Assessment of mean annual NO_2 concentration based on a partial dataset

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Abstract: NO_2 is a pollutant harmful to both health and the environment. The European Union and the World Health Organization have developed guidelines in terms of pollutant. The value of 40 µg/m^3 is set by both entities as the annual mean NO_2 concentration not to be exceeded to prevent risks for human health. To assess this given value, yearlong in situ measurements are required. However, sometimes only partial data are available, such as having only NO_x (NO + NO_2) information, on the one hand, and, on the other hand, brief NO_2 measurements performed over few months. To overcome the first hurdle, several methods exist in the literature to transform NO_x data into NO_2 data. The method of Derwent and Middleton is the most appropriate for France with less than 8% of deviation and even less deviation when considering rural and urban sites. For all values, NO_x concentrations behave as expected with higher concentrations in autumn and winter than in spring and summer. However, for NO_2 this trend changes around 80 µg/m^3 for which the spring and summer values are higher. Therefore, to maximize measurements to assess an upper limit on annual NO_2 concentration over a short period of time, those measurements should be done in winter if an annual concentration of less than 80 µg/m3 is expected, otherwise they should carry out in summer. To tackle the second issue, a second order polynomial approach is built on a Paris dataset covering years between 2013-2017 to determine annual mean concentrations with monthly mean concentrations and gives an overall error of 10%. The law built on Paris was then tested on several regions in France for the same period and resulted in predicted values with a mean error of about 15 % compared to the measured ones. In the end, the presented methodology allows covering twelve times more ground with a single NO_2 or NO_x sensor with an acceptable error.

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

Highlights:

- The Derwent and Middleton function enables converting annual NO_x into NO_2 in France.
- NO_2 and NO_x exhibit strong seasonal and monthly variabilities.
- The behavior of NO_2 concentrations related to seasons depends on their levels.
- Functions are presented to assess annual NO_2 concentration using monthly ones.

1. Introduction

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

Nitrogen dioxide (NO_2) is, with nitric oxide (NO), one of the two components forming nitrogen oxides. In the European Union (EU) and more generally around the world, NO_2 is the most measured component. Indeed, NO_2 can have significant harmful effects on health, inducing numerous diseases like bronchitis, pneumonias, etc. (Purvis and Ehrlich, 1963), but it can also increase the risks of viral and bacterial infections (Chauhan et al., 1998).

To obtain standard values for the purposes of comparison, the European Union (EU) and the World Health Organization (WHO) have issued critical values that should not be exceeded to protect the public from the health effect of gaseous NO_2. For this purpose, two standard values have been enforced : a hourly mean of 200 $\mu g/m^3$ and an annual mean of 40 $\mu g/m^3$ not to exceed given by both the WHO (WHO, 2017) and the EU (Directive 2008/50/EC). Studies have shown that the annual standard is generally more stringent than the hourly one (Chaloulakou et al., 2008; Jenkin, 2004). However, year-round measurements are needed to gather concentrations values that can be compared directly to this standard. This requirement is not a constraint when monitoring stations are located permanently in one area. Nonetheless, it becomes constraining when the objective is to evaluate urban planning projects over a limited period: the heterogeneity of urban areas requires controls related to the standard at several key locations where no permanent stations have been installed and where only temporary measurements are economically viable. Moreover, these temporary measurements may only provide information on NO_x concentrations but no direct information on NO_2. Thus, one question arises in such situation: how can annual mean NO_2 concentrations be determined using only a short measurement period of NO_2 or NO_x concentrations ?

The Leighton relationship provides information on the ratio between NO and NO_2 concentrations as a function of O_3, a chemical constant rate and a photolysis rate considering the photochemical steady state (Leighton, 1961). Unfortunately, it was demonstrated that using this method with more than 10 ppb of O_3 leads to an increasing error by not taking into account VOC chemistry (Sanchez et al., 2016). Different methods were proposed to evaluate the photolysis rate (Wiegand and Bo, 2000), but computing an annual representative photolysis rate can still lead to a wrong evaluation of the seasonal dependencies between NO_x and NO_2. Numerical computation based on complex chemical mechanisms involving more than 300 reactions with more than 100 species gives more accurate evaluations of NO_2 (Bright et al., 2013; Kim et al., 2012). Nevertheless, when NO_2 concentration measures are missing there is little chance that this information is known on other species such as VOCs. However, such information is needed in the numerical computations.

Furthermore, seasonal variability of NO_2 and NO_x concentrations differs considerably between summer and winter because NO_2 concentrations depend on photolysis conditions, and NO_x molecules play a role in several chemical mechanisms in the troposphere, involving ozone (O_3) and volatile organic compounds (VOC) (Seinfeld and Pandis, 2016). Robert-Semple et al. showed that there is a relative standard deviation of more than 50% when calculating the mean annual concentrations of both NO_2 and NO_x (Roberts–Semple et al., 2012). Moreover, Kendrick et al. showed that there is a seasonal variability in NO_2 concentration even with constant hourly seasonal traffic (Kendrick et al., 2015). Thus, these results show that a few months of NO_2 monitoring are generally not representative of a mean annual concentration despite existing only slight seasonal variations of the main source, namely traffic-related emissions.

The aim of this study is first to evaluate whether one-parameter methods without any explicit chemical mechanism found in the literature are sufficiently accurate to determine NO_2 concentrations based on monitored NO_x data in France. The second aim is to present a method capable of providing the mean annual NO_2 concentration from one-month period of monitoring.

In this article, the different areas of study as well as the measurement method and the approach to turn NO_x into NO_2 used are presented in section 2. Then, the results of the study on the NO_x-based NO_2 concentration calculation in France, and the method presented for the mean annual NO_2 concentration calculation based on monthly measurement periods, are presented in section 3.

2. Material and methods

2.1. Study location

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

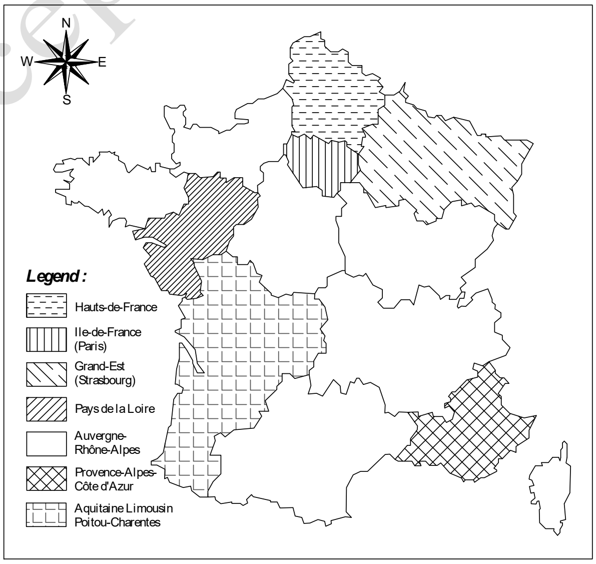

Fig. 1. Location of the different study areas used.

2.2. Data availability

The data used in this work were obtained via the open access database provided by the different air quality monitoring authorities known as AASQA, the French acronym for "Approved Air Quality Monitoring Associations". In particular, the data were provided by the organisations Atmo Haut-de-France (Haut-de-France), Atmo Grand-Est (Strasbourg region), AIRPARIF (Paris region), Air Pays de la Loire (Pays de la Loire), Atmo Auvergne-Rhône-Alpes (Auvergne-Rhône-Alpes), Atmo PACA (Provence-Alpes-Côte d'Azur) and Atmo Nouvelle-Aquitaine (Aquitaine Limousin Poitou-Charentes). The data are mainly mean annual NO_2 and NO_x concentrations over a five-year period from 2013 to 2017, but other data such as hourly measured concentrations for the Strasbourg region in 2018 were also obtained. Additional contacts were also made with AIRPARIF to obtain more specific data for the Paris Region like hourly measured concentrations from 2013 to 2017 with their corresponding uncertainties. A summary of the available data, corresponding to about 270 different sensors, is presented in Table 2.

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

2.3. Data range

The annual and monthly concentrations range from 10 to 340 µg/m^3 for NO_x and from 5 to 95 µg/m^3 for NO_2, considering the complete dataset (all years, types and locations of stations included). According to these wide ranges, different types of stations were considered in this work including rural, suburban, urban and traffic stations. The dataset for the Paris region comprises 2% rural, 13% suburban, 54% urban and 31% traffic stations. The type of station was not always directly provided in the global France dataset. Thus, the percentage of each type of station was estimated based on the range of concentrations for each type of station in Paris. The corresponding results were 29%, 22%, 31% and 18% for rural, suburban, urban and traffic stations, respectively.

2.4. Monitoring method

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

The reference method used for the measurement of nitrogen dioxide and oxides of nitrogen is known as chemiluminescence. Two chemiluminescence methods exist: on the one hand, chemiluminescence based on luminol reaction, and, on the other hand, chemiluminescence based on NO/O_3 reaction. The second method is the one used in

France. In particular AIRPARIF uses the AC32M EN model from ENVE and the 42i model from THERMO SCIENTIFIC.

The principle of the method was well-described by Navas et al. (1997) and is based on the reaction (1) between NO and O_3. This reaction produces an excited nitrogen dioxide (NO_2^*) that emits infrared radiations when returning to a stable state. The luminous radiation emitted and then measured is directly proportional to the NO concentration.

$$\mathrm{NO} + \mathrm{O_3} \rightarrow \mathrm{NO_2^*} + \mathrm{O_2} \qquad (1)$$

$$\mathrm{NO_2^*} \rightarrow \mathrm{NO_2} + h\nu \qquad (2)$$

To obtain information on the NO_x concentration, it is first necessary to convert all the NO_2 into NO before the measurement. After that, the resulting NO corresponding to the initial NO and the NO derived from NO_2 are measured and the NO_x concentration is obtained. Combining both the measured NO and NO_x concentrations provides the NO_2 concentration. Thus, the uncertainties on NO_2 measurement are higher than those on NO or NO_x because the results are obtained from both NO and NO_x measurements.

Based on the work of Navas et al., this kind of technique has very low detection limits, making it a good tool for evaluating the concentration of nitrogen compounds for atmospheric purposes (Navas et al., 1997). According to a personal communication with AIRPARIF, the maximal uncertainty on the mean annual NO_2 concentration from 2015 to 2017 was lower than 10% with a mean uncertainty of 6%.

2.5. Empirical methods to convert concentration from NO_x to NO_2

Several one-parametric empirical methods can be found in the literature to give an estimation of NO_2 concentration based on NO_x concentration. Three methods were compared with the entire France dataset:

- Derwent and Middleton function, a polynomial-logarithmic function linking hourly averaged NO_x and NO_2 concentrations for NO_x concentrations in the range of 9.0 to 1145.1 ppb (Derwent and Middleton, 1996).
- Romberg et al. function, a rational function linking annual averaged NO_x and NO_2 (Romberg et al., 1996).
- Bächlin et al., another rational function linking annual averaged NO_x and NO_x (Bächlin et al., 2008).

