



# 1 Assessment of mean annual NO<sub>2</sub> concentration based on a partial 2 dataset

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16

## 17 Abstract:

18 NO<sub>2</sub> 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/m<sup>3</sup> is set by both entities as the annual mean NO<sub>2</sub> 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<sub>x</sub> (NO + NO<sub>2</sub>)  
23 information, on the one hand, and, on the other hand, brief NO<sub>2</sub> measurements performed over  
24 few months. To overcome the first hurdle, several methods exist in the literature to transform  
25 NO<sub>x</sub> data into NO<sub>2</sub> 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<sub>x</sub> concentrations behave as expected with higher concentrations in  
28 autumn and winter than in spring and summer. However, for NO<sub>2</sub> this trend changes around 80  
29 µg/m<sup>3</sup> for which the spring and summer values are higher. Therefore, to maximize  
30 measurements to assess an upper limit on annual NO<sub>2</sub> concentration over a short period of time,  
31 those measurements should be done in winter if an annual concentration of less than 80 µg/m<sup>3</sup>  
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 NO<sub>2</sub> or NO<sub>x</sub> 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<sub>x</sub> into NO<sub>2</sub> in  
45 France.
- 46 • NO<sub>2</sub> and NO<sub>x</sub> exhibit strong seasonal and monthly variabilities.
- 47 • The behavior of NO<sub>2</sub> concentrations related to seasons depends on their levels.
- 48 • Functions are presented to assess annual NO<sub>2</sub> concentration using monthly ones.

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## 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 (NO<sub>2</sub>) 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<sub>x</sub> 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<sub>x</sub> comes from traffic-related emissions and 18% from the tertiary and residential  
80 sectors (AIRPARIF, 2016).

81 Nitrogen dioxide (NO<sub>2</sub>) 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, NO<sub>2</sub> is the most  
83 measured component. Indeed, NO<sub>2</sub> 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 NO<sub>2</sub>. For this purpose, two standard values  
89 have been enforced : a hourly mean of 200 µg/m<sup>3</sup> and an annual mean of 40 µg/m<sup>3</sup> 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<sub>x</sub> concentrations but no direct information on NO<sub>2</sub>. Thus, one question arises in such  
100 situation: how can annual mean NO<sub>2</sub> concentrations be determined using only a short  
101 measurement period of NO<sub>2</sub> or NO<sub>x</sub> concentrations ?



102 The Leighton relationship provides information on the ratio between NO and NO<sub>2</sub>  
103 concentrations as a function of O<sub>3</sub>, 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 O<sub>3</sub> 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<sub>x</sub> and NO<sub>2</sub>.  
109 Numerical computation based on complex chemical mechanisms involving more than 300  
110 reactions with more than 100 species gives more accurate evaluations of NO<sub>2</sub> (Bright et al.,  
111 2013; Kim et al., 2012). Nevertheless, when NO<sub>2</sub> 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 NO<sub>2</sub> and NO<sub>x</sub> concentrations differs considerably between  
115 summer and winter because NO<sub>2</sub> concentrations depend on photolysis conditions, and NO<sub>x</sub>  
116 molecules play a role in several chemical mechanisms in the troposphere, involving ozone (O<sub>3</sub>)  
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 NO<sub>2</sub> and NO<sub>x</sub> (Roberts–Semple et al., 2012). Moreover, Kendrick  
120 et al. showed that there is a seasonal variability in NO<sub>2</sub> concentration even with constant hourly  
121 seasonal traffic (Kendrick et al., 2015). Thus, these results show that a few months of NO<sub>2</sub>  
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 NO<sub>2</sub>  
126 concentrations based on monitored NO<sub>x</sub> data in France. The second aim is to present a method  
127 capable of providing the mean annual NO<sub>2</sub> 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<sub>x</sub> into NO<sub>2</sub> used are presented in section 2. Then, the results of the study on the NO<sub>x</sub>-  
130 based NO<sub>2</sub> concentration calculation in France, and the method presented for the mean annual  
131 NO<sub>2</sub> concentration calculation based on monthly measurement periods, are presented in section  
132 3.

