



HAL
open science

Assessment of mean annual NO₂ concentration based on a partial dataset

Xavier Jurado, Nicolas Reiminger, José Vazquez, Cédric Wemmert, Matthieu Dufresne, Nadège Blond, Jonathan Wertel

► To cite this version:

Xavier Jurado, Nicolas Reiminger, José Vazquez, Cédric Wemmert, Matthieu Dufresne, et al.. Assessment of mean annual NO₂ concentration based on a partial dataset. *Atmospheric Environment*, 2020, 221, pp.117087. 10.1016/j.atmosenv.2019.117087 . hal-02398708

HAL Id: hal-02398708

<https://hal.science/hal-02398708>

Submitted on 10 Dec 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



1 Assessment of mean annual NO₂ concentration based on a partial 2 dataset

3
4 Xavier Jurado^{1,2†*}, Nicolas Reiminger^{1,2*}, José Vazquez², Cédric Wemmert², Matthieu Dufresne¹,
5 Nadège Blond³, Jonathan Wertel¹

6
7 ¹AIR&D, 67400, Illkirch-Graffenstaden, France

8 ²ICUBE Laboratory, CNRS/University of Strasbourg, 67000, Strasbourg, France

9 ³LIVE Laboratory, CNRS/University of Strasbourg, 67000, Strasbourg, France

10 *These authors contributed equally to this work

11 †Corresponding author: Tel. +33 (0)3 69 06 49 40, Mail. xjurado@air-d.fr

12
13 Please cite this paper as : Jurado, X. , Reiminger, N., Vazquez, J., Wemmert, C., Dufresne, M.,
14 Blond, N., Wertel, J., 2020. Assessment of mean annual NO₂ concentration based on a partial
15 dataset. Atmospheric Environment 221, 117087. DOI: 10.1016/j.atmosenv.2019.117087

17 Abstract:

18 NO₂ is a pollutant harmful to both health and the environment. The European Union and the
19 World Health Organization have developed guidelines in terms of pollutant. The value of 40
20 µg/m³ is set by both entities as the annual mean NO₂ concentration not to be exceeded to prevent
21 risks for human health. To assess this given value, yearlong in situ measurements are required.
22 However, sometimes only partial data are available, such as having only NO_x (NO + NO₂)
23 information, on the one hand, and, on the other hand, brief NO₂ measurements performed over
24 few months. To overcome the first hurdle, several methods exist in the literature to transform
25 NO_x data into NO₂ data. The method of Derwent and Middleton is the most appropriate for
26 France with less than 8% of deviation and even less deviation when considering rural and urban
27 sites. For all values, NO_x concentrations behave as expected with higher concentrations in
28 autumn and winter than in spring and summer. However, for NO₂ this trend changes around 80
29 µg/m³ for which the spring and summer values are higher. Therefore, to maximize
30 measurements to assess an upper limit on annual NO₂ concentration over a short period of time,
31 those measurements should be done in winter if an annual concentration of less than 80 µg/m³
32 is expected, otherwise they should carry out in summer. To tackle the second issue, a second
33 order polynomial approach is built on a Paris dataset covering years between 2013-2017 to
34 determine annual mean concentrations with monthly mean concentrations and gives an overall
35 error of 10%. The law built on Paris was then tested on several regions in France for the same



36 period and resulted in predicted values with a mean error of about 15 % compared to the
37 measured ones. In the end, the presented methodology allows covering twelve times more
38 ground with a single NO₂ or NO_x sensor with an acceptable error.

39

40 **Keywords:** Air pollution, Nitrogen oxides, Seasonal variations, Monthly variations, Annual
41 concentration assessment.

42

43 **Highlights:**

- 44 • The Derwent and Middleton function enables converting annual NO_x into NO₂ in
45 France.
- 46 • NO₂ and NO_x exhibit strong seasonal and monthly variabilities.
- 47 • The behavior of NO₂ concentrations related to seasons depends on their levels.
- 48 • Functions are presented to assess annual NO₂ concentration using monthly ones.

49

50

51

52

53

54

55

56

57

58

59

60

61

62

63

64

65

66

67

68

69 1. Introduction

70 While many measures are implemented to improve air quality, atmospheric pollution still
71 exceeds the thresholds of health standards. Next to particulate matter or ozone, nitrogen dioxide
72 (NO₂) has been selected as an air pollutant with the highest priority whose monitoring must be
73 routinely carried out (WHO, 2005). Nitrogen oxides are known to be a source of respiratory
74 symptoms and diseases (Kagawa, 1985), and they are also harmful to the environment as they
75 play the role of precursor in nitric acid production, leading to acid rains (Likens et al., 1979).
76 These air pollutants are mainly due to anthropogenic sources. Indeed Thunis (2018) showed
77 that in several cities in Europe, NO_x is mainly emitted by transport and industrial sources, with
78 varying contributions depending on the city. For example, in dense urban areas such as Paris,
79 56% of NO_x comes from traffic-related emissions and 18% from the tertiary and residential
80 sectors (AIRPARIF, 2016).

81 Nitrogen dioxide (NO₂) is, with nitric oxide (NO), one of the two components forming nitrogen
82 oxides. In the European Union (EU) and more generally around the world, NO₂ is the most
83 measured component. Indeed, NO₂ can have significant harmful effects on health, inducing
84 numerous diseases like bronchitis, pneumonias, etc. (Purvis and Ehrlich, 1963), but it can also
85 increase the risks of viral and bacterial infections (Chauhan et al., 1998).

86 To obtain standard values for the purposes of comparison, the European Union (EU) and the
87 World Health Organization (WHO) have issued critical values that should not be exceeded to
88 protect the public from the health effect of gaseous NO₂. For this purpose, two standard values
89 have been enforced : a hourly mean of 200 µg/m³ and an annual mean of 40 µg/m³ not to exceed
90 given by both the WHO (WHO, 2017) and the EU (Directive 2008/50/EC). Studies have shown
91 that the annual standard is generally more stringent than the hourly one (Chaloulakou et al.,
92 2008; Jenkin, 2004). However, year-round measurements are needed to gather concentrations
93 values that can be compared directly to this standard. This requirement is not a constraint when
94 monitoring stations are located permanently in one area. Nonetheless, it becomes constraining
95 when the objective is to evaluate urban planning projects over a limited period: the
96 heterogeneity of urban areas requires controls related to the standard at several key locations
97 where no permanent stations have been installed and where only temporary measurements are
98 economically viable. Moreover, these temporary measurements may only provide information
99 on NO_x concentrations but no direct information on NO₂. Thus, one question arises in such
100 situation: how can annual mean NO₂ concentrations be determined using only a short
101 measurement period of NO₂ or NO_x concentrations ?



102 The Leighton relationship provides information on the ratio between NO and NO₂
103 concentrations as a function of O₃, a chemical constant rate and a photolysis rate considering
104 the photochemical steady state (Leighton, 1961). Unfortunately, it was demonstrated that using
105 this method with more than 10 ppb of O₃ leads to an increasing error by not taking into account
106 VOC chemistry (Sanchez et al., 2016). Different methods were proposed to evaluate the
107 photolysis rate (Wiegand and Bo, 2000), but computing an annual representative photolysis rate
108 can still lead to a wrong evaluation of the seasonal dependencies between NO_x and NO₂.
109 Numerical computation based on complex chemical mechanisms involving more than 300
110 reactions with more than 100 species gives more accurate evaluations of NO₂ (Bright et al.,
111 2013; Kim et al., 2012). Nevertheless, when NO₂ concentration measures are missing there is
112 little chance that this information is known on other species such as VOCs. However, such
113 information is needed in the numerical computations.

114 Furthermore, seasonal variability of NO₂ and NO_x concentrations differs considerably between
115 summer and winter because NO₂ concentrations depend on photolysis conditions, and NO_x
116 molecules play a role in several chemical mechanisms in the troposphere, involving ozone (O₃)
117 and volatile organic compounds (VOC) (Seinfeld and Pandis, 2016). Robert-Semple et al.
118 showed that there is a relative standard deviation of more than 50% when calculating the mean
119 annual concentrations of both NO₂ and NO_x (Roberts–Semple et al., 2012). Moreover, Kendrick
120 et al. showed that there is a seasonal variability in NO₂ concentration even with constant hourly
121 seasonal traffic (Kendrick et al., 2015). Thus, these results show that a few months of NO₂
122 monitoring are generally not representative of a mean annual concentration despite existing
123 only slight seasonal variations of the main source, namely traffic-related emissions.

124 The aim of this study is first to evaluate whether one-parameter methods without any explicit
125 chemical mechanism found in the literature are sufficiently accurate to determine NO₂
126 concentrations based on monitored NO_x data in France. The second aim is to present a method
127 capable of providing the mean annual NO₂ concentration from one-month period of monitoring.
128 In this article, the different areas of study as well as the measurement method and the approach
129 to turn NO_x into NO₂ used are presented in section 2. Then, the results of the study on the NO_x-
130 based NO₂ concentration calculation in France, and the method presented for the mean annual
131 NO₂ concentration calculation based on monthly measurement periods, are presented in section
132 3.

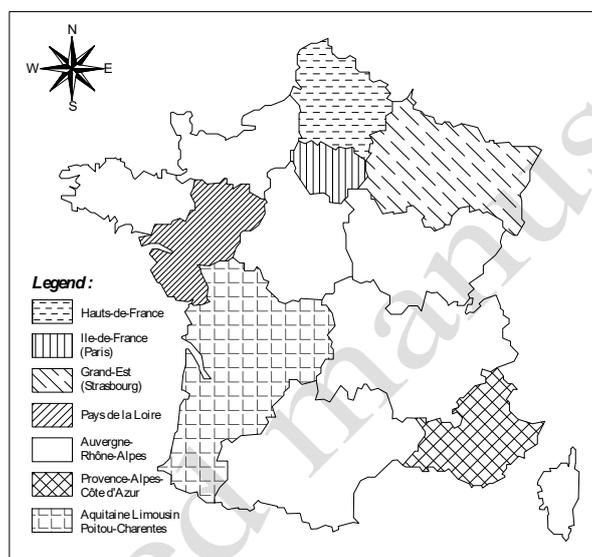
133

134

135 2. Material and methods

136 2.1. Study location

137 This work uses NO_2 and NO_x concentrations monitored in a large number of regions in France,
 138 including from North to South: Hauts-de-France, Grand-Est (Strasbourg region), Ile-de-France
 139 (Paris region), Pays de la Loire, Auvergne-Rhône-Alpes and Provence-Alpes-Côte d’Azur.
 140 These areas were chosen for the availability of data and to better cover the minimum and
 141 maximum latitudes and longitudes of France. The location of these regions is presented in
 142 Fig. 1.



143
 144 Fig. 1. Location of the different study areas used.

145 2.2. Data availability

146 The data used in this work were obtained via the open access database provided by the different
 147 air quality monitoring authorities known as AASQA, the French acronym for “Approved Air
 148 Quality Monitoring Associations”. In particular, the data were provided by the organisations
 149 Atmo Haut-de-France (Haut-de-France), Atmo Grand-Est (Strasbourg region), AIRPARIF
 150 (Paris region), Air Pays de la Loire (Pays de la Loire), Atmo Auvergne-Rhône-Alpes
 151 (Auvergne-Rhône-Alpes), Atmo PACA (Provence-Alpes-Côte d’Azur) and Atmo Nouvelle-
 152 Aquitaine (Aquitaine Limousin Poitou-Charentes). The data are mainly mean annual NO_2 and
 153 NO_x concentrations over a five-year period from 2013 to 2017, but other data such as hourly
 154 measured concentrations for the Strasbourg region in 2018 were also obtained. Additional
 155 contacts were also made with AIRPARIF to obtain more specific data for the Paris Region like
 156 hourly measured concentrations from 2013 to 2017 with their corresponding uncertainties. A

157 summary of the available data, corresponding to about 270 different sensors, is presented in
 158 Table 2.

159 Table 2. Summary of the available data

Region	Data availability (years)	NO _x			NO ₂			Number of stations
		A	M	H	A	M	H	
Ile-de-France (Paris)	2013 - 2017			•			•	≈ 40
Grand-Est (Strasbourg)	2018			•			•	≈ 50
Hauts-de-France	2013 - 2017	•			•			≈ 15
Pays de la Loire	2013 - 2017	•			•			≈ 50
Auvergne Rhône-Alpes	2013 - 2017	•			•	•		≈ 60
Provence-Alpes-Côte d'Azur	2013 - 2017	•			•	•		≈ 25
Aquitaine Limousin Poitou-Charentes	2013 - 2017	•			•	•		≈ 30

160

161 2.3. Data range

162 The annual and monthly concentrations range from 10 to 340 $\mu\text{g}/\text{m}^3$ for NO_x and from 5 to
 163 95 $\mu\text{g}/\text{m}^3$ for NO₂, considering the complete dataset (all years, types and locations of stations
 164 included). According to these wide ranges, different types of stations were considered in this
 165 work including rural, suburban, urban and traffic stations. The dataset for the Paris region
 166 comprises 2% rural, 13% suburban, 54% urban and 31% traffic stations. The type of station
 167 was not always directly provided in the global France dataset. Thus, the percentage of each type
 168 of station was estimated based on the range of concentrations for each type of station in Paris.
 169 The corresponding results were 29%, 22%, 31% and 18% for rural, suburban, urban and traffic
 170 stations, respectively.

171 2.4. Monitoring method

172 The EU imposes a maximal uncertainty of 15% on AASQA for individual measurements
 173 averaged over the period considered regarding the limit values monitored by sensors. Thus, to
 174 satisfy the requirements, all AASQA use the same monitoring method in accordance with this
 175 constraint.

176 The reference method used for the measurement of nitrogen dioxide and oxides of nitrogen is
 177 known as chemiluminescence. Two chemiluminescence methods exist: on the one hand,
 178 chemiluminescence based on luminol reaction, and, on the other hand, chemiluminescence
 179 based on NO/O₃ reaction. The second method is the one used in France. In particular
 180 AIRPARIF uses the AC32M EN model from ENVE and the 42i model from THERMO
 181 SCIENTIFIC.

182 The principle of the method was well-described by Navas et al. (1997) and is based on the
183 reaction (1) between NO and O₃. This reaction produces an excited nitrogen dioxide (NO₂^{*}) that
184 emits infrared radiations when returning to a stable state. The luminous radiation emitted and
185 then measured is directly proportional to the NO concentration.



188 To obtain information on the NO_x concentration, it is first necessary to convert all the NO₂ into
189 NO before the measurement. After that, the resulting NO corresponding to the initial NO and
190 the NO derived from NO₂ are measured and the NO_x concentration is obtained. Combining both
191 the measured NO and NO_x concentrations provides the NO₂ concentration. Thus, the
192 uncertainties on NO₂ measurement are higher than those on NO or NO_x because the results are
193 obtained from both NO and NO_x measurements.

194 Based on the work of Navas et al., this kind of technique has very low detection limits, making
195 it a good tool for evaluating the concentration of nitrogen compounds for atmospheric purposes
196 (Navas et al., 1997). According to a personal communication with AIRPARIF, the maximal
197 uncertainty on the mean annual NO₂ concentration from 2015 to 2017 was lower than 10% with
198 a mean uncertainty of 6%.

199

200 2.5. Empirical methods to convert concentration from NO_x to NO₂

201 Several one-parametric empirical methods can be found in the literature to give an estimation
202 of NO₂ concentration based on NO_x concentration. Three methods were compared with the
203 entire France dataset:

- 204 • Derwent and Middleton function, a polynomial-logarithmic function linking hourly
205 averaged NO_x and NO₂ concentrations for NO_x concentrations in the range of 9.0 to
206 1145.1 ppb (Derwent and Middleton, 1996).
- 207 • Romberg et al. function, a rational function linking annual averaged NO_x and NO₂
208 (Romberg et al., 1996).
- 209 • Bächlin et al., another rational function linking annual averaged NO_x and NO_x (Bächlin
210 et al., 2008).

211 According to the above authors, the corresponding equations are (3), (4) and (5) respectively,
 212 with the hourly averaged NO_x and NO_2 noted $[\text{NO}_x]_h$ and $[\text{NO}_2]_h$ and annual averaged NO_x
 213 and NO_2 for the two other functions noted $[\text{NO}_x]_a$ and $[\text{NO}_2]_a$. All concentrations presented
 214 below are in $\mu\text{g}/\text{m}^3$ and $A = \log_{10}([\text{NO}_x]_h/1.91)$.

$$215 \quad [\text{NO}_2]_h = \left(2.166 - \frac{[\text{NO}_x]_h}{1.91} (1.236 - 3.348A + 1.933A^2 - 0.326A^3) \right) \times 1.91 \quad (3)$$

$$216 \quad [\text{NO}_2] = \frac{103 \cdot [\text{NO}_x]_a}{[\text{NO}_x]_a + 130} + 0.005 \times [\text{NO}_x]_a \quad (4)$$

$$217 \quad [\text{NO}_2] = \frac{29 \cdot [\text{NO}_x]_a}{[\text{NO}_x]_a + 35} + 0.217 \times [\text{NO}_x]_a \quad (5)$$

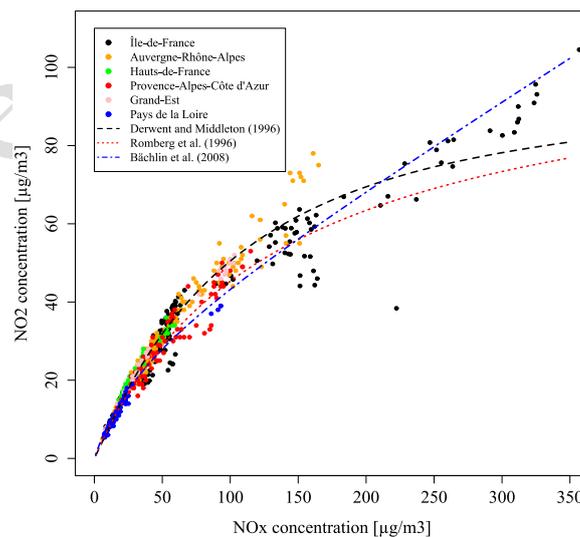
218 For the purpose of this work, mean annual concentrations were used instead of hourly averaged
 219 concentrations for the Derwent and Middleton function.

220 3. Results

221 3.1. Evaluation of annual NO_2 concentration based on NO_x data

222 3.1.1. Best fitting function in France

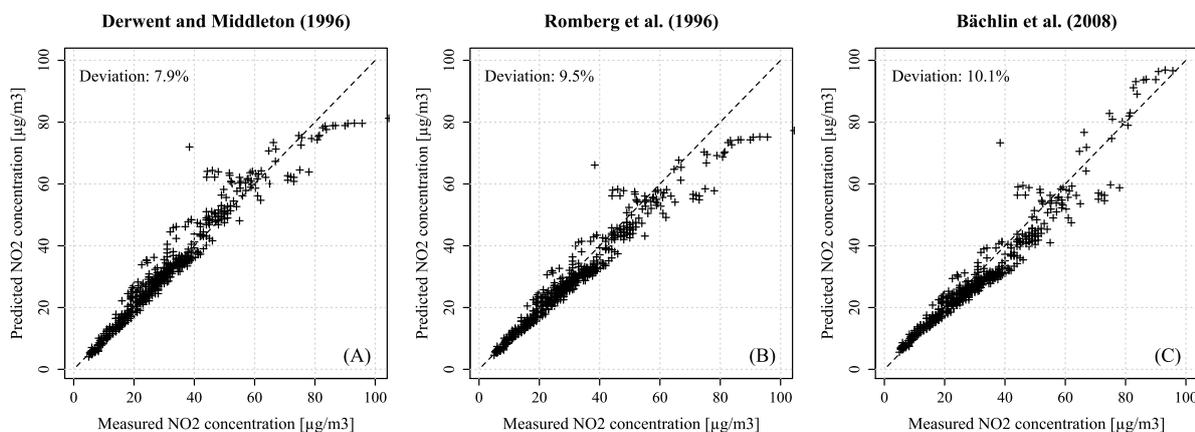
223 Fig. 2. shows the evolution of mean annual NO_2 concentration as a function of the mean annual
 224 NO_x concentration considering the total dataset (measurements from 2013 to 2017 for the six
 225 regions considered and all types of station included). The three empirical methods cited
 226 previously are also plotted.



227
 228 Fig. 2. Evolution of NO_2 concentration as a function of NO_x concentration and comparison with empirical functions

229 To obtain a better comparison between the three functions, predicted NO_2 concentrations
 230 calculated with measured NO_x concentrations were plotted against measured NO_2

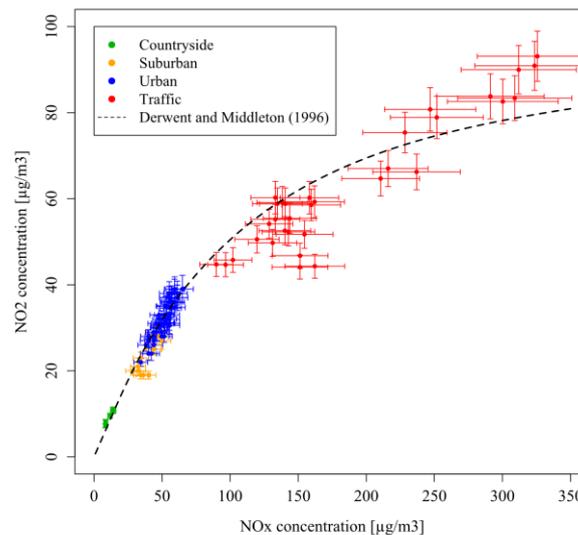
231 concentrations. The corresponding results are presented in Fig. 3. with the first bisector
 232 corresponding to ideal results. As shown in Fig. 3., the function from Bächlin et al. is the most
 233 appropriate for high NO_2 , thus high NO_x concentrations. However, based on Fig. 3. (A) and
 234 Fig. 3. (B) the results for lower NO_2 concentrations (less than $50 \mu\text{g}/\text{m}^3$) are better when using
 235 the function proposed by Derwent and Middleton (1996), and Romberg et al. (1996).
 236 Considering the difference between the predicted and measured concentrations, the function of
 237 Derwent and Middleton is the most appropriate with a deviation of less than 8%, whereas that
 238 of Romberg et al. (1996) leads to a deviation of 9.5%. Moreover, in this work, the function of
 239 Romberg et al. (1996) tends to slightly underpredict NO_2 concentrations. When choosing
 240 between two functions giving about the same deviation, the precautionary approach is to
 241 choose the function that overestimates NO_2 rather than the one which underestimates it. Hence,
 242 in France, Derwent and Middleton's function has been chosen and is advised by the authors to
 243 assess the NO_2 concentrations based on NO_x data. This is especially the case for the monitoring
 244 both in urban and rural sites. It should also be noted that these comparisons included several
 245 years of measurements and locations (various latitudes and longitudes), thus in principle giving
 246 independence to these parameters. However, for high NO_2 concentrations (higher than 70
 247 $\mu\text{g}/\text{m}^3$) the method fits less and less well.



248
 249 Fig. 3. Comparison between predicted and measured NO_2 concentrations for (A) the Derwent and Middleton function, (B) the
 250 Romberg et al. function, and (C) the Bächlin et al. function.

251 3.1.2. Application to Paris region

252 The information obtained in the Paris region was more detailed and included uncertainties as
 253 well as the type of station. Fig. 4. presents the mean annual NO_2 concentration for the Paris
 254 region dataset as a function of NO_x concentration with a distinction between the different types
 255 of station. Derwent and Middleton's function is also plotted.



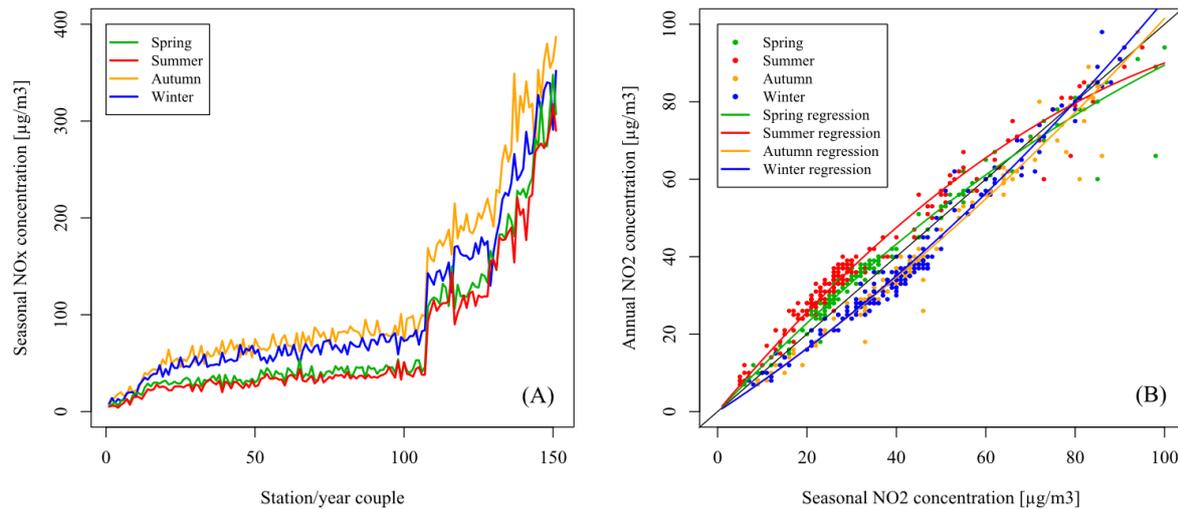
256

257 Fig. 4. Evolution of NO₂ concentration as a function of NO_x concentration for the Paris region dataset and comparison with
 258 Derwent and Middleton's function.

259 These results show that in accordance with previous observations, the best range of application
 260 for Derwent and Middleton's function is for NO_x concentrations lower than 80 µg/m³. As can
 261 be seen in Fig 4. this limit corresponds to the difference between urban and traffic stations for
 262 Parisian region. Thus, Derwent and Middleton's method applies best for rural, suburban and
 263 urban stations whereas the results are less accurate for traffic. Indeed, there are 92% of the data
 264 that are within the uncertainties range both in the countryside and in urban areas, while for
 265 traffic data it falls to 71%. The mean error on predicted NO₂ concentrations is 9% with a 95th
 266 percentile of 27%.

267 3.2. Seasonal variability of NO₂ concentration

268 The seasonal variability of NO₂ was studied using the Paris region dataset. Hourly NO₂
 269 concentrations were averaged for each station and each year of data, giving five mean
 270 concentrations per station and per year (one annual concentration and four seasonal
 271 concentrations). Fig. 5. (A) shows the differences between seasonal mean NO_x concentrations
 272 for each couple of year and station. Fig. 5. (B) shows the evolution of seasonal NO₂
 273 concentrations as a function of the annual NO₂ concentration for the same year of measurement.



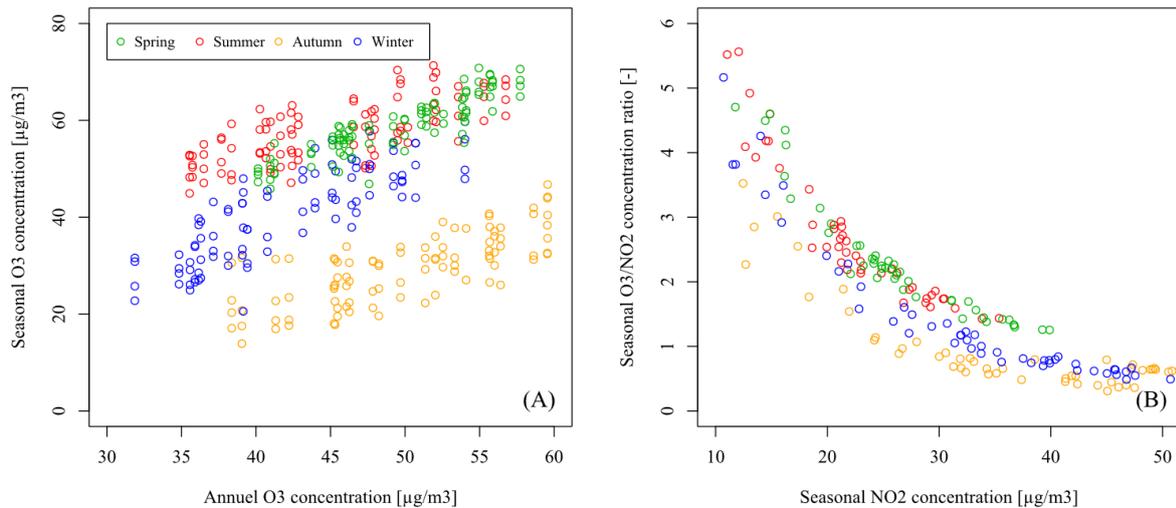
274
 275 Fig. 5. Comparison between seasonal NO_x concentrations for a given station and year of measurement in the Paris region (A)
 276 and the evolution of the annual NO₂ concentration as a function of seasonal NO₂ concentrations (B).

277 According to Fig. 5. (A), NO_x concentrations are strongly dependent on the season. Indeed,
 278 although summer and spring NO_x concentrations are similar, the concentrations are higher in
 279 winter and autumn by up to a factor of 2. These differences can be explained by several
 280 disparities between these seasons: lower boundary layer height, lower temperatures and new
 281 sources of emission due to residential heating, increased emissions by cold-started vehicles, etc.
 282 Since the results show that NO_x concentrations are higher in winter and autumn, for a given
 283 NO_x concentration the seasonal NO₂ concentrations should also be higher in autumn and winter
 284 than in summer and spring. However, the results for the Paris region show a different trend.
 285 The result in Fig. 5. (B) indicates a change of behavior when the annual NO₂ concentration
 286 increases, with the summer and spring NO₂ concentrations becoming higher than in autumn and
 287 winter. These results can be associated with those of other authors. Indeed, Kendrick et al.
 288 showed that NO₂ concentrations are higher in winter and autumn than in spring and summer,
 289 with a mean annual NO₂ concentration lower than 80 μg/m³ and for three different types of
 290 station (Kendrick et al., 2015). On the contrary, Mavroidis and Ilia showed that for a traffic
 291 station (i.e. giving high NO₂ concentrations), NO₂ concentrations are generally higher during
 292 the summer and spring months than in autumn and winter, with in their case a mean annual NO₂
 293 concentration higher than 80 μg/m³ (Mavroidis and Ilia, 2012). Thus, the evolution of seasonal
 294 NO₂ concentrations as a function of annual NO₂ concentration is not well represented by a linear
 295 method unable to catch these varying trends and is much better fitted by a quadratic one. With
 296 this interpolation, the spring and summer results are described by a concave quadratic function
 297 whereas the autumn and winter ones are described by a convex quadratic function. In this case,
 298 these concavities and convexities result in a NO₂ concentration of about 80 μg/m³, where the

299 seasonal NO₂ concentrations are equal to the annual NO₂ concentration. This concentration of
300 80 µg/m³ corresponds to the value for which, in the case of a measurement station giving an
301 annual average NO₂ concentration lower than this value, the concentrations for winter and
302 autumn are higher than the spring and summer concentrations. Therefore, to obtain maximized
303 measurements in order to assess an upper limit on annual NO₂ concentration over a short period
304 of time, the measurements should be carried out in winter, in case where an annual
305 concentration of less than 80 µg/m³ is expected, otherwise measurements should be carried out
306 in summer.

307 These observations are consistent with those of other research papers, despite being counter
308 intuitive on the first point of view. Indeed, a previous observation was that NO_x concentrations
309 are higher during autumn and winter, in theory giving higher NO₂ concentrations. Moreover, in
310 summer and spring, the zenithal angles are generally lower, leading to increased photochemistry
311 with higher photolysis, including NO₂ photolysis, and the production of radicals. As shown in
312 Fig. 6. (A), O₃ concentrations are globally much lower in autumn than in winter, and in winter
313 than in spring and summer. These concentrations are about the same between spring and
314 summer. Fig. 6. (B) gives supplementary information on how much ozone is available to react
315 with NO₂, by giving the evolution of the ratio of the seasonal O₃ concentration over the seasonal
316 NO₂ concentration as a function of the seasonal NO₂ concentration.

317 The first observation is that more O₃ molecules are available in spring and summer than in
318 winter and autumn for any NO₂ concentration. This statement is always true even when the
319 seasonal NO₂ concentration increases, leading to a systemic reduction of available O₃. For
320 example, for a seasonal NO₂ concentration of 15 µg/m³, the ratio of seasonal O₃ concentration
321 over seasonal NO₂ concentration is around 3 for autumn, 4 for winter and almost 5 for spring
322 and summer. Increasing the seasonal NO₂ concentration to 30 µg/m³ gives ratios of 1 and 1.5
323 for autumn and winter respectively and almost 2 for both spring and summer. The explanation
324 of why the seasonal NO₂ concentration is higher in spring and summer than in winter and
325 autumn for high NO₂ concentrations can be obtained from these two observations. For low NO₂
326 concentrations, O₃ is readily available and the reaction is not limited by the O₃ concentration
327 but by several other factors that lead to the commonly accepted result: NO₂ concentrations are
328 higher in winter and autumn than in spring and summer. However, when the NO₂ concentration
329 increases, O₃ becomes less and less available until reaching a state in which it becomes the
330 limiting reagent of the production reaction of NO₂ from NO_x. This state is reached earlier in
331 winter and autumn than in spring and summer, leading to a higher NO₂ concentration in summer
332 and spring than in autumn and winter.



333
 334 Fig. 6. Evolution of the seasonal O₃ concentration as a function of the annual O₃ concentration (A) in the Paris region and the
 335 evolution of the ratio between seasonal O₃ and NO₂ concentrations as a function seasonal NO₂ concentrations (B).
 336

337 3.3. Assessment of annual NO₂ concentration

338 3.3.1. Assessment of annual NO₂ concentration from monthly NO₂ concentrations

339 As mentioned above with regards to seasonal variability, seasonal concentrations cannot be
 340 used directly as an annual concentration. However, they seem to fit a trend and it may be
 341 possible to assess the annual mean concentration from a short period of measurement.

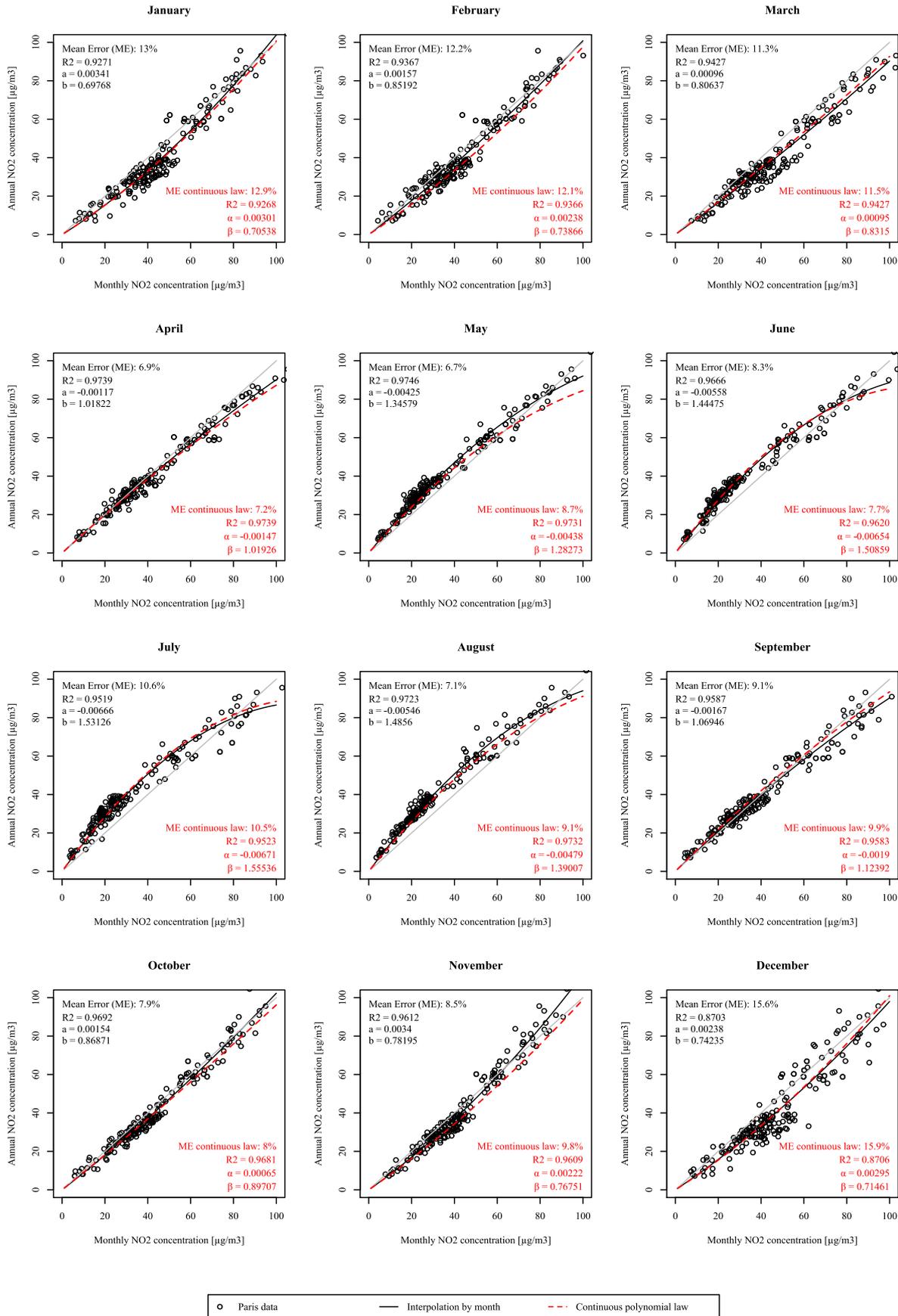
342 The NO₂ concentrations over the Paris region were first averaged for each month and then
 343 compared with annual NO₂ concentrations. The results, presented with black circles in Fig. 7,
 344 show that, like seasonal NO₂ concentrations, monthly averaged NO₂ concentrations as a
 345 function of annual NO₂ concentrations seem to be better fitted by a quadric function than by a
 346 linear function. These fittings are also presented with black lines in Fig. 7. as well as the
 347 polynomial interpolation coefficients, and the mean error between measured data and
 348 interpolation, also in black. The polynomial equation corresponds to (6) with $[NO_2]_a$ and
 349 $[NO_2]_m$ being the annual mean NO₂ concentration and the monthly averaged NO₂
 350 concentration respectively in µg/m³, and a and b the different polynomial coefficients for each
 351 month.

$$352 \quad [NO_2]_a = a \cdot [NO_2]_m^2 + b \cdot [NO_2]_m \quad (6)$$

353 The polynomial methods obtained have different concavities and convexities, consistent with
 354 those obtained for seasonal variability. The maximum convexity is obtained around December
 355 and January, corresponding to the transition from autumn to winter. The maximum concavity

356 is obtained around June and July, corresponding to the transition from spring to summer. Lastly,
357 minimal concavity and convexity is obtained around March and September, corresponding to
358 the transition from winter to spring and from summer to autumn, respectively. For these months,
359 monthly averaged NO₂ concentrations are almost equal to annual NO₂ concentrations.
360 According to these polynomial methods, the maximal mean error is around 15% and
361 corresponds to December, and the minimal mean error is around 7% and corresponds to March.
362 The mean error averaged over all months is below 10%.

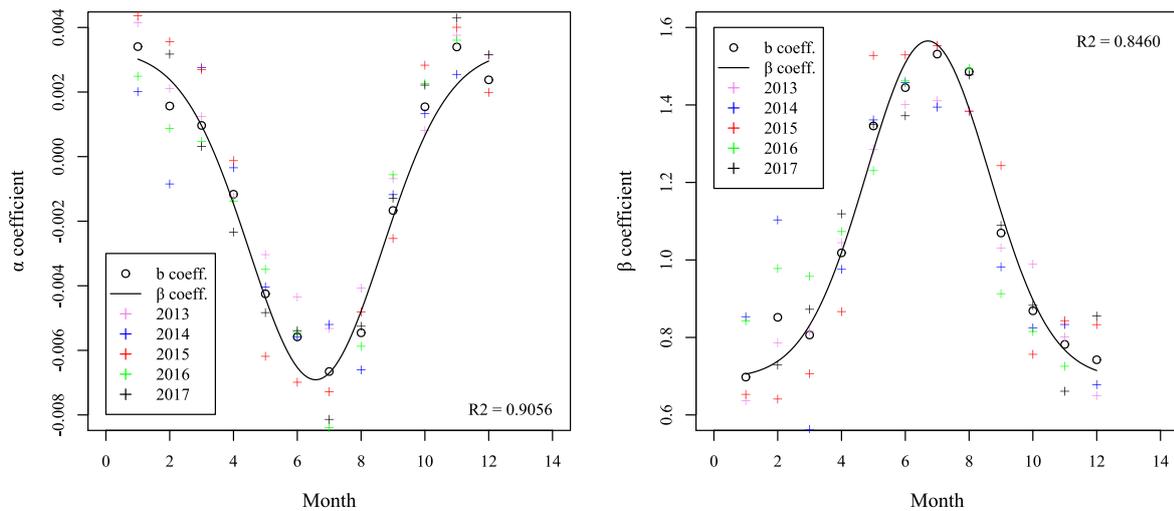
363 These polynomial methods can be used to assess the annual NO₂ concentration based on only
364 one month of measurements. However, the problem is that measurements from the first day to
365 the last day of a month are required. If one month of data is acquired that overlaps two distinct
366 months, say from 15th January to 15th February, the interpolation is no longer appropriate. An
367 additional study was carried out to change from discrete to continuous interpolation. To achieve
368 this, the resulting polynomial coefficients a and b were plotted as a function of the month with
369 1 corresponding to January and 12 to December. Fig. 8. shows the corresponding results.



370

371

Fig. 7. Evolution and interpolation of annual NO₂ concentration as a function of monthly NO₂ concentration.



372

373 Fig. 8. Interpolation of a and b coefficients (for each year considered and the subsequent mean) and resulting continuous α
374 and β coefficients.

375 As shown in Fig. 8., both coefficients a and b seem to follow a cyclic trend. However, the
376 evolution of the coefficients is inversed with a minimal value of a around June, corresponding
377 to a maximal value of b . On the contrary, the maximal value of a is reached around January,
378 corresponding to a minimal value of b . Considering the trends of a and b observed, a Gaussian
379 function was used to obtain continuous values bringing two new coefficients, α and β ,
380 respectively, corresponding to the coefficients obtained from the continuous method. The
381 corresponding equations for α and β are (7) and (8), respectively, with m being the month
382 corresponding to the available data (e.g. $m = 1$ for the data from the first to the last day of
383 January, $m = 3.5$ for the data from the middle of March to the middle of April, etc.).

$$384 \quad \alpha = 0.0033 - 0.0102 \cdot \exp\left[\frac{-(m - 6.5749)^2}{8.6962}\right] \quad (7)$$

$$385 \quad \beta = 0.6945 + 0.8708 \cdot \exp\left[\frac{-(m - 6.7076)^2}{7.4328}\right] \quad (8)$$

386 The new curves obtained for each month with (4), and the calculated α and β corresponding to
387 a and b respectively, are presented in red dashed lines in Fig. 7, in addition to the corresponding
388 values of α and β , R^2 and the mean error (ME) compared to the Paris data. When comparing
389 these new curves with the previous ones obtained with a and b , they are globally the same
390 except for May and November, for which the curves start to deviate from each other for high
391 monthly NO_2 concentrations. Nonetheless, the mean error for these two months is still
392 acceptable, with in both cases a mean error of less than 10%. The mean errors for each month



393 are approximatively equal between both cases and give an overall error of 10% and a maximal
394 error of 16% in December.

395 In view to assessing the reliability of the equations, the polynomial methods were applied to
396 several regions of France, including Aquitaine Limousin Poitou-Charentes, Auvergne-Rhône-
397 Alpes and Provence-Alpes-Côte d'Azur from 2013 to 2017. For each month of these years, the
398 mean annual NO₂ concentrations were calculated based on each month of data. The discrete
399 polynomial methods were used here because the information was available for each month. The
400 calculated annual concentrations were then compared to the measured concentrations and a
401 mean error was obtained. The mean errors are summarized in Table 2. This table also gives
402 information on the error obtained when the monthly NO₂ concentration is taken directly as an
403 annual NO₂ concentration (called direct approach), and on the improvements between this
404 direct approach and the approach using the suggested methods. For the three regions
405 considered, the mean error using the discrete method is higher than for the Paris region, ranging
406 from 12% to 20%. The errors obtained when using the direct approach range from 18% to 32%.
407 The improvement between the two approaches depends on the regions considered and ranges
408 from 26% to 46% with an overall improvement of 38%. According to these results, the method
409 presented in this paper is reliable and can be used outside the Paris region in France. Overall,
410 this simple applicable polynomial method improves the results in comparison to a direct
411 approach by up to a factor two.

412

413

414

415

416

417

418

419

420

421

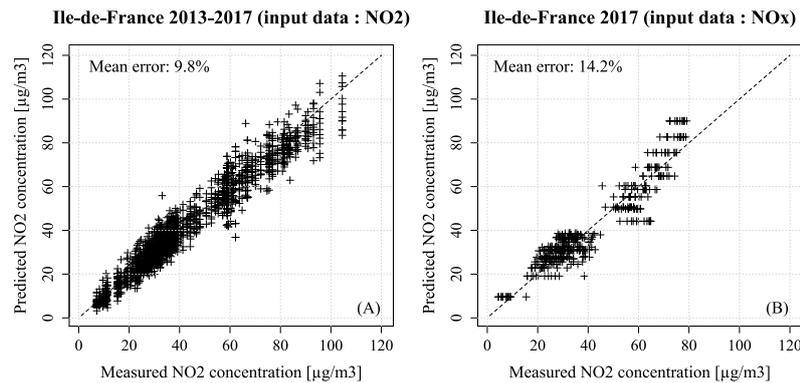
422 Table 2. Global results of the polynomial discrete method over regions in southern France and improvements compared to the
 423 direct utilization of monthly concentrations as annual concentrations.

Region	Year	Number of stations with a full year of data	Annual mean direct error (%)	Annual mean discrete method error (%)	Improvement between direct and discrete method error (%)	Mean annual direct error (%)	Mean annual discrete method error (%)	Mean improvement (%)
Aquitaine Limousin Poitou- Charentes	2013	31	29	17	41	30	17	43
	2014	29	27	15	46			
	2015	29	32	17	46			
	2016	35	28	16	44			
	2017	29	32	19	42			
Auvergne- Rhône- Alpes	2013	50	29	18	39	30	18	40
	2014	65	29	17	41			
	2015	58	30	18	39			
	2016	68	30	20	35			
	2017	57	30	19	38			
Provence- Alpes-Côte d'Azur	2013	21	19	14	27	19	13	31
	2014	22	19	12	38			
	2015	29	19	13	29			
	2016	27	20	14	26			
	2017	27	18	12	31			

424

425 *3.3.2. Assessment of annual NO₂ concentration from monthly NO_x concentrations.*

426 The final study was performed to give an estimation of the total error when calculating annual
 427 NO₂ concentration using monthly measured NO_x data. To manage this, data for the Paris region
 428 for the year 2017 were used. Firstly, the monthly NO₂ concentrations were calculated based on
 429 monthly NO_x concentrations measurements using the Derwent and Middleton function (3).
 430 Then, annual NO₂ concentrations were calculated using (6), (7) and (8). The resulting annual
 431 NO₂ concentrations were plotted against measured annual NO₂ concentrations and are
 432 presented in Fig. 9. (B). The previous results for Paris from 2013 to 2017 and for which the
 433 calculated annual NO₂ concentrations are based on monitored monthly NO₂ concentrations are
 434 also provided in Fig. 9. (A). According to Fig. 9. (A), a global error of 10% for Paris region is
 435 obtained and it can also be seen that the maximal errors occur for the highest NO₂
 436 concentrations. The same observation can be made when comparing this result with those for
 437 Paris assessed with the monthly NO_x concentrations for 2017. The global error in this case
 438 increases but does not exceed 15%.



439

440 Fig. 9. Comparison between calculated and measured annual NO₂ concentrations for the Paris region from 2013 to 2017 (A)
 441 and for the Paris region based on monthly 2017 NO_x concentrations (B).

442 4. Discussion

443 The seasonal variability of NO₂ concentrations was shown and leads to higher or lower seasonal
 444 NO₂ concentrations compared to annual NO₂ concentrations. An explanation for these
 445 observations was proposed and seems to be linked to the seasonal variability of ozone
 446 concentrations as well as the seasonal variability of available ozone to react with NO₂.
 447 However, this link must be quantified to better explain the phenomenon and evaluate if these
 448 observations can be fully generalized. The first hypothesis is that this phenomenon may only
 449 be generalizable to countries whose seasonal variability in ozone concentrations are like those
 450 observed in France. Thus, in countries having other types of seasons like Indonesia, with only
 451 a dry and a monsoon season or India, with winter, summer, monsoon and post-monsoon
 452 seasons, the results would be very different, and the equations presented in this paper may not
 453 be relevant. However, it may be possible to apply the methodology and adapt the coefficients
 454 of the equations to obtain good results in these countries. Nevertheless, this would require long
 455 periods of measurements.

456 It should also be noted that for some specific periods, monthly NO₂ concentrations are
 457 representative of annual NO₂ concentrations. Indeed, averaging monthly concentrations
 458 measured in March, April, September or October could give good estimations of the mean
 459 annual concentrations directly. For these months, it might not be necessary to use the previous
 460 methodology to assess the annual NO₂ concentration.

461 Lastly, the different equations obtained that could be used to assess annual NO₂ concentrations,
 462 were built for and applied to regions having around the same latitudes, from 43° to 50°. For a
 463 very different latitude, the coefficients of the equations might not be optimized, and greater
 464 errors could occur.

465 5. Conclusion

466 The assessment of annual NO₂ concentrations with partial data was studied from two main
467 approaches. The first one was to determine the annual mean NO₂ concentration with only
468 annual mean NO_x concentration information. The second was to determine the annual mean
469 NO₂ concentration with only a one-month period measurement. The main conclusions are as
470 follows:

- 471 (a) Three functions giving annual NO₂ concentrations based on NO_x data were compared.
472 These functions correspond to the methods of Derwent and Middleton, Romberg et
473 al., and Bächlin et al. The results show that the method proposed by Derwent and
474 Middleton is the better suited to assess the annual NO₂ concentration based on NO_x
475 concentrations for several regions of France and for several years both for rural and
476 urban areas in particular. However, this method has some limitations for high NO_x
477 concentrations and gives less accurate results for traffic stations with annual NO_x
478 concentrations higher than 70 µg/m³. The global error of this method for the regions
479 of France considered is around 8%.
- 480 (b) NO₂ concentrations are seasonally variable and depend on the concentrations of NO_x
481 and their ratio with VOC concentrations, and on the photochemistry conditions.
482 Hence, making it impossible to give an annual concentration directly from a seasonal
483 concentration: for annual NO₂ concentrations lower than 80 µg/m³, summer and
484 spring NO₂ concentrations are lower than autumn and winter concentrations; for
485 higher annual NO₂ concentrations, it is the summer and the spring NO₂ concentrations
486 that become higher than the autumn and winter concentrations. Thus, to evaluate an
487 upper limit on annual NO₂ concentration over a short period of time, measurements
488 should be done in winter if an annual concentration of less than 80 µg/m³ is expected,
489 otherwise they should be carried out in summer
- 490 (c) Monthly NO₂ concentrations follow the same variability trends as the seasonal
491 concentrations which were quantified for each month. A discrete function was
492 proposed to assess annual NO₂ concentrations based on monthly NO₂ concentrations,
493 yielding a global error of 10% for the Paris region. The corresponding function was
494 made continuous using two Gaussian methods to facilitate its use, leading also to a
495 global error of 10% for the Paris region. The discrete methods applied to the southern
496 regions of France yielded an overall error of 15% and provided an improvement
497 ranging from 26% to 46% compared to the utilization of the direct approach.

498 (d) Using both the Derwent and Middleton method and the quadratic equations method
499 both presented in this work it is possible to assess annual NO₂ concentrations from
500 monthly NO_x concentrations measurements. Those methods led to an overall error of
501 15% for the Paris region for the year 2017.

502 All the results and observations discussed in this paper concern NO_x and NO₂ concentrations
503 and it was shown that interesting results can be obtained to reduce measurement periods and
504 estimate NO₂ concentrations from NO_x data without introducing any chemical considerations.
505 This methodology could be extended to other pollutants like particulate matter, which even if
506 not highly chemically active, are subject to specific phenomena like deposition, resuspensions,
507 etc.

508

509 **Acknowledgments**

510 The authors would like to thank all the AASQA for the open access data they provided, and
511 which were used to perform the present work. Special thanks are addressed to AIRPARIF for
512 their support and availability. They also thank the ANRT (Association nationale de la recherche
513 et de la technologie) for their support.

514 **References**

515 AIRPARIF, 2016. Inventaire régional des émissions en Île-de-France - Année de référence 2012 -
516 éléments synthétiques - Édition mai 2016 32.

517 Bächlin, W., Bössinger, R., Brandt, A., Schultz, T., 2008. Überprüfung des NO-NO₂-
518 Umwandlungsmodells für die Anwendung bei Immissionsprognosen für bodennahe
519 Stickoxidfreisetzung. *Reinhaltung der Luft* 66, 154–157.

520 Bright, V.B., Bloss, W.J., Cai, X., 2013. Urban street canyons: Coupling dynamics, chemistry and
521 within-canyon chemical processing of emissions. *Atmospheric Environment* 68, 127–142.
522 <https://doi.org/10.1016/j.atmosenv.2012.10.056>

523 Chaloulakou, A., Mavroidis, I., Gavriil, I., 2008. Compliance with the annual NO₂ air quality standard
524 in Athens. Required NO_x levels and expected health implications. *Atmospheric Environment*
525 42, 454–465. <https://doi.org/10.1016/j.atmosenv.2007.09.067>

526 Chauhan, A.J., Krishna, M.T., Frew, A.J., Holgate, S.T., 1998. Exposure to nitrogen dioxide (NO₂) and
527 respiratory disease risk. *Rev Environ Health* 13, 73–90.



- 528 Derwent, R.G., Middleton, D.R., 1996. An empirical function for the ratio [NO₂]:[NO_x]. *Clean Air* 26,
529 57–60.
- 530 Jenkin, M.E., 2004. Analysis of sources and partitioning of oxidant in the UK—Part 1: the NO_x-
531 dependence of annual mean concentrations of nitrogen dioxide and ozone. *Atmospheric*
532 *Environment* 38, 5117–5129. <https://doi.org/10.1016/j.atmosenv.2004.05.056>
- 533 Kagawa, J., 1985. Evaluation of biological significance of nitrogen oxides exposure. *Tokai J. Exp. Clin.*
534 *Med.* 10, 348–353.
- 535 Kendrick, C.M., Koonce, P., George, L.A., 2015. Diurnal and seasonal variations of NO, NO₂ and PM
536 2.5 mass as a function of traffic volumes alongside an urban arterial. *Atmospheric Environment*
537 122, 133–141. <https://doi.org/10.1016/j.atmosenv.2015.09.019>
- 538 Kim, M.J., Park, R.J., Kim, J.-J., 2012. Urban air quality modeling with full O₃–NO_x–VOC chemistry:
539 Implications for O₃ and PM air quality in a street canyon. *Atmospheric Environment* 47, 330–
540 340. <https://doi.org/10.1016/j.atmosenv.2011.10.059>
- 541 Leighton, P.A., 1961. Photochemistry of air pollution, *Physical chemistry*. New-York Acad.
- 542 Likens, G.E., Wright, R.F., Galloway, J.N., Butler, T.J., 1979. Acid Rain. *Scientific American* 241, 43–
543 51.
- 544 Mavroidis, I., Iliá, M., 2012. Trends of NO_x, NO₂ and O₃ concentrations at three different types of air
545 quality monitoring stations in Athens, Greece. *Atmospheric Environment* 63, 135–147.
546 <https://doi.org/10.1016/j.atmosenv.2012.09.030>
- 547 Navas, M.J., Jiménez, A.M., Galán, G., 1997. Air analysis: determination of nitrogen compounds by
548 chemiluminescence. *Atmospheric Environment* 31, 3603–3608. [https://doi.org/10.1016/S1352-2310\(97\)00153-2](https://doi.org/10.1016/S1352-2310(97)00153-2)
- 550 Purvis, M.R., Ehrlich, R., 1963. Effect of Atmospheric Pollutants on Susceptibility to Respiratory
551 Infection: II. Effect of Nitrogen Dioxide. *The Journal of Infectious Diseases* 113, 72–76.
- 552 Roberts–Semple, D., Song, F., Gao, Y., 2012. Seasonal characteristics of ambient nitrogen oxides and
553 ground–level ozone in metropolitan northeastern New Jersey. *Atmospheric Pollution Research*
554 3, 247–257. <https://doi.org/10.5094/APR.2012.027>
- 555 Romberg, E., Bösinger, R., Lohmeyer, A., Ruhnke, R., 1996. NO–NO₂–Umwandlung für die
556 Anwendung bei Immissionsprognosen für Kfz–Abgase. *Reinhaltung der Luft* 56, 215–218.



- 557 Sanchez, B., Santiago, J.-L., Martilli, A., Palacios, M., Kirchner, F., 2016. CFD modeling of reactive
558 pollutant dispersion in simplified urban configurations with different chemical mechanisms.
559 Atmospheric Chemistry and Physics 16, 12143–12157. [https://doi.org/10.5194/acp-16-12143-](https://doi.org/10.5194/acp-16-12143-2016)
560 2016
- 561 Seinfeld, J.H., Pandis, S.N., 2016. Atmospheric Chemistry and Physics: From Air Pollution to Climate
562 Change, 3rd Edition, Wiley-Blackwell. ed.
- 563 Thunis, P., 2018. On the validity of the incremental approach to estimate the impact of cities on air
564 quality. Atmospheric Environment 173, 210–222.
565 <https://doi.org/10.1016/j.atmosenv.2017.11.012>
- 566 WHO, 2017. Evolution of WHO air quality guidelines past, present and future, Copenhagen: WHO
567 Regional Office for Europe.
- 568 WHO, 2005. WHO Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur
569 dioxide. Global update 2005. WHO.
- 570 Wiegand, A.N., Bo, N.D., 2000. Review of empirical methods for the calculation of the diurnal NO₂
571 photolysis rate coefficient. Atmospheric Environment 10. [https://doi.org/10.1016/S1352-](https://doi.org/10.1016/S1352-2310(99)00294-0)
572 2310(99)00294-0
- 573