According to the above authors, the corresponding equations are (3), (4) and (5) respectively, with the hourly averaged NO_x and NO_2 noted $[NOx]_h$ and $[NO2]_h$ and annual averaged NO_x and NO_2 for the two other functions noted $[NOx]_a$ and $[NO2]_a$. All concentrations presented below are in μg/m^3 and $A=\log_{10}([NO_x]_h/1.91)$.

$$[NO_2]_h = \left(2.166 - \frac{[NO_x]_h}{1.91}(1.236 - 3.348A + 1.933A^2 - 0.326A^3)\right) \times 1.91 \qquad (3)$$

$$[NO_2] = \frac{103.[NO_x]_a}{[NO_x]_a + 130} + 0.005 \times [NO_x]_a \qquad (4)$$

$$[NO_2] = \frac{29.[NO_x]_a}{[NO_x]_a + 35} + 0.217 \times [NO_x]_a \qquad (5)$$

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

3. Results

3.1. Evaluation of annual NO_2 concentration based on NO_x data

3.1.1. Best fitting function in France

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

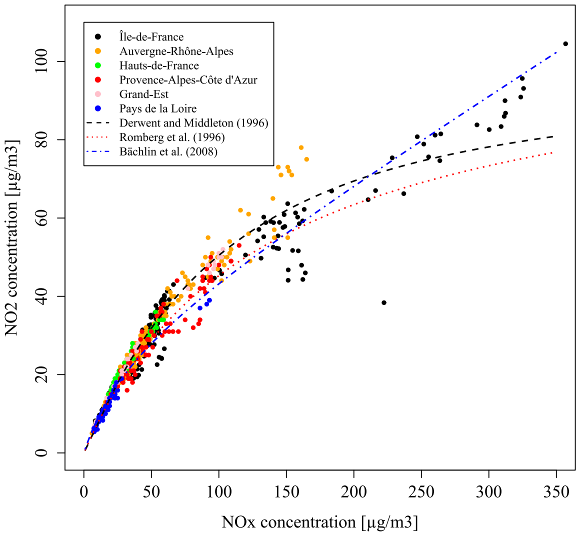

Fig. 2. Evolution of NO_2 concentration as a function of NO_x concentration and comparison with empirical functions

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

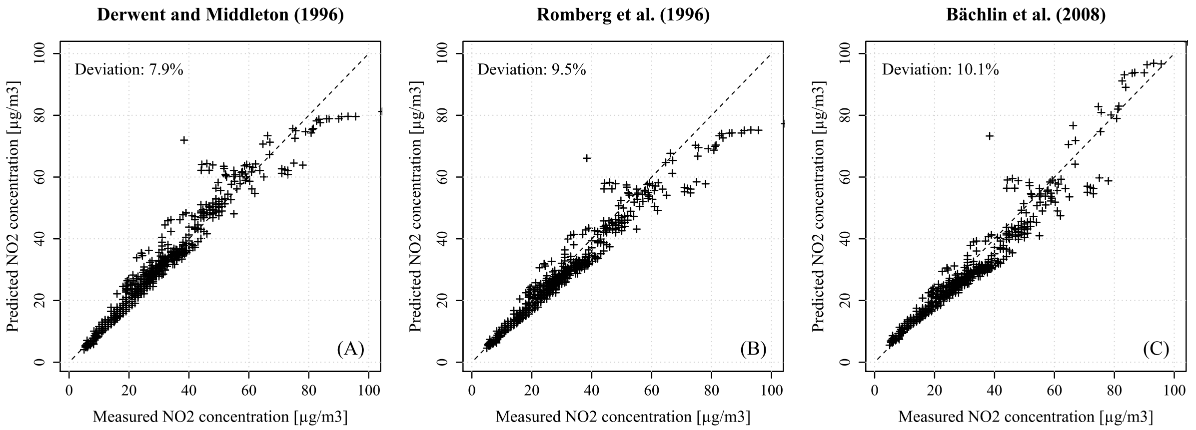

Fig. 3. Comparison between predicted and measured NO_2 concentrations for (A) the Derwent and Middleton function, (B) the Romberg et al. function, and (C) the Bächlin et al. function.

3.1.2. Application to Paris region

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

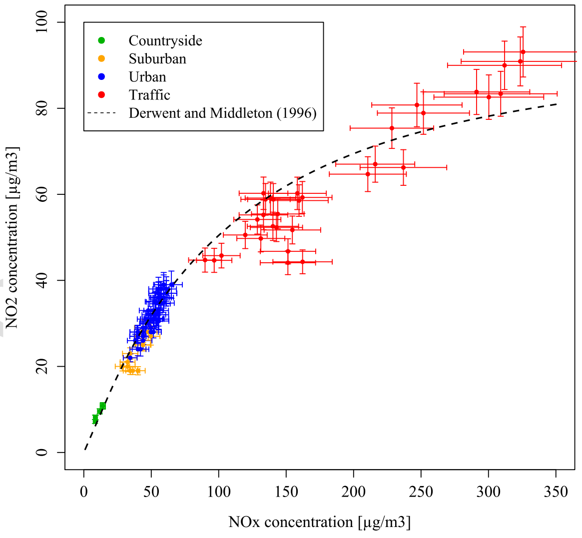

Fig. 4. Evolution of NO_2 concentration as a function of NO_x concentration for the Paris region dataset and comparison with Derwent and Middleton's function.

These results show that in accordance with previous observations, the best range of application for Derwent and Middleton's function is for NO_x concentrations lower than 80 µg/m^3. As can be seen in Fig 4. this limit corresponds to the difference between urban and traffic stations for Parisian region. Thus, Derwent and Middleton's method applies best for rural, suburban and urban stations whereas the results are less accurate for traffic. Indeed, there are 92% of the data that are within the uncertainties range both in the countryside and in urban areas, while for traffic data it falls to 71%. The mean error on predicted NO_2 concentrations is 9% with a 95th percentile of 27%.

3.2. Seasonal variability of NO_2 concentration

The seasonal variability of NO_2 was studied using the Paris region dataset. Hourly NO_2 concentrations were averaged for each station and each year of data, giving five mean concentrations per station and per year (one annual concentration and four seasonal concentrations). Fig. 5. (A) shows the differences between seasonal mean NO_x concentrations for each couple of year and station. Fig. 5. (B) shows the evolution of seasonal NO_2 concentrations as a function of the annual NO_2 concentration for the same year of measurement.

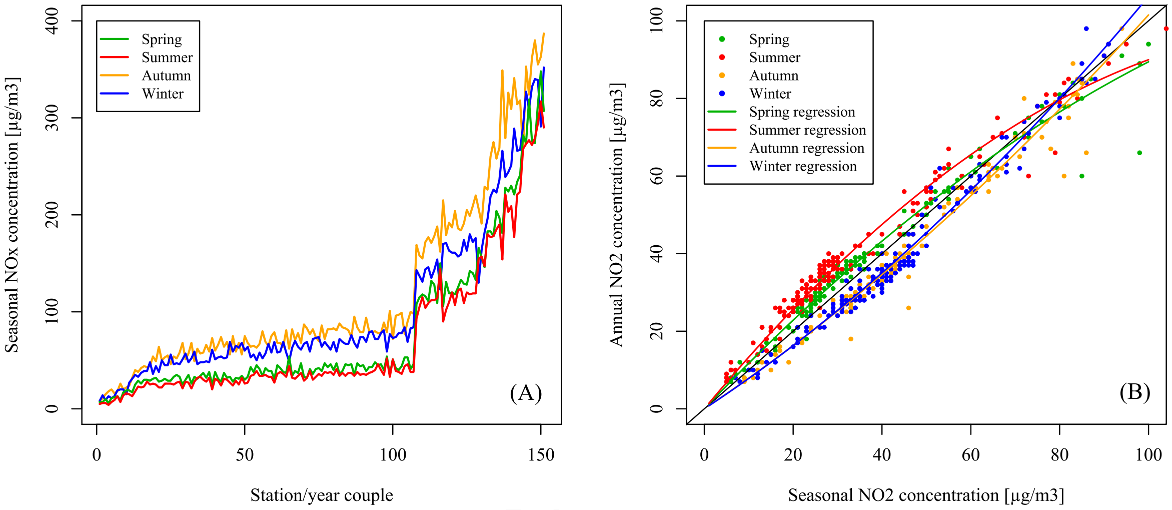

Fig. 5. Comparison between seasonal NO_x concentrations for a given station and year of measurement in the Paris region (A) and the evolution of the annual NO_2 concentration as a function of seasonal NO_2 concentrations (B).

According to Fig. 5. (A), NO_x concentrations are strongly dependent on the season. Indeed, although summer and spring NO_x concentrations are similar, the concentrations are higher in winter and autumn by up to a factor of 2. These differences can be explained by several disparities between these seasons: lower boundary layer height, lower temperatures and new sources of emission due to residential heating, increased emissions by cold-started vehicles, etc.

Since the results show that NO_x concentrations are higher in winter and autumn, for a given NO_x concentration the seasonal NO_2 concentrations should also be higher in autumn and winter than in summer and spring. However, the results for the Paris region show a different trend. The result in Fig. 5. (B) indicates a change of behavior when the annual NO_2 concentration increases, with the summer and spring NO_2 concentrations becoming higher than in autumn and winter. These results can be associated with those of other authors. Indeed, Kendrick et al. showed that NO_2 concentrations are higher in winter and autumn than in spring and summer, with a mean annual NO_2 concentration lower than 80 $\mu g/m^3$ and for three different types of station (Kendrick et al., 2015). On the contrary, Mavroidis and Ilia showed that for a traffic station (i.e. giving high NO_2 concentrations), NO_2 concentrations are generally higher during the summer and spring months than in autumn and winter, with in their case a mean annual NO_2 concentration higher than 80 μg/m^3 (Mavroidis and Ilia, 2012). Thus, the evolution of seasonal NO_2 concentrations as a function of annual NO_2 concentration is not well represented by a linear method unable to catch these varying trends and is much better fitted by a quadratic one. With this interpolation, the spring and summer results are described by a concave quadratic function whereas the autumn and winter ones are described by a convex quadratic function. In this case, these concavities and convexities result in a NO_2 concentration of about 80 μg/m^3, where the seasonal NO_2 concentrations are equal to the annual NO_2 concentration. This concentration of 80 μg/m^3 corresponds to the value for which, in the case of a measurement station giving an annual average NO_2 concentration lower than this value, the concentrations for winter and autumn are higher than the spring and summer concentrations. Therefore, to obtain maximized measurements in order to assess an upper limit on annual NO_2 concentration over a short period of time, the measurements should be carried out in winter, in case where an annual concentration of less than 80 μg/m3 is expected, otherwise measurements should be carried out in summer.

These observations are consistent with those of other research papers, despite being counter intuitive on the first point of view. Indeed, a previous observation was that NO_x concentrations are higher during autumn and winter, in theory giving higher NO_2 concentrations. Moreover, in summer and spring, the zenithal angles are generally lower, leading to increased photochemistry with higher photolysis, including NO_2 photolysis, and the production of radicals. As shown in Fig. 6. (A), O_3 concentrations are globally much lower in autumn than in winter, and in winter than in spring and summer. These concentrations are about the same between spring and summer. Fig. 6. (B) gives supplementary information on how much ozone is available to react with NO_2, by giving the evolution of the ratio of the seasonal O_3 concentration over the seasonal NO_2 concentration as a function of the seasonal NO_2 concentration.

The first observation is that more O_3 molecules are available in spring and summer than in winter and autumn for any NO_2 concentration. This statement is always true even when the seasonal NO_2 concentration increases, leading to a systemic reduction of available O_3. For example, for a seasonal NO_2 concentration of 15 μg/m3, the ratio of seasonal O_3 concentration over seasonal NO_2 concentration is around 3 for autumn, 4 for winter and almost 5 for spring and summer. Increasing the seasonal NO_2 concentration to 30 μg/m^3 gives ratios of 1 and 1.5 for autumn and winter respectively and almost 2 for both spring and summer. The explanation of why the seasonal NO_2 concentration is higher in spring and summer than in winter and autumn for high NO_2 concentrations can be obtained from these two observations. For low NO_2 concentrations, O_3 is readily available and the reaction is not limited by the O_3 concentration but by several other factors that lead to the commonly accepted result: NO_2 concentrations are higher in winter and autumn than in spring and summer. However, when the NO_2 concentration increases, O_3 becomes less and less available until reaching a state in which it becomes the limiting reagent of the production reaction of NO_2 from NO_x. This state is reached earlier in winter and autumn than in spring and summer, leading to a higher NO_2 concentration in summer and spring than in autumn and winter.

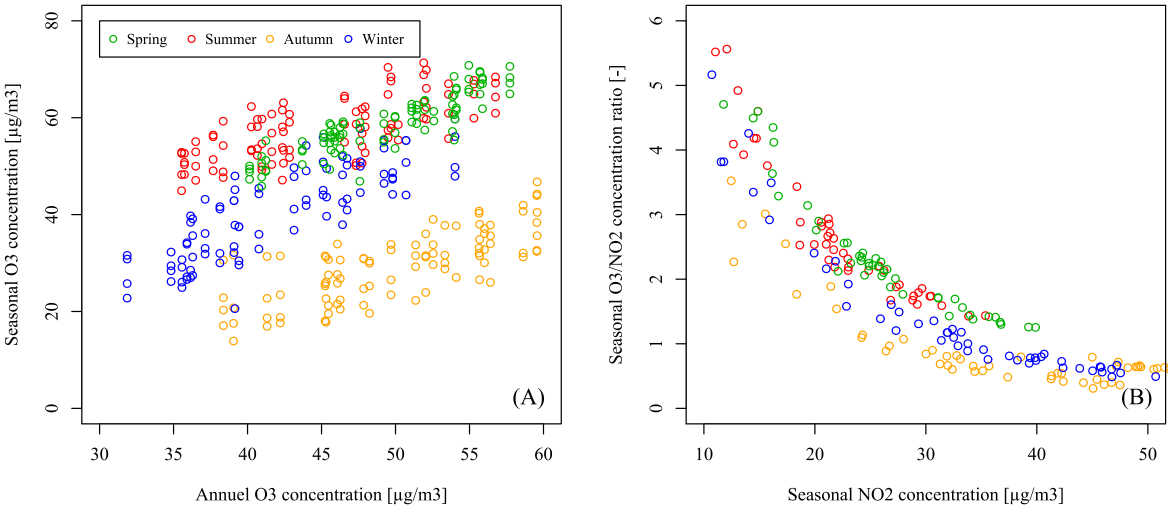

Fig. 6. Evolution of the seasonal O_3 concentration as a function of the annual O_3 concentration (A) in the Paris region and the evolution of the ratio between seasonal O_3 and NO_2 concentrations as a function seasonal NO_2 concentrations (B).

3.3. Assessment of annual NO_2 concentration

3.3.1. Assessment of annual NO_2 concentration from monthly NO_2 concentrations

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

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

$$[NO_2]_a = a.[NO_2]_m{}^2 + b.[NO_2]_m \qquad (4)$$

The polynomial methods obtained have different concavities and convexities, consistent with those obtained for seasonal variability. The maximum convexity is obtained around December and January, corresponding to the transition from autumn to winter. The maximum concavity is obtained around June and July, corresponding to the transition from spring to summer. Lastly, minimal concavity and convexity is obtained around March and September, corresponding to the transition from winter to spring and from summer to autumn, respectively. For these months, monthly averaged NO_2 concentrations are almost equal to annual NO_2 concentrations. According to these polynomial methods, the maximal mean error is around 15% and corresponds to December, and the minimal mean error is around 7% and corresponds to March. The mean error averaged over all months is below 10%.

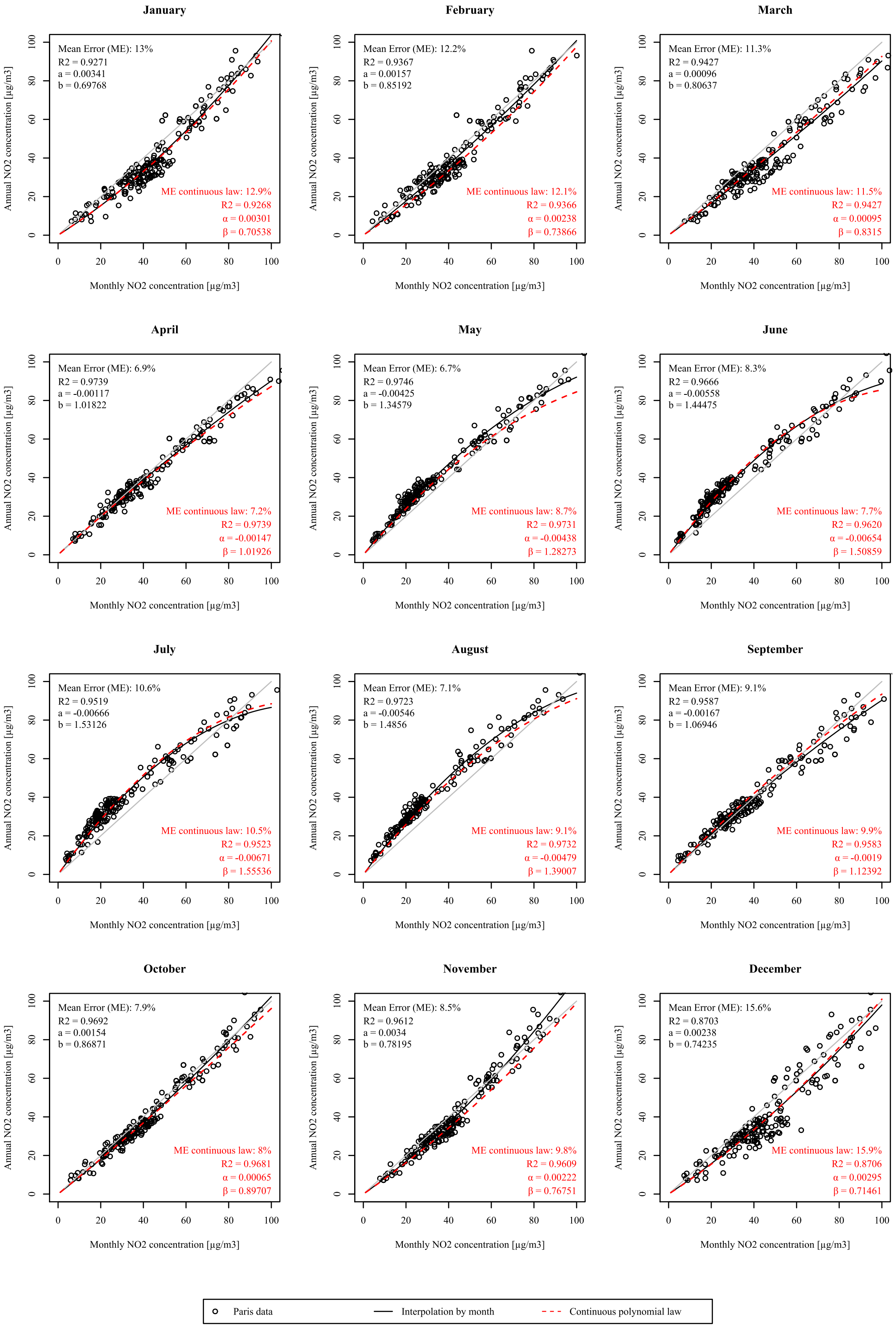

Fig. 7. Evolution and interpolation of annual NO_2 concentration as a function of monthly NO_2 concentration.

These polynomial methods can be used to assess the annual NO_2 concentration based on only one month of measurements. However, the problem is that measurements from the first day to the last day of a month are required. If one month of data is acquired that overlaps two distinct months, say from 15th January to 15th February, the interpolation is no longer appropriate. An additional study was carried out to change from discrete to continuous interpolation. To achieve this, the resulting polynomial coefficients *a* and *b* were plotted as a function of the month with 1 corresponding to January and 12 to December. Fig. 8. shows the corresponding results.

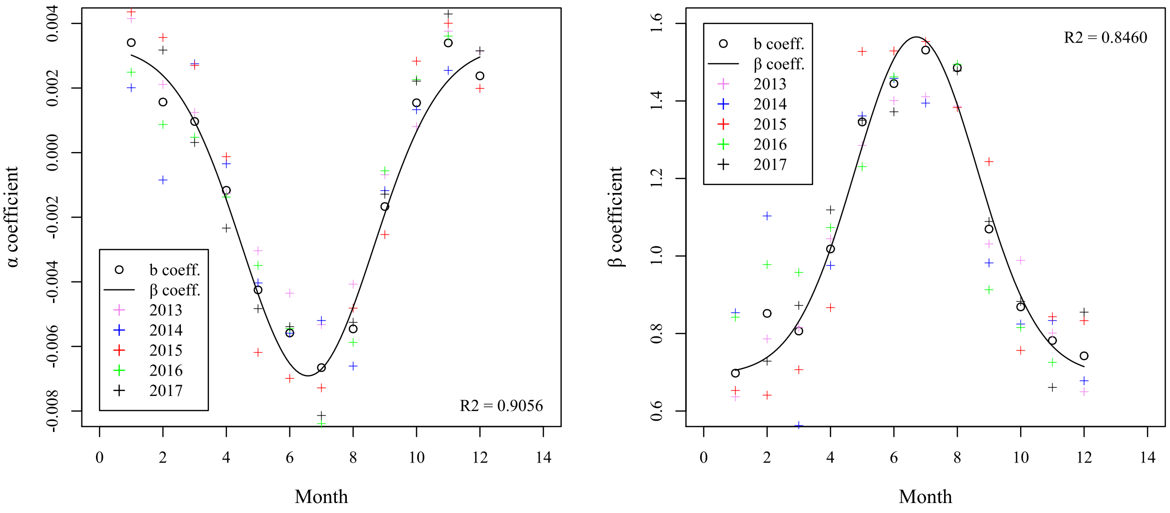

Fig. 8. Interpolation of a and b coefficients (for each year considered and the subsequent mean) and resulting continuous α and β coefficients.

As shown in Fig. 8., both coefficients *a* and *b* seem to follow a cyclic trend. However, the evolution of the coefficients is inversed with a minimal value of *a* around June, corresponding to a maximal value of *b*. On the contrary, the maximal value of *a* is reached around January, corresponding to a minimal value of *b*. Considering the trends of *a* and *b* observed, a Gaussian function was used to obtain continuous values bringing two new coefficients, α and β, respectively, corresponding to the coefficients obtained from the continuous method. The corresponding equations for α and β are (5) and (6), respectively, with *m* being the month corresponding to the available data (e.g. m = 1 for the data from the first to the last day of January, m = 3.5 for the data from the middle of March to the middle of April, etc.).

$$\alpha = 0.0033 - 0.0102.\exp\left[\frac{-(m-6.5749)^2}{8.6962}\right] \qquad (5)$$

$$\beta = 0.6945 + 0.8708.\exp\left[\frac{-(m-6.7076)^2}{7.4328}\right] \qquad (6)$$

The new curves obtained for each month with (4), and the calculated α and β corresponding to *a* and *b* respectively, are presented in red dashed lines in Fig. 7, in addition to the corresponding values of α and β, R2 and the mean error (ME) compared to the Paris data. When comparing these new curves with the previous ones obtained with *a* and *b*, they are globally the same except for May and November, for which the curves start to deviate from each other for high monthly NO_2 concentrations.

Nonetheless, the mean error for these two months is still acceptable, with in both cases a mean error of less than 10%. The mean errors for each month are approximatively equal between both cases and give an overall error of 10% and a maximal error of 16% in December.

In view to assessing the reliability of the equations, the polynomial methods were applied to several regions of France, including Aquitaine Limousin Poitou-Charentes, Auvergne-Rhône-Alpes and Provence-Alpes-Côte d'Azur from 2013 to 2017. For each month of these years, the mean annual NO_2 concentrations were calculated based on each month of data. The discrete polynomial methods were used here because the information was available for each month. The calculated annual concentrations were then compared to the measured concentrations and a mean error was obtained. The mean errors are summarized in Table 2. This table also gives information on the error obtained when the monthly NO_2 concentration is taken directly as an annual NO_2 concentration (called direct approach), and on the improvements between this direct approach and the approach using the suggested methods. For the three regions considered, the mean error using the discrete method is higher than for the Paris region, ranging from 12% to 20%. The errors obtained when using the direct approach range from 18% to 32%. The improvement between the two approaches depends on the regions considered and ranges from 26% to 46% with an overall improvement of 38%. According to these results, the method presented in this paper is reliable and can be used outside the Paris region in France. Overall, this simple applicable polynomial method improves the results in comparison to a direct approach by up to a factor two.

Table 2. Global results of the polynomial discrete method over regions in southern France and improvements compared to the 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			

3.3.2. Assessment of annual NO_2 concentration from monthly NO_x concentrations.

The final study was performed to give an estimation of the total error when calculating annual NO_2 concentration using monthly measured NO_x data. To manage this, data for the Paris region for the year 2017 were used. Firstly, the monthly NO_2 concentrations were calculated based on monthly NO_x concentrations measurements using the Derwent and Middleton function (3). Then, annual NO_2 concentrations were calculated using (4), (5) and (6). The resulting annual NO_2 concentrations were plotted against measured annual NO_2 concentrations and are presented in Fig. 9. (B). The previous results for Paris from 2013 to 2017 and for which the calculated annual NO_2 concentrations are based on monitored monthly NO_2 concentrations are also provided in Fig. 9. (A). According to Fig. 9. (A), a global error of 10% for Paris region is obtained and it can also be seen that the maximal errors occur for the highest NO_2 concentrations. The same observation can be made when comparing this result with those for Paris assessed with the monthly NO_x concentrations for 2017. The global error in this case increases but does not exceed 15%.

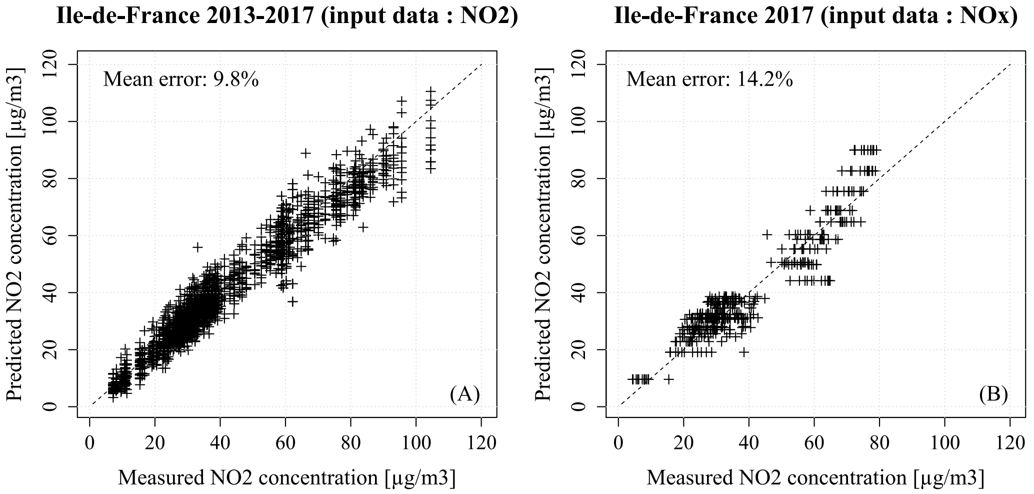

Fig. 9. Comparison between calculated and measured annual NO_2 concentrations for the Paris region from 2013 to 2017 (A) and for the Paris region based on monthly 2017 NO_x concentrations (B).

4. Discussion

The seasonal variability of NO_2 concentrations was shown and leads to higher or lower seasonal NO_2 concentrations compared to annual NO_2 concentrations. An explanation for these observations was proposed and seems to be linked to the seasonal variability of ozone concentrations as well as the seasonal variability of available ozone to react with NO_2. However, this link must be quantified to better explain the phenomenon and evaluate if these observations can be fully generalized. The first hypothesis is that this phenomenon may only be generalizable to countries whose seasonal variability in ozone concentrations are like those observed in France. Thus, in countries having other types of seasons like Indonesia, with only a dry and a monsoon season or India, with winter, summer, monsoon and post-monsoon seasons, the results would be very different, and the equations presented in this paper may not be relevant. However, it may be possible to apply the methodology and adapt the coefficients of the equations to obtain good results in these countries. Nevertheless, this would require long periods of measurements.

It should also be noted that for some specific periods, monthly NO_2 concentrations are representative of annual NO_2 concentrations. Indeed, averaging monthly concentrations measured in March, April, September or October could give good estimations of the mean annual concentrations directly. For these months, it might not be necessary to use the previous methodology to assess the annual NO_2 concentration.

Lastly, the different equations obtained that could be used to assess annual NO_2 concentrations, were built for and applied to regions having around the same latitudes, from 43° to 50°. For a very different latitude, the coefficients of the equations might not be optimized, and greater errors could occur.

5. Conclusion

The assessment of annual NO_2 concentrations with partial data was studied from two main approaches. The first one was to determine the annual mean NO_2 concentration with only annual mean NO_x concentration information. The second was to determine the annual mean NO_2 concentration with only a one-month period measurement. The main conclusions are as follows:

(a) Three functions giving annual NO_2 concentrations based on NO_x data were compared. These functions correspond to the methods of Derwent and Middleton, Romberg et al., and Bächlin et al. The results show that the method proposed by Derwent and Middleton is the better suited to assess the annual NO_2 concentration based on NO_x concentrations for several regions of France and for several years both for rural and urban areas in particular. However, this method has some limitations for high NO_x concentrations and gives less accurate results for traffic stations with annual NO_x concentrations higher than 70 $\mu g/m^3$. The global error of this method for the regions of France considered is around 8%.

(b) NO_2 concentrations are seasonally variable and depend on the concentrations of NO_x and their ratio with VOC concentrations, and on the photochemistry conditions. Hence, making it impossible to give an annual concentration directly from a seasonal concentration: for annual NO_2 concentrations lower than 80 $\mu g/m^3$, summer and spring NO_2 concentrations are lower than autumn and winter concentrations; for higher annual NO_2 concentrations, it is the summer and the spring NO_2 concentrations that become higher than the autumn and winter concentrations. Thus, to evaluate an upper limit on annual NO_2 concentration over a short period of time, measurements should be done in winter if an annual concentration of less than 80 µg/m3 is expected, otherwise they should be carried out in summer

(c) Monthly NO_2 concentrations follow the same variability trends as the seasonal concentrations which were quantified for each month. A discrete function was proposed to assess annual NO_2 concentrations based on monthly NO_2 concentrations, yielding a global error of 10% for the Paris region. The corresponding function was made continuous using two Gaussian methods to facilitate its use, leading also to a global error of 10% for the Paris region. The discrete methods applied to the southern regions of France yielded an overall error of 15% and provided an improvement ranging from 26% to 46% compared to the utilization of the direct approach.

(d) Using both the Derwent and Middleton method and the quadratic equations method both presented in this work it is possible to assess annual NO_2 concentrations from monthly NO_x concentrations measurements. Those methods led to an overall error of 15% for the Paris region for the year 2017.

All the results and observations discussed in this paper concern NO_x and NO_2 concentrations and it was shown that interesting results can be obtained to reduce measurement periods and estimate NO_2 concentrations from NO_x data without introducing any chemical considerations. This methodology could be extended to other pollutants like particulate matter, which even if not highly chemically active, are subject to specific phenomena like deposition, resuspensions, etc.

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