Photochemical regimes in urban atmospheres: The influence of dispersion

Cécile Honoré, Robert Vautard, Matthias Beekmann

► To cite this version:

Cécile Honoré, Robert Vautard, Matthias Beekmann. Photochemical regimes in urban atmospheres: The influence of dispersion. *Geophysical Research Letters*, 2000, 27 (13), pp.1895-1898. 10.1029/1999GL011050 . hal-02925721

HAL Id: hal-02925721

<https://hal.science/hal-02925721>

Submitted on 30 Aug 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.

Photochemical regimes in urban atmospheres: The influence of dispersion

Cécile Honoré and Robert Vautard¹

Laboratoire de Météorologie Dynamique, Ecole Normale Supérieure, Paris, France

Matthias Beekmann

Service d'Aéronomie, Université Pierre et Marie Curie, Paris, France

Abstract. The dependence on emissions of urban photochemistry is studied under meteorological conditions favouring pollution episodes. We use a simple chemistry-transport model, yet realistic with respect to the main chemical and physical processes and considering the diurnal cycle of forcing parameters. For a range of NO_x emissions, the diurnal equilibria of the system are searched for. It is shown that, if the photochemistry over a large city mostly exhibits a negative sensitivity to NO_x emissions, there are meteorological situations under which it becomes (positively) NO_x sensitive, the dispersion time scale being a key parameter. We show that, under specific conditions, the urban atmosphere might reach two very different diurnal equilibria. We demonstrate that the sensitivity to NO_x emissions evolves with time: under specific conditions, the urban atmosphere becomes NO_x sensitive within two days.

Introduction

For several years, controlling urban air quality has turned out to be of primary importance as many cities violate air quality standards, especially with respect to photooxidant (NO_2 and O_3) levels. These species build up from NO_x ($\text{NO} + \text{NO}_2$) and Volatile Organic Compounds (VOC) which, at the urban scale, result mostly from human activities [Chameides *et al.*, 1992]. It seems possible to decrease urban photooxidant levels by controlling anthropic precursor emissions at a local scale.

In rural areas, photooxidant levels depend on NO_x emissions and it is admitted that photooxidant build-up downwind of major cities eventually depends on the amount of urban NO_x emissions [Jacob *et al.*, 1993; Roselle and Schere, 1995; Sillman *et al.*, 1990; Trainer *et al.*, 1995]. By contrast, the urban O_3 peak sensitivity to NO_x versus VOC emissions is controversial [Sillman, 1999]. This stems from the double role of NO_x as producing O_x ($\text{NO}_2 + \text{O}_3$) from radicals resulting from VOC oxidation and as reducing OH concentrations

through nitric acid formation [Kleinman, 1991, 1997; Lin *et al.*, 1988]. We show that the sensitivity of urban O_x concentrations to local NO_x emissions critically depends on meteorological conditions, and specifically dispersion (horizontal or vertical transport). By using a chemistry-transport box model, this is demonstrated for the diurnal equilibria of urban photochemistry as well as for its transient behaviour. Another aspect of the nonlinear character of photochemistry is the existence of multiple photochemical states. The existence of a hysteresis has been noticed in the context of the free troposphere, using simplified chemistry and idealized box models [Kleinman, 1994; Stewart, 1993, 1995; White and Dietz, 1984]. This feature has never been found for an urban environment, in more realistic models with diurnal cycle of forcing parameters. It is showed here that for specific meteorological and emissions conditions, the urban atmosphere can reach two different diurnal equilibria, depending on initial conditions.

Model Description

We use a chemistry-transport box model with simplified physics and realistic gas-phase chemistry. The chemical mechanism is an updated and extended version of the EMEP mechanism [Simpson *et al.*, 1993], suited to polluted as well as unpolluted environments. The urban area is modeled by a 30 km wide one-dimensional box and the boundary layer is divided into three layers (see Fig. 1). This geometry implies each layer is well-mixed and the concentrations may be thought of as mean concentrations. The species concentrations vary due to horizontal transport (constant in time), vertical mixing, entrainment from residual into mixed layer, dry deposition, emissions, and chemistry. A flux budget is computed within each layer. The diurnal cycle of some meteorological parameters is taken into account as well as variation of the zenithal angle, typical of a summer day near solstice over Paris ($49^\circ\text{N}, 2.5^\circ\text{E}$). Some parameters are given in Table 1.

