXERA XR HPLCDAD apparatus. Separation
183 was conducted using a phenomenex reversed phase C18 column (100 mm \times 2.1 mm, 2.6 μ m particle size)
184 and a binary solvent system composed of 10% acetonitrile and 90% water at a flow of 0.2 mL/min.
185 Analysis time was 10 minutes. HPLC analyses allowed the monitoring of thymol disappearance as well as
186 its absorption spectrum.

187 *Scanning electron microscopy (SEM)*. The structure of thyme cuticular surfaces before and after ozonation
188 were characterized using scanning electron microscope. Leaves were mounted on aluminum stubs using
189 double-sided adhesive tape and sputter-coated with 10-15 nm gold-palladium (20 s, 25 mA, partial argon
190 pressure 60 mTorr, Denton Desk V. The samples were investigated with a field-emission scanning
191 electron microscope (SH 4000 M) using a 20 kV acceleration voltage and a 10 mm working distance.
192 Pictures were taken from adaxial and abaxial leaf surfaces.

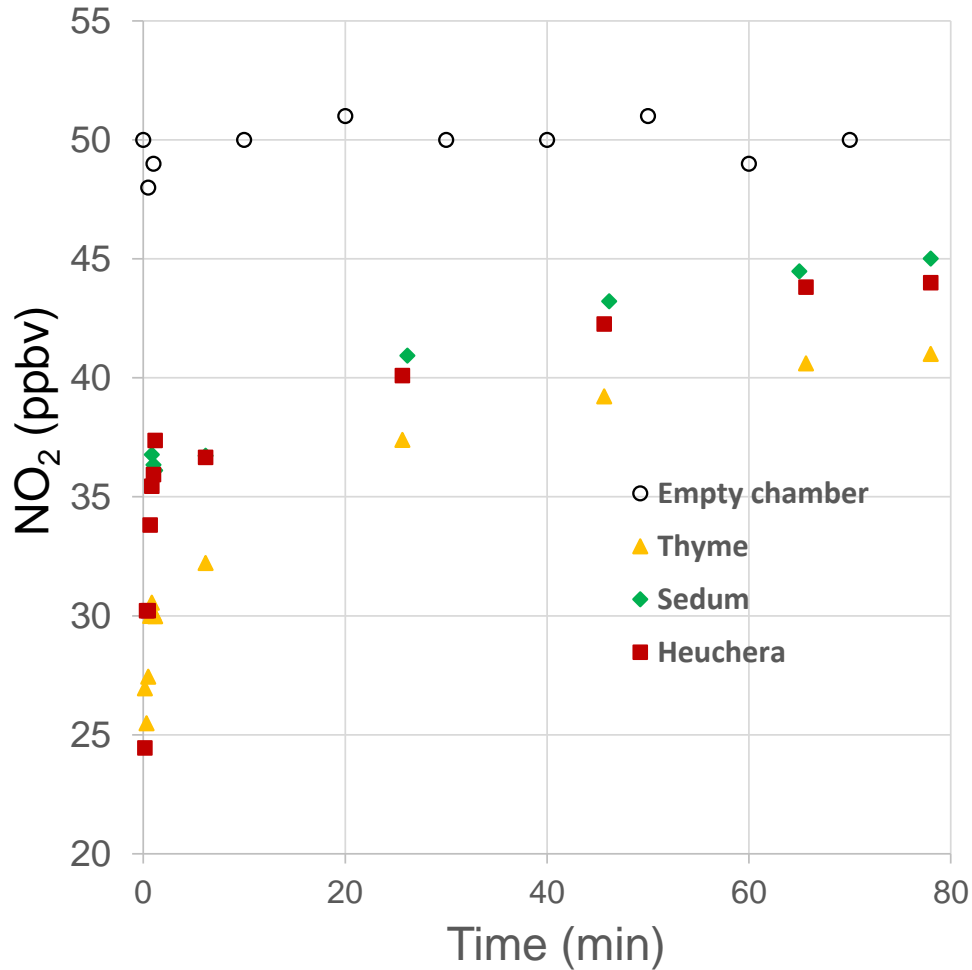
193 **3. RESULTS AND DISCUSSION**

194 3.1. Depollution capacity of detached leaves

195 3.1.1. NO₂ uptake

196 A maximum of 1 g of leaves was irradiated in the reactor for 1 hr while being ventilated with pure
197 synthetic air at a flow rate of 0.8 L/min (green line in Fig. 2) under visible light allowing the plant to adapt
198 to the conditions given before measuring the uptake. During this period, NO₂ generated by IMD was