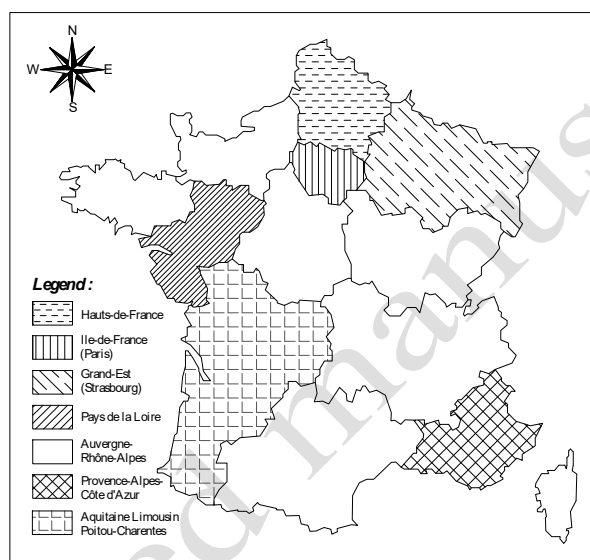
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## 135 2. Material and methods

### 136 2.1. Study location

137 This work uses  $\text{NO}_2$  and  $\text{NO}_x$  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  $\text{NO}_2$  and  
 153  $\text{NO}_x$  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 <sub>x</sub>			NO <sub>2</sub>			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

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### 161 2.3. Data range

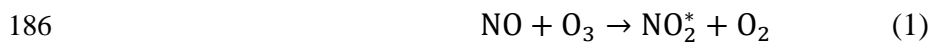
162 The annual and monthly concentrations range from 10 to 340  $\mu\text{g}/\text{m}^3$  for NO<sub>x</sub> and from 5 to  
 163 95  $\mu\text{g}/\text{m}^3$  for NO<sub>2</sub>, considering the complete dataset (all years, types and locations of stations  
 164 included). According to these wide ranges, 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/O<sub>3</sub> 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 O<sub>3</sub>. This reaction produces an excited nitrogen dioxide (NO<sub>2</sub><sup>\*</sup>) 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<sub>x</sub> concentration, it is first necessary to convert all the NO<sub>2</sub> into  
189 NO before the measurement. After that, the resulting NO corresponding to the initial NO and  
190 the NO derived from NO<sub>2</sub> are measured and the NO<sub>x</sub> concentration is obtained. Combining both  
191 the measured NO and NO<sub>x</sub> concentrations provides the NO<sub>2</sub> concentration. Thus, the  
192 uncertainties on NO<sub>2</sub> measurement are higher than those on NO or NO<sub>x</sub> because the results are  
193 obtained from both NO and NO<sub>x</sub> 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 NO<sub>2</sub> 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<sub>x</sub> to NO<sub>2</sub>

201 Several one-parametric empirical methods can be found in the literature to give an estimation  
202 of NO<sub>2</sub> concentration based on NO<sub>x</sub> 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<sub>x</sub> and NO<sub>2</sub> concentrations for NO<sub>x</sub> 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<sub>x</sub> and NO<sub>2</sub>  
208 (Romberg et al., 1996).
- 209 • Bächlin et al., another rational function linking annual averaged NO<sub>x</sub> and NO<sub>x</sub> (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  $\text{NO}_x$  and  $\text{NO}_2$  noted  $[\text{NO}_x]_h$  and  $[\text{NO}_2]_h$  and annual averaged  $\text{NO}_x$   
 213 and  $\text{NO}_2$  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  $A = \log_{10}([\text{NO}_x]_h/1.91)$ .

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

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

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

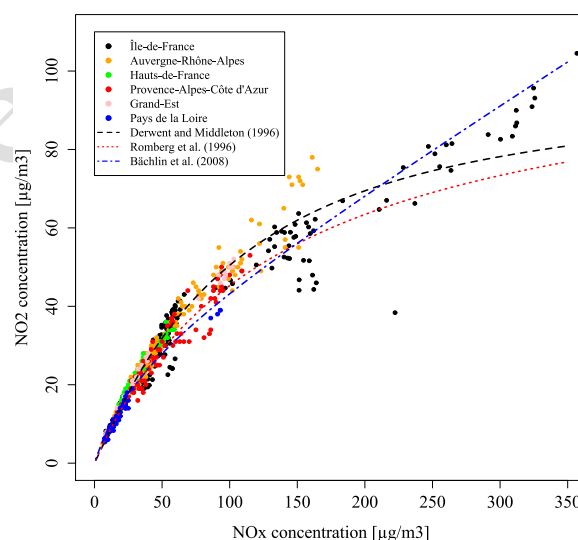
218 For the purpose of this work, mean annual concentrations were used instead of hourly averaged  
 219 concentrations for the Derwent and Middleton function.

### 220 3. Results

#### 221 3.1. Evaluation of annual $\text{NO}_2$ concentration based on $\text{NO}_x$ data

##### 222 3.1.1. Best fitting function in France

223 Fig. 2. shows the evolution of mean annual  $\text{NO}_2$  concentration as a function of the mean annual  
 224  $\text{NO}_x$  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.

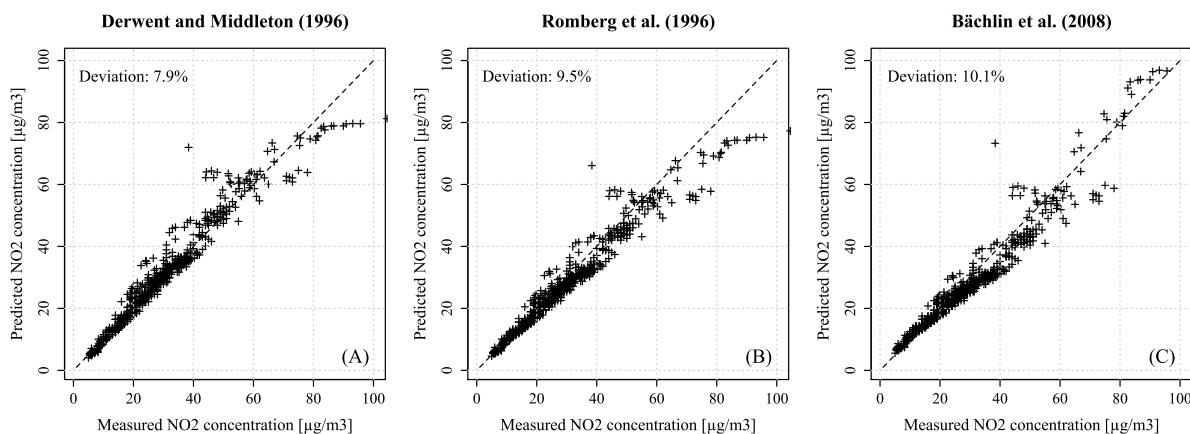


227  
 228 Fig. 2. Evolution of  $\text{NO}_2$  concentration as a function of  $\text{NO}_x$  concentration and comparison with empirical functions

229 To obtain a better comparison between the three functions, predicted  $\text{NO}_2$  concentrations  
 230 calculated with measured  $\text{NO}_x$  concentrations were plotted against measured  $\text{NO}_2$



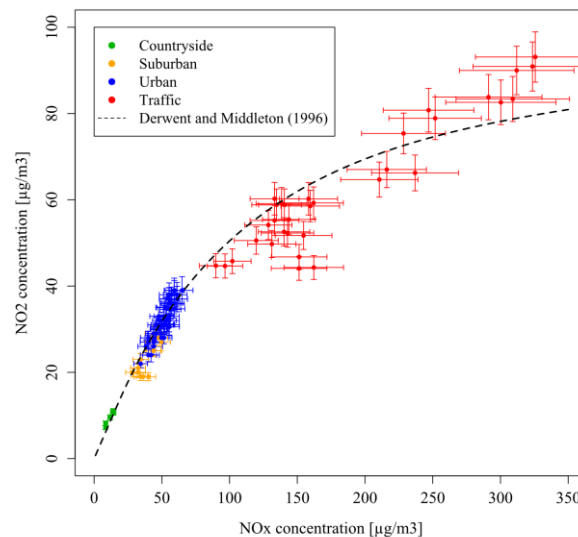
231 concentrations. The corresponding results are presented in Fig. 3. with the first bisector  
 232 corresponding to ideal results. As shown in Fig. 3., the function from Bächlin et al. is the most  
 233 appropriate for high NO<sub>2</sub>, thus high NO<sub>x</sub> concentrations. However, based on Fig. 3. (A) and  
 234 Fig. 3. (B) the results for lower NO<sub>2</sub> concentrations (less than 50 µg/m<sup>3</sup>) 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<sub>2</sub> concentrations. When choosing  
 240 between two functions giving about the same deviation, the precautionary approach is to  
 241 choose the function that overestimates NO<sub>2</sub> 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<sub>2</sub> concentrations based on NO<sub>x</sub> 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<sub>2</sub> concentrations (higher than 70  
 247 µg/m<sup>3</sup>) the method fits less and less well.



248  
 249 Fig. 3. Comparison between predicted and measured NO<sub>2</sub> 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<sub>2</sub> concentration for the Paris  
 254 region dataset as a function of NO<sub>x</sub> concentration with a distinction between the different types  
 255 of station. Derwent and Middleton's function is also plotted.



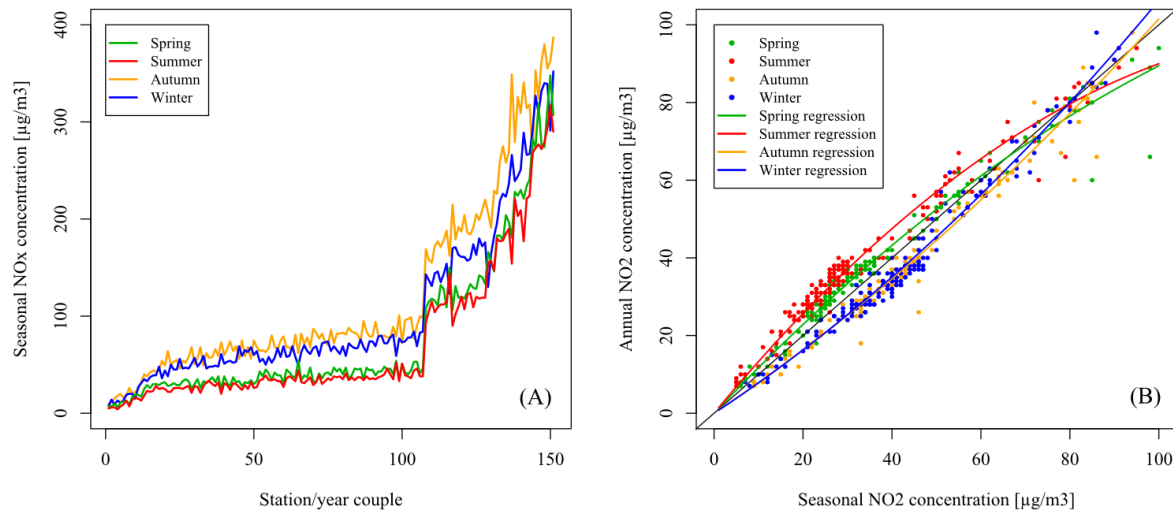
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257 Fig. 4. Evolution of NO<sub>2</sub> concentration as a function of NO<sub>x</sub> concentration for the Paris region dataset and comparison with  
 258 Derwent and Middleton's function.

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<sub>x</sub> concentrations lower than 80 µg/m<sup>3</sup>. 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 NO<sub>2</sub> concentrations is 9% with a 95<sup>th</sup>  
 266 percentile of 27%.

### 267 3.2. Seasonal variability of NO<sub>2</sub> concentration

268 The seasonal variability of NO<sub>2</sub> was studied using the Paris region dataset. Hourly NO<sub>2</sub>  
 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<sub>x</sub> concentrations  
 272 for each couple of year and station. Fig. 5. (B) shows the evolution of seasonal NO<sub>2</sub>  
 273 concentrations as a function of the annual NO<sub>2</sub> concentration for the same year of measurement.



274  
275 Fig. 5. Comparison between seasonal NO<sub>x</sub> concentrations for a given station and year of measurement in the Paris region (A)  
276 and the evolution of the annual NO<sub>2</sub> concentration as a function of seasonal NO<sub>2</sub> concentrations (B).

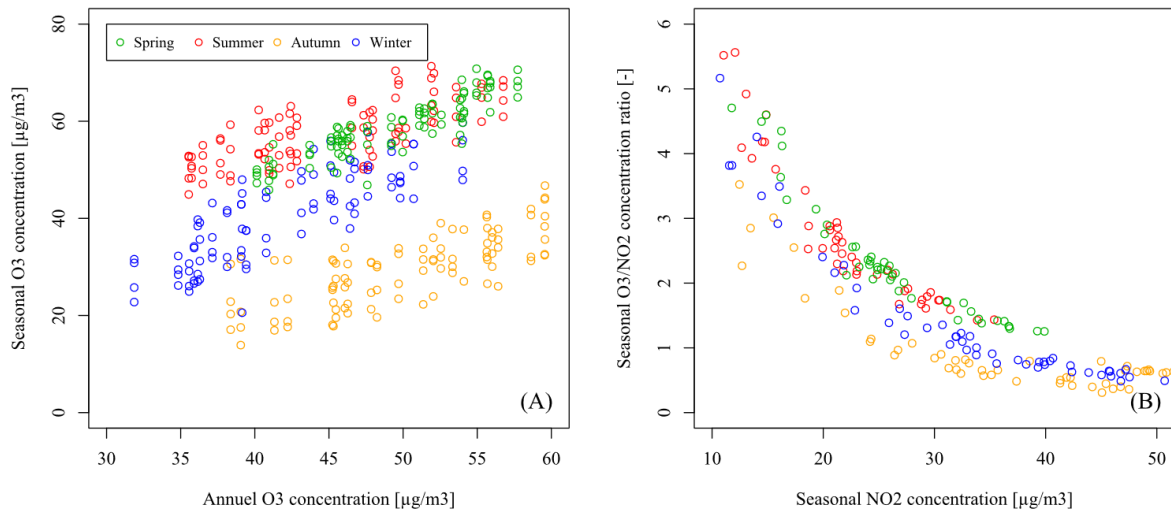
277 According to Fig. 5. (A), NO<sub>x</sub> concentrations are strongly dependent on the season. Indeed,  
278 although summer and spring NO<sub>x</sub> concentrations are similar, the concentrations are higher in  
279 winter and autumn by up to a factor of 2. These differences can be explained by 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<sub>x</sub> concentrations are higher in winter and autumn, for a given  
283 NO<sub>x</sub> concentration the seasonal NO<sub>2</sub> 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 NO<sub>2</sub> concentration  
286 increases, with the summer and spring NO<sub>2</sub> 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 NO<sub>2</sub> concentrations are higher in winter and autumn than in spring and summer,  
289 with a mean annual NO<sub>2</sub> concentration lower than 80 μg/m<sup>3</sup> 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 NO<sub>2</sub> concentrations), NO<sub>2</sub> concentrations are generally higher during  
292 the summer and spring months than in autumn and winter, with in their case a mean annual NO<sub>2</sub>  
293 concentration higher than 80 μg/m<sup>3</sup> (Mavroidis and Ilia, 2012). Thus, the evolution of seasonal  
294 NO<sub>2</sub> concentrations as a function of annual NO<sub>2</sub> 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 NO<sub>2</sub> concentration of about 80 μg/m<sup>3</sup>, where the



299 seasonal NO<sub>2</sub> concentrations are equal to the annual NO<sub>2</sub> concentration. This concentration of  
300 80 µg/m<sup>3</sup> corresponds to the value for which, in the case of a measurement station giving an  
301 annual average NO<sub>2</sub> 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 NO<sub>2</sub> 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/m<sup>3</sup> 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<sub>x</sub> concentrations  
309 are higher during autumn and winter, in theory giving higher NO<sub>2</sub> concentrations. Moreover, in  
310 summer and spring, the zenithal angles are generally lower, leading to increased photochemistry  
311 with higher photolysis, including NO<sub>2</sub> photolysis, and the production of radicals. As shown in  
312 Fig. 6. (A), O<sub>3</sub> 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 NO<sub>2</sub>, by giving the evolution of the ratio of the seasonal O<sub>3</sub> concentration over the seasonal  
316 NO<sub>2</sub> concentration as a function of the seasonal NO<sub>2</sub> concentration.

317 The first observation is that more O<sub>3</sub> molecules are available in spring and summer than in  
318 winter and autumn for any NO<sub>2</sub> concentration. This statement is always true even when the  
319 seasonal NO<sub>2</sub> concentration increases, leading to a systemic reduction of available O<sub>3</sub>. For  
320 example, for a seasonal NO<sub>2</sub> concentration of 15 µg/m<sup>3</sup>, the ratio of seasonal O<sub>3</sub> concentration  
321 over seasonal NO<sub>2</sub> concentration is around 3 for autumn, 4 for winter and almost 5 for spring  
322 and summer. Increasing the seasonal NO<sub>2</sub> concentration to 30 µg/m<sup>3</sup> 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 NO<sub>2</sub> concentration is higher in spring and summer than in winter and  
325 autumn for high NO<sub>2</sub> concentrations can be obtained from these two observations. For low NO<sub>2</sub>  
326 concentrations, O<sub>3</sub> is readily available and the reaction is not limited by the O<sub>3</sub> concentration  
327 but by several other factors that lead to the commonly accepted result: NO<sub>2</sub> concentrations are  
328 higher in winter and autumn than in spring and summer. However, when the NO<sub>2</sub> concentration  
329 increases, O<sub>3</sub> becomes less and less available until reaching a state in which it becomes the  
330 limiting reagent of the production reaction of NO<sub>2</sub> from NO<sub>x</sub>. This state is reached earlier in  
331 winter and autumn than in spring and summer, leading to a higher NO<sub>2</sub> concentration in summer  
332 and spring than in autumn and winter.



333  
 334 Fig. 6. Evolution of the seasonal O<sub>3</sub> concentration as a function of the annual O<sub>3</sub> concentration (A) in the Paris region and the  
 335 evolution of the ratio between seasonal O<sub>3</sub> and NO<sub>2</sub> concentrations as a function seasonal NO<sub>2</sub> concentrations (B).  
 336

### 337 3.3. Assessment of annual NO<sub>2</sub> concentration

#### 338 3.3.1. Assessment of annual NO<sub>2</sub> concentration from monthly NO<sub>2</sub> 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.

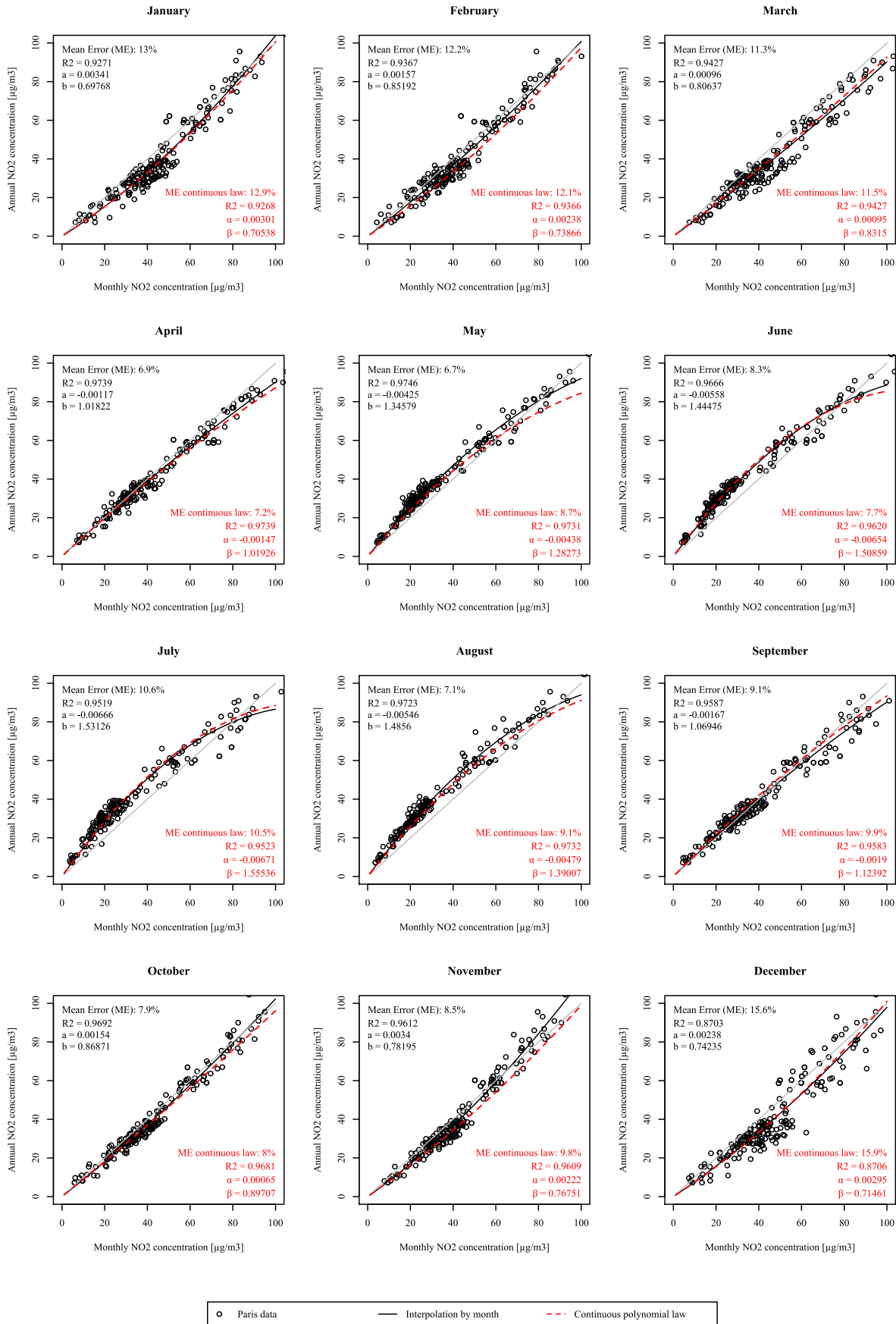
342 The NO<sub>2</sub> concentrations over the Paris region were first averaged for each month and then  
 343 compared with annual NO<sub>2</sub> concentrations. The results, presented with black circles in Fig. 7,  
 344 show that, like seasonal NO<sub>2</sub> concentrations, monthly averaged NO<sub>2</sub> concentrations as a  
 345 function of annual NO<sub>2</sub> 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 NO<sub>2</sub> concentration and the monthly averaged NO<sub>2</sub>  
 350 concentration respectively in µg/m<sup>3</sup>, 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 NO<sub>2</sub> concentrations are almost equal to annual NO<sub>2</sub> 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%.

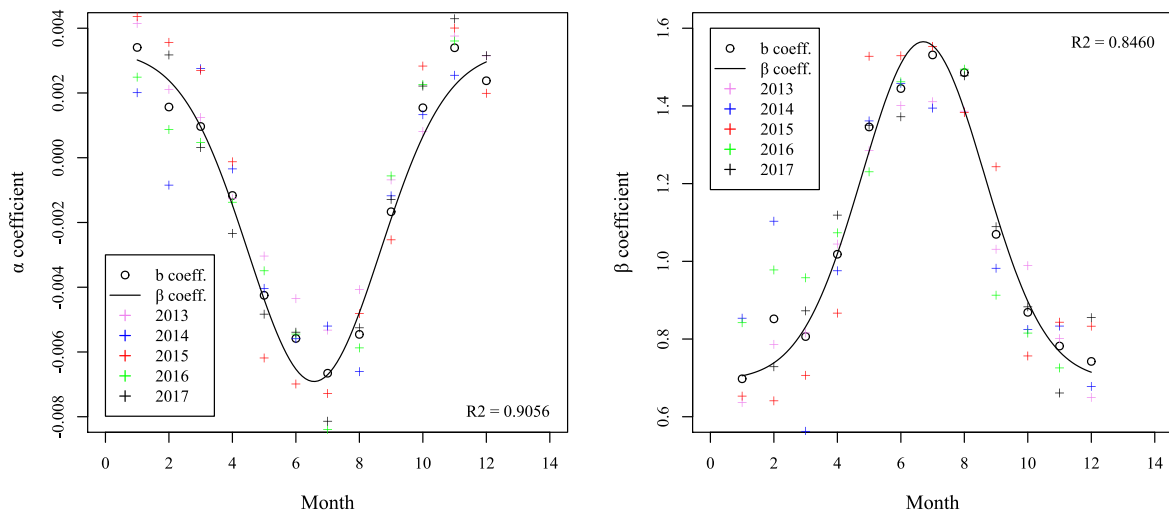
363 These polynomial methods can be used to assess the annual NO<sub>2</sub> concentration based on only  
364 one month of measurements. However, the problem is that measurements from the first day to  
365 the last day of a month are required. If one month of data is acquired that overlaps two distinct  
366 months, say from 15<sup>th</sup> January to 15<sup>th</sup> 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 NO<sub>2</sub> concentration as a function of monthly NO<sub>2</sub> concentration.



372

373 Fig. 8. Interpolation of  $a$  and  $b$  coefficients (for each year considered and the subsequent mean) and resulting continuous  $\alpha$   
 374 and  $\beta$  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,  $\alpha$  and  $\beta$ ,  
 380 respectively, corresponding to the coefficients obtained from the continuous method. The  
 381 corresponding equations for  $\alpha$  and  $\beta$  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  $\alpha$  and  $\beta$  corresponding to  
 387  $a$  and  $b$  respectively, are presented in red dashed lines in Fig. 7, in addition to the corresponding  
 388 values of  $\alpha$  and  $\beta$ ,  $R^2$  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  $\text{NO}_2$  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 NO<sub>2</sub> 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 NO<sub>2</sub> concentration is taken directly as an  
403 annual NO<sub>2</sub> 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.