Emissions derive from different databases [CITEPA, 1993; GENEMIS, 1994; Salles *et al.*, 1996] for 16 model species, according to the aggregation procedure of Middleton *et al.* [1990]. They contain anthropic and biogenic sources [Simpson *et al.*, 1995] and follow a diurnal cycle, with traffic peaks at 7 h and 16 h UT. Typical

¹Now at Laboratoire de Météorologie Dynamique, Ecole Polytechnique, 91128 Palaiseau Cedex, France.

Figure 1. Modeled urban atmosphere. The surface layer height is constant. The mixed layer evolution is prescribed. It reaches its maximum height at 14 h UT, remains well-developed as long as turbulent mixing is fed and collapses at 18 h UT, with a minimum height during night. The top of the residual layer defines the top of the urban atmosphere. As the mixed layer develops, entrainment of air occurs from residual into mixed layer. At the end of the afternoon and all night long, chemical species formed during daytime in the mixed layer are trapped in the residual layer.

'clean' concentrations are taken for CH_4 (1.8 ppm), CO (0.1 ppm) and O_3 (30 ppb) at the domain boundaries.

Chemical Regimes and Multiple Diurnal Equilibria

The sensitivity of urban photochemistry to NO_x emissions is investigated by varying these emissions in the model. To test the effect of dispersion, we consider two scenarios: A very stagnant case, with wind speed of 0.1 m/s in the surface layer (0.2 m/s above) corresponding to a residence time of air in the urban area of about 42 hours; A moderately stagnant case (wind speeds multiplied by ten). The latter case is typical of polluted conditions in Paris, while the former is less realistic. For each scenario and various NO_x emissions, the model is run until equilibrium (see legend of Fig. 2). Since forcing has a diurnal cycle, concentrations also display a diurnal cycle. We study concentrations at 14 h UT, the approximate O_3 peak hour. Fig. 2a and 2b show some photooxidant concentrations versus NO_x emission weight ENO_x , for the two dispersion scenarios. In both cases, O_3 and NO_2 first increase with increasing NO_x emissions. Then, O_3 decreases with still increasing NO_x emissions and NO_2 increases up to a saturation value. O_x behaves like O_3 for low NO_x emissions, but finally converges to NO_2 for higher NO_x emissions. It also appears that the transition between the two sensitivity regimes depends on wind speed: It shifts from $\text{ENO}_x = 0.7$ for the moderately stagnant case to $\text{ENO}_x = 1.4$ for the very stagnant case. Under the latter configuration, for standard NO_x emissions ($\text{ENO}_x = 1.0$), the urban photochemistry is NO_x sensitive: A decrease in NO_x emissions results in a decrease in O_3 and O_x peaks. In the former case, O_3 sensitivity is negative: An increase of NO_x emissions results in a decrease of O_3 and O_x .

This positive NO_x emissions sensitivity for very low wind speed is contradictory to several studies showing that areas close to large NO_x sources are associated with VOC rather than NO_x sensitivity [Jacob *et al.*, 1993; Roselle and Schere, 1995; Trainer *et al.*, 1995]. However, in a very stagnant situation, it seems possible for an air mass to age photochemically, so that it becomes NO_x sensitive *within* the urban area [Sillman, 1999]. This *in situ* photochemical aging is due to the difference of reactivity of VOC and NO_x relative to OH, resulting in higher VOC/ NO_x ratios in the very stagnant case than in the moderately stagnant case, regardless of NO_x emissions (not shown). A consequence is higher radical concentrations and better efficiency of radical-radical reactions relative to the ' $\text{NO}_2 + \text{OH}$ ' pathway in removing radicals, as confirmed by radical budget performed for both dispersion cases as a function of NO_x emissions (Fig. 2c and 2d). Radical loss pathways are associated with sensitivity regimes, the two loss curves intersecting almost exactly at the same ENO_x as those of the change in sensitivity regimes. The change of sensitivity regime with dispersion for standard NO_x emissions can thus be explained by a change of relative importance of radical loss pathways: In the very stagnant case, radical loss is dominated by radical recombinations, additional NO_x emissions do not affect radical budget but increase O_x . In the other case, it is dominated by nitric acid formation, additional NO_x emissions titrate even more OH.