199 directly monitored and its average concentration was found to be relatively stable around 50 ± 2 ppbv.
200 Following the 1 h pre-conditioning of the plant, NO₂ gas flow was introduced into the reactor containing
201 the detached leaves and the NO₂ concentration was monitored initially every 10 seconds and then
202 regularly until reaching a steady-state to calculate the NO₂ uptake. In control experiment, NO₂ flow was
203 passed through empty chamber (no leaves) and its concentration showed negligible drop suggesting a
204 negligible background removal of NO₂ due to chamber walls (See Fig. 3). In the presence of detached
205 leaves of green roof species, the chamber exit concentration of NO₂ concentration increases quickly in the
206 first minute as the chamber is filled with constant level NO₂ followed by a slower and progressive
207 increases until approaching a steady-state after 1h of exposure. At the end of the experiment, thyme
208 showed the highest NO₂ uptake with a reduction of about 9 ppbv in NO₂ concentration followed by sedum
209 and heuchera with a reduction of about 5-6 ppbv. The near steady-state deposition velocities for the three
210 plants were calculated by averaging the last 15 min of the exposure.



211 **Fig.3.** Empty chamber and outlet NO₂ concentration for sedum, thyme, and heuchera.

212 **Table 1** shows the near steady-state NO₂ deposition velocities and corresponding uptake coefficients
 213 for the three plant species tested. While Heuchera seems to perform as good as sedum according to Fig. 3,
 214 the exposed surface of its leaves was twice higher than that for Sedum and Thyme due to its large leaves.
 215 Yang et al [16] estimated the removal capacity of 71 green roofs using a big leaf dry deposition model and
 216 reported an average uptake coefficient of 260 μg/m²/h for NO₂ which is comparable to the values reported
 217 in this study. In addition, the calculated $v_{d(p)}^t$ (1.70 – 5.56) fall also within the range of v_d in their model
 218 (0.36 – 21.6 m/h). Our values are also in agreement with those reported by Currie and Bass [20] who used
 219 the UFORE model (urban forest effects model) and grass as a proxy unit for green roofs and reported an
 220 NO₂ uptake of 300 μg/m²/h.

221 **Table.1.** Near steady-state NO₂ deposition velocities and plant uptake coefficients

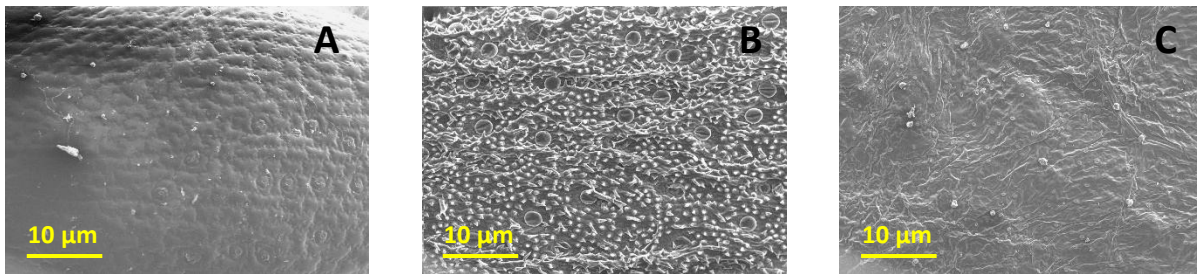
Plant	$v_{d(p)}^t$ (m/h)	U_p^t ($\mu\text{g}/\text{m}^2/\text{h}$)
Sedum	2.99	282
Thyme	5.56	523
Heuchera	1.70	160

222 To better understand the uptake mechanisms and the difference between studied species, several
223 experimental factors such as the stomata, water and chemical reactions were investigated.

224

225 - **Effect of stomata**

226 Leaf stomates are very important organs on the leaf surface as they control exchange of plants with
227 the environment. In general, green plants affect air pollutants by taking up gaseous pollutants primarily
228 through leaf stomates. The higher the density, the more CO₂ and gaseous pollutants can be absorbed or
229 released [30].



230 **Fig.4.** SEM Images of the three studied plants: sedum (A), thyme (B), and heuchera (C).

231 Using SEM, we observed the stomates on each leaf and estimated the stomatal density and average
232 stomatal areas by taking into consideration abaxial and adaxial sides. Highest stomata density was seen
233 with heuchera followed by thyme and sedum ($40 \text{ mm}^{-2} \pm 2$, $6 \text{ mm}^{-2} \pm 2$, and $4 \text{ mm}^{-2} \pm 2$ respectively).
234 However, thyme exhibited the largest stomatal area ($8400 \pm 150 \mu\text{m}^2$) while those of sedum and heuchera
235 were equal to $5700 \pm 150 \mu\text{m}^2$ and 1400 ± 150 respectively. This finding suggests that the higher stomatal
236 area for thyme could be responsible for its better performance in removing NO₂.

237 - **Effect of transpiration (surface reaction)**

238 A fraction of the consumption of NO₂ could be due to reactions with VOCs emitted by the plants. In
239 general, NO₂ has a low reactivity towards VOCs. However, NO_x might generate O₃ by photolysis under
240 UV. As UV was not present, this pathway should be negligible. An alternative possibility is the decay of
241 NO₂ through reaction with water leading to the formation of nitrous acid or HONO (process 1).

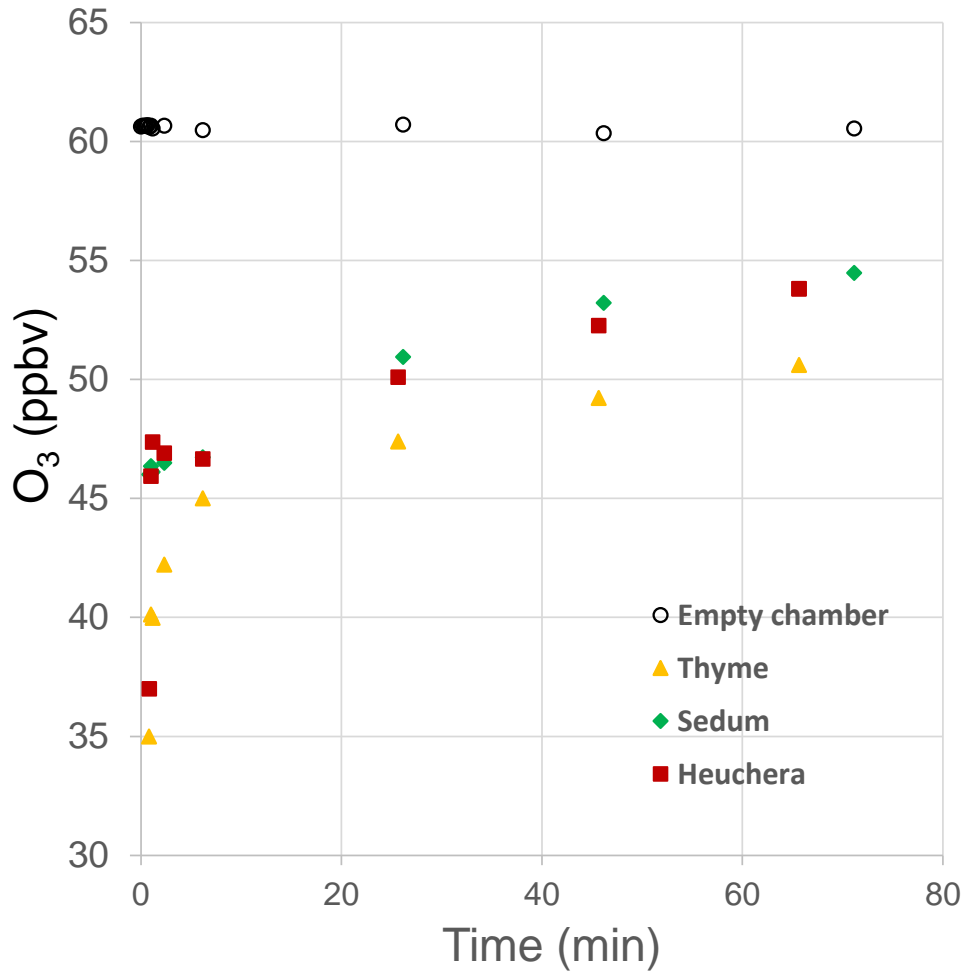


243 Such reaction is possible in the case of sedum particularly as it is an evergreen plant with moist leaves
244 and transpiration can occur. In our experiments, sedum might release moisture after being irradiated and
245 its water might react with NO₂ to yield HONO. We checked this hypothesis by performing experiments
246 aiming to monitor the formation of HONO. This was done by including Na₂CO₃ trap to sample HONO as
247 described in the experimental section. In the same conditions as before, 1 g of leaves was irradiated under
248 visible light for 1 h and the NO₂ uptake was monitored using sodium carbonate as a trap. The difference in
249 the NO₂ uptake in the presence and absence of the trap reveals the uptake due to the reaction between NO₂
250 and water. Comparing the NO₂ values with and without the trap, we conclude that 55% of the uptake
251 capacity was due to the reaction as shown in **process 1**. In the case of other species, no significant HONO
252 production was observed, confirming that NO₂ uptake in the case of sedum is enhanced by surface water
253 and its reaction with NO₂. This finding highlights the importance of chemical reaction in addition to
254 stomatal uptake in the overall performance of plant species and could have implication on the
255 photochemistry of air pollutants since HONO can undergo direct photolysis to produce hydroxyl radicals
256 (OH[•]).

257 3.1.2. O₃ uptake

258 **Fig.5.** illustrates the time evolution of the outlet concentration of O₃ in the case of an empty chamber
259 and in presence of the three studied plants. The same steps were followed as the ones in part 2.1 using

260 same plants, irradiation system, and duration (1 hour of pre-conditioning in the chamber). As for the
 261 experiment with NO₂, thyme showed the highest O₃ uptake with a reduction of about 10 ppbv followed by
 262 sedum and heuchera with a reduction of about 6-7 ppbv. **Table.2** shows the near steady-state O₃
 263 deposition velocities and plant uptake coefficients for the three studied plants calculated by averaging the
 264 last 20 min of the exposure.



265 **Fig.5.** Empty chamber and outlet O₃ concentration for sedum, thyme, and heuchera.

266

267 **Table.2.** Near steady-state O₃ deposition velocities and plant uptake coefficients.

Plant	$v_{d(p)}^t$ (m/h)	U_p^t (μg/m ² /h)

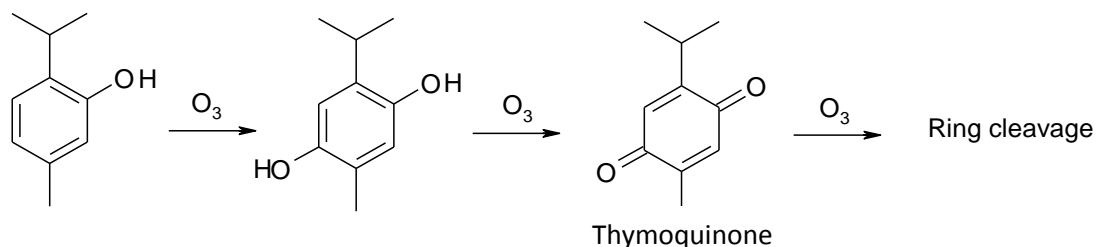
Sedum	2.69	317
Thyme	4.82	569
Heuchera	1.60	189
Yang et.al [10]	1.8	100-6500
Curie et. Bass [11]	0.18	-

268 The calculated values in our study are in agreement with those reported by Yang et al. [16] whereas
269 the study of Curie et Bass [20] showed lower values compared to those found here.

270 - **Effect of thyme volatile metabolites**

271 While the higher stomatal area can be responsible for the better performance of thyme in removing O₃,
272 O₃ can potentially react with plant volatile metabolites particularly in the case of thyme which is known to
273 release several terpenes in addition to thymol. For these reasons, thyme was selected as the main species
274 to study in the following experiments. For a simpler approach, experiments were undertaken with one of
275 the major emitted VOC, thymol (a phenolic derivative), first in solution to examine the feasibility of
276 thymol degradation by O₃ and to facilitate the identification of by-products. O₃ reactions in solutions can
277 be easier to perform and could provide a first indication of possible heterogeneous reactions between
278 thymol and O₃ on leaves. Water can also be present on leaf surface and could participate in the reaction
279 mechanisms. Following this feasibility test, additional experiments on thyme leaves were carried out to
280 mimic realistic conditions and to investigate the heterogeneous reactivity of thyme volatiles with O₃.

281 *Reaction of thymol with ozone in solution.* We prepared a 20 ml solution of thymol (2x10⁻⁴ M) in ACN
282 and O₃ at a concentration of 4 ppm was bubbled into it for almost 6 h. Results were monitored by HPLC-
283 DAD analysis that showed that 50 % of thymol was degraded. The percentage of degradation is related to
284 ozone and thymol concentrations. According to a study on the catalytic ozonation of thymol, the
285 simplified proposed degradation mechanism is the following: the *para* and *ortho* positions of the
286 hydroxyl on thymol are attacked by O₃ and hydroxyl radical. This leads to diols with a backbone of
287 cymene (**Fig.6**). Several reactions then can take place prompting mineralization [25].



288 **Fig.6.** Thymol degradation pathway via the reaction with O₃.

289 The GC-MS analysis of an experiment conducted on thymol and O₃ revealed the production of
 290 Thymoquinone which corroborates the proposed mechanism.

291 *Reaction of thyme VOCs with ozone.* Two samples of detached thyme leaves (2 g) were introduced into
 292 Pyrex flow-reactors, under irradiation with visible light. To monitor the effect of O₃, the first sample (S1)
 293 was not exposed to O₃ while the second (S2) was exposed to O₃ (153 ppbv). In both cases, the production
 294 of VOC was monitored via sampling on sorbent tubes followed by ATD-GC-MS analysis.

295 **Table.3.** shows the four major terpenes emitted in addition to thymol. After 1 h of ozonation, their
 296 levels decreased drastically as expected since terpenes are known to undergo oxidation by O₃. This was
 297 associated with the identification of various oxidation products such as linalool-oxide, keto-
 298 limononaldehyde and thymoquinone. This finding confirms the role that plays thyme VOC metabolites in
 299 the observed good performance for the removal of O₃. However, while the uptake of ozone can be
 300 enhanced by the emission of terpenes, one should consider the consequences of O₃ reactions with terpenes
 301 since it can lead to the formation of secondary organic aerosols (SOA) [31]. Unfortunately, this was not
 302 confirmed here but future experiments are needed to measure the possible emission of ultrafine particles
 303 due to reaction of O₃ with thyme volatiles, and to estimate its impact on air pollution.

304

305 **Table.3.** Major VOC products identified in S1 and S2.

Sample	VOC collected mass (ng)				
	<i>Cymene</i>	<i>Limonene</i>	<i>Thymol</i>	<i>Eucalyptol</i>	<i>Linalool</i>
S1 (no O₃)	12.6	8.5	22.5	13.2	31.3
S2 (with O₃)	0.4	Non detected	Non detected	0.3	1.6

306 3.2. Depollution capacity of thyme full-size plant

307 3.2.1. NO₂/O₃ uptakes

308 These following experiments were conducted using a small thyme plant (with an estimated total leaf
309 area of 500 cm²) which was pre-conditioned in the big reactor (12 L) with 1 h visible light irradiation
310 while soil was fully covered during experiments to ensure the least interference possible. After 1h of
311 exposure to NO₂ (50 ppbv) the NO₂ concentration dropped to reach a near-steady state around 10 ppbv.
312 Using eq.(1) and (2) we calculated a $v_{d(p)}^t$ of 3.84 m/h. In the case of O₃, same conditions were used as
313 with detached leaves with the exception of O₃ inlet concentration which was increased to 110 ± 3 ppbv to
314 reduce measurement uncertainty. Under these conditions, O₃ concentration dropped by around 91 ppbv to
315 reach 19 ppbv after 1h of exposure (Fig. SI-4). Assuming a near steady-state condition we obtained a
316 $v_{d(p)}^t$ of 4.65 m/h. These values are comparable with those obtained using detached leaves particularly
317 when considering the uncertainty in the estimation of total leaf area, presence of soil, emission of volatile
318 metabolites and the measurement uncertainty. It is noteworthy that a small production of NO was
319 observed when thyme plant was irradiated which was not detected with detached leaves. NO is a key
320 signaling molecule in plant physiology. However, its production in photosynthetic organisms remains
321 partially unresolved. The best characterized NO production route involves the reduction of nitrite (NO₂⁻)
322 to NO via different non-enzymatic or enzymatic mechanisms. To better characterize the role of soil in the
323 production of NO and the uptake of pollutants, additional experiments using soil only were carried out.

324 - **Effect of soil on NO_x production and uptake and of O₃ uptake**

325 Soil, as well, is used on green roofs so its uptake towards NO_2 and O_3 in addition to its NO_x
326 production were studied. In these experiments the same soil used for thyme was studied here.

327 *NO_x production.* After 1 h of visible light irradiation, a mixture of N_2 and O_2 (pure synthetic air) was
328 passed through the reactor containing the soil to monitor the NO/NO_2 production. Studied soil was either
329 wet or dry, but the steps were the same in both cases. Only NO was produced at a level of ≈ 20 ppbv in the
330 case of dry soil, and ≈ 10 ppbv in that of wet soil (**Fig.SI-5**). Irrigation, N-fertilizers, and bacteria are
331 known to be responsible for NO_2 production [32]. In our experiments, the adsorbed NO_2 is probably
332 undergoing reactions producing $\text{NO}_{(\text{g})}$ in case of both dry and wet soils; or reacting with water producing
333 ions e.g. NO_2^- and NO_3^- (case of wet soil).

334 *NO₂/O₃ uptake.* The same experimental steps were followed as in section 3.2. In the case of O_3
335 (see Fig. SI-4), the reduction in concentration (Δ) for exposed soil ranged between 85 (dry) and 88 (wet)
336 ppbv which is very close to that observed with thyme (91 ppbv). This suggests that soil can also be as
337 effective in removing O_3 and could contribute to increase the overall performance of green roofs. On the
338 other hand, soil contributed to the removal of 15 ppbv (wet) to 35 ppbv (dry) of NO_2 as compared with
339 about 40 ppbv for thyme (Fig. SI-6) indicating that the thyme plant is more effective in removing NO_2 .
340 The higher NO_2 uptake by dry soil is likely associated with the higher surface area available for adsorption
341 as compared with wet soil which can be partially saturated with water.

342 4. CONCLUSION

343 Natural air pollution mitigation approaches are needed to help improve air quality especially in
344 urbanized areas. One promising recommended approach is the use of green roofs. In this study, we
345 developed a new NO_2/O_3 bench-scale experimental system to measure the depollution performance of
346 different green roofs species.

347 After the screening of several species, 3 species were found to be the most efficient for the
348 NO_2/O_3 uptakes: *sedum sexangulare*, *thymus vulgaris*, and *heuchera americana L.* They offer a diversity

349 between being aesthetically pleasant, drought tolerant, climate resilient, and exhibiting good uptakes. NO₂
350 uptake coefficients ranged from 160 to 523 μg/m²/h while that of O₃ varied between 189 and 569 μg/m²/h.
351 These findings are in accordance with previously reported data using the big-leaf dry deposition models.
352 Nevertheless, values were relatively higher in our experiments possibly due to other mechanisms than dry
353 deposition (adsorption) such as the reactions between the VOCs and O₃ especially in the case of thyme,
354 and between NO₂ and water in the case of the evergreen plant: sedum -which are not considered yet in
355 models. If we apply our experimental results using the existing model [16] by taking the average
356 deposition velocity in our experiments (0.095 m/h for NO₂ and 0.084 m/h for O₃), the total uptake by the 3
357 species (sedum, thyme, and heuchera) could reach 9 kg/ha/year of NO₂ and around 13.6 kg/ha/year of O₃.
358 Assuming that Paris has around 76 ha of green roofs and walls (2016) [33], and if the three species
359 investigated in this study were to be used, one can estimate that 683 kg/year of NO₂ and 1037 kg/year of
360 O₃ can be mitigated.

361 While our study focused only on the uptake of two air pollutants, additional research should be
362 carried to measure the performance of green roof species towards PM_{2.5} and to investigate the potential
363 formation of SOA. In addition, our experimental design does not consider some important variables such
364 as the effects of humidity, lighting spectrum/intensity changes, nor the diurnal and seasonal cycles of the
365 plant. In addition, field evaluation of laboratory results should be carried in order to better understand the
366 effects of seasonality and weather conditions on the depollution performance of green roofs.

367 **5. ASSOCIATED CONTENT**

368 **Supporting information (e-component) 6 figures**

369 The Volatile Organic Compounds emitted by thyme obtained by headspace-GC-MS. The small
370 and big reactors containing the detached leaves and the full-size plant/soil. The light spectrum of the
371 lamps used in our experiments for irradiation. O₃ uptakes by Thyme and soil (wet and dry) after

372 irradiation. NO production by the soil (wet and dry) after being irradiated by visible light for 1 h. NO₂
373 uptakes by the soil (wet and dry) after 1 h of visible light irradiation.

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