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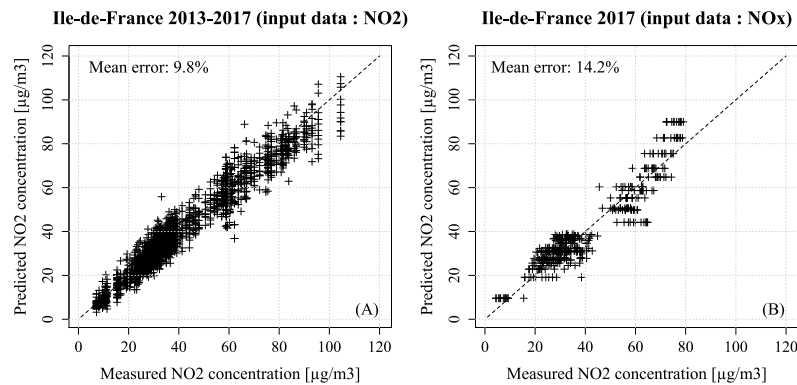
422 Table 2. Global results of the polynomial discrete method over regions in southern France and improvements compared to the  
 423 direct utilization of monthly concentrations as annual concentrations.

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 $NO_2$ concentration from monthly $NO_x$ concentrations.

426 The final study was performed to give an estimation of the total error when calculating annual  
 427  $NO_2$  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  $NO_2$  concentrations were calculated based on  
 429 monthly  $NO_x$  concentrations measurements using the Derwent and Middleton function (3).  
 430 Then, annual  $NO_2$  concentrations were calculated using (6), (7) and (8). The resulting annual  
 431  $NO_2$  concentrations were plotted against measured annual  $NO_2$  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  $NO_2$  concentrations are based on monitored monthly  $NO_2$  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  $NO_2$   
 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 NO<sub>2</sub> concentrations for the Paris region from 2013 to 2017 (A)  
 441 and for the Paris region based on monthly 2017 NO<sub>x</sub> concentrations (B).

#### 442 4. Discussion

443 The seasonal variability of NO<sub>2</sub> concentrations was shown and leads to higher or lower seasonal  
 444 NO<sub>2</sub> concentrations compared to annual NO<sub>2</sub> 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 NO<sub>2</sub>.  
 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 NO<sub>2</sub> concentrations are  
 457 representative of annual NO<sub>2</sub> 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 NO<sub>2</sub> concentration.

461 Lastly, the different equations obtained that could be used to assess annual NO<sub>2</sub> 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 NO<sub>2</sub> concentrations with partial data was studied from two main  
467 approaches. The first one was to determine the annual mean NO<sub>2</sub> concentration with only  
468 annual mean NO<sub>x</sub> concentration information. The second was to determine the annual mean  
469 NO<sub>2</sub> concentration with only a one-month period measurement. The main conclusions are as  
470 follows:

- 471 (a) Three functions giving annual NO<sub>2</sub> concentrations based on NO<sub>x</sub> 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 NO<sub>2</sub> concentration based on NO<sub>x</sub>  
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<sub>x</sub>  
477 concentrations and gives less accurate results for traffic stations with annual NO<sub>x</sub>  
478 concentrations higher than 70 µg/m<sup>3</sup>. The global error of this method for the regions  
479 of France considered is around 8%.
- 480 (b) NO<sub>2</sub> concentrations are seasonally variable and depend on the concentrations of NO<sub>x</sub>  
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 NO<sub>2</sub> concentrations lower than 80 µg/m<sup>3</sup>, summer and  
484 spring NO<sub>2</sub> concentrations are lower than autumn and winter concentrations; for  
485 higher annual NO<sub>2</sub> concentrations, it is the summer and the spring NO<sub>2</sub> concentrations  
486 that become higher than the autumn and winter concentrations. Thus, to evaluate an  
487 upper limit on annual NO<sub>2</sub> concentration over a short period of time, measurements  
488 should be done in winter if an annual concentration of less than 80 µg/m<sup>3</sup> is expected,  
489 otherwise they should be carried out in summer
- 490 (c) Monthly NO<sub>2</sub> 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 NO<sub>2</sub> concentrations based on monthly NO<sub>2</sub> 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 NO<sub>2</sub> concentrations from  
500 monthly NO<sub>x</sub> 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<sub>x</sub> and NO<sub>2</sub> concentrations  
503 and it was shown that interesting results can be obtained to reduce measurement periods and  
504 estimate NO<sub>2</sub> concentrations from NO<sub>x</sub> 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

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