Another remarkable point that stems from Fig. 2 is the existence of multiple diurnal equilibria in the very

Table 1. Some model parameters

Parameter and unit	SL	ML, RL
Cloudiness (%)	0	0
O_3 deposition velocity (cm/s)	0.25 *	-
Exchange rate with free troposphere (cm/s)	-	0.4
Humidity (ppb)	2e+07	1.65e+07
Temperature (K)	300 *	300
NO emissions	3.3e+12 *	-
NO_2 emissions	1.7e+11 *	-
CO emissions	5.0e+13 *	-
CH_4 emissions	2.8e+12 *	-
C_2H_6 emissions	2.6e+12 *	-
$\text{n-C}_4\text{H}_{10}$ emissions	3.1e+12 *	-
C_2H_4 emissions	5.7e+11 *	-
C_3H_8 emissions	1.3e+12 *	-
C_5H_8 emissions	6.6e+11 *	-
<i>o</i> -xylene emissions	7.2e+11 *	-
HCHO emissions	1.3e+11 *	-
CH_3CHO emissions	4.6e+11 *	-
Methyl ethyl ketone emissions	1.6e+11 *	-
CH_3OH emissions	2.1e+11 *	-
$\text{C}_2\text{H}_5\text{OH}$ emissions	3.7e+09 *	-

SL, ML, RL denote respectively the surface, mixed and residual layer. Parameters with a diurnal cycle are mentioned by a *. In this case, the maximum value is given, except for emissions (values at 12 h UT, in $\text{molec}/\text{cm}^2/\text{s}$).

Figure 2. Some photooxidant concentrations at 14 h UT versus NO_x emissions, in the very (a) and moderately (b) stagnant case, for the urban photochemical system at (diurnal) equilibrium. NO_x emissions are normalized by standard NO_x emissions (see Table 1). Diurnal equilibrium is reached by running the model until $\|C(h_0 + T) - C(h_0)\| \leq \epsilon$, where C is the concentration vector, h_0 a fixed hour in the day, ϵ a required accuracy and $T = 24$ h. For each new ENO_x , the last equilibrium found is used as initial concentrations. Increment of ENO_x is done once by increasing emissions, once by decreasing them. Concentrations are averages over the model layers. Also displayed, radical budget versus ENO_x , in the very (c) and moderately (d) stagnant case. Values are averages over the model layers and over whole day. 'Rad+Rad' denotes all radical-radical reactions. The 'PAN' curve (resp. 'AlkNit') represents the net radical budget related to peroxyacetylnitrates (resp. alkylnitrates) chemistry.

stagnant case. For $\text{ENO}_x \approx 3.0$, the model urban atmosphere can reach two different equilibria, depending on initial concentrations. These multiple diurnal equilibria exist throughout the day within the same NO_x emissions range. At 14 h UT, the O_3 peak can reach 130 ppb or be as low as 40 ppb. As wind speed increases, the multiple diurnal equilibria region disappears.

Transient Behaviour of the Urban Photochemical System

Under real conditions, due to the variability of forcing parameters, one could hardly expect to observe such a behaviour as the one underlined previously, since it takes several days for the system to reach diurnal equi-

librium. The urban photochemical system is now studied on a short period, starting from a non polluted situation. We do not wait until diurnal equilibrium but investigate *transient* behaviour. Not only do we study sensitivity to NO_x emissions but also the influence of the dispersion on this sensitivity.

We use the same box model as before. Given NO_x emissions and dispersion conditions, we compute the O_3 peak in the urban mixed layer, on the first, second and third day of the simulations. For all simulations, initial concentrations are typical of an urban area. To be as general as possible, three types of environments are considered: Weakly polluted (VOC and NO_x standard emissions twice as low as Paris emissions), moderately polluted (VOC and NO_x standard Paris emissions) and highly polluted (VOC and NO_x standard emissions twice as large as Paris emissions). Each row (resp. column) in Fig. 3 refers to a given day (resp. environment). In each panel, the O_3 peak is displayed as a function of NO_x emissions weight ENO_x and residence time so that the results do not depend on the size of the city under consideration.

It clearly stems from Fig. 3 that whatever the urban environment, several sensitivity regimes exist. First, for low residence times (below 10 h), the O_3 peak is rather insensitive to NO_x emissions over a wide range of conditions. Second, for higher residence times, the transition between a positive and a negative NO_x sensitive regime evolves with time. On the first day, transition is independent on dispersion. This is not the case on the

Figure 3. Modeled O_3 peak (in ppb) in mixed layer as a function of NO_x emission weight (x axis) and residence time in the urban area, in hours (y axis). Isolines every 25 ppb. Each panel correspond to a given environment (weakly, moderately, strongly polluted) and day (first, second, third) of simulations.

second and even more on the third day, where it shifts to higher NO_x emission weights, due to photochemical aging. For example, in the moderately polluted case, for standard NO_x emissions ($\text{ENO}_x = 1.0$), the mixed layer O_3 peak is negatively NO_x sensitive on the first day. If residence time exceeds 35 h (resp. 24 h), it becomes NO_x sensitive on the second (resp. third) day. Finally, as the environment is more polluted, the transition shifts to lower NO_x emission weights and the O_3 peak becomes more sensitive to the studied parameters. For example, in the strongly polluted case and for standard NO_x emissions, urban photochemistry remains negatively NO_x sensitive over the three days.

Considering a specific point in Fig. 3, defined by its NO_x emission weight (0.7) and residence time (30 hours), one gets an insight into the difficulty of characterizing the sensitivity of an urban area. On the first day, it can be in any sensitivity regime, depending on environment. In the strongly polluted case, it is positively or negatively sensitive to NO_x , depending on the day. Finally, when changing the residence time for given emissions and day, the sensitivity regime also differs.

Conclusion

The results shown in this paper suggest that no universal abatement strategy can be efficient to reduce photochemical smog over a large urban area. Not only sensitivity to NO_x emissions depends on emissions, but also on meteorological parameters such as dispersion. This has been shown for an urban photochemical system at (diurnal) equilibrium but also for its transient behaviour. A systematic analysis with varying emissions, VOC/ NO_x emission ratios and residence times has made evident the existence of a region of parameters space in which sensitivity to NO_x depends on dispersion, larger residence time favouring positive sensitivity due to photochemical aging. Paris, such as possibly other large cities, appears to be located in this region. The rather crude model geometry, uncertainties in emissions, VOC mix reactivity and chemical scheme make a precise estimation of the transition between chemical regimes difficult. Still it is expected that the results will qualitatively hold against these limitations.

An additional result is the theoretical existence of multiple diurnal equilibria in an urban atmosphere. Although this phenomenon is brought to light for an urban area such as Paris, for very low dispersion conditions, it might hold for larger cities for more realistic dispersion conditions. This may be of great practical importance, especially with respect to air quality forecasts. However, the time taken by the urban atmosphere to shift from one state to the other is of several days, so that for this phenomenon to be observed, low wind speed would have to persist for several days.

References

- Chameides, W.L. *et al.*, Ozone precursor relationships in the ambient atmosphere, *J. Geophys. Res.*, **97**, 6037-6055, 1992.
- CITEPA, Inventaire des émissions de SO_2 , NO_x , poussières, COVNM, CH_4 dans l'atmosphère en Ile-de-France en 1990, *CITEPA study for AIRPARIF*, 1993.
- GENEMIS (Generation of European Emission Data for Episodes) project, *EUROTRAC annual report 1993*, part 5, EUROTRAC international scientific secretariat, Garmish-Partenkirchen, 1994.
- Jacob, D.J. *et al.*, Factors regulating ozone over the United States and its export to the global atmosphere, *J. Geophys. Res.*, **98**, 14817-14826, 1993.
- Kleinman, L.I., Seasonal dependence of boundary layer peroxide concentration: The low and high NO_x regimes, *J. Geophys. Res.*, **96**, 20721-20733, 1991.
- Kleinman, L.I., Low and high NO_x tropospheric photochemistry, *J. Geophys. Res.*, **99**, 16831-16838, 1994.
- Kleinman, L.I., Dependence of ozone production on NO and hydrocarbons in the troposphere, *Geophys. Res. Lett.*, **24**, 2299-2302, 1997.
- Lin, X., Trainer, M. and S.C. Liu, On the nonlinearity of the tropospheric ozone production, *J. Geophys. Res.*, **93**, 15879-15888, 1988.
- Middleton, P., Stockwell, W.R. and W.P. Carter, Aggregation and analysis of volatile organic compound emissions for regional modelling, *Atmos. Environ.*, **24**, 1107-1133, 1990.
- Roselle, S.J. and K.L. Schere, Modeled response of photochemical oxidants to systematic reductions in anthropogenic volatile organic compound and NO_x emissions, *J. Geophys. Res.*, **100**, 22929-22941, 1995.
- Salles, J., Janischewski, J., Jaeger-Voirol, A. and B. Martin, Mobile source emissions inventory model: Application to the Paris area, *Atmos. Environ.*, **30**, 1965-1975, 1996.
- Sillman, S., Logan, J.A. and S.C. Wofsy, The sensitivity of ozone to nitrogen oxides and hydrocarbons in regional ozone episodes, *J. Geophys. Res.*, **95**, 1837-1851, 1990.
- Sillman, S., The relation between ozone, NO_x and hydrocarbons in urban and polluted rural environments, *Atmos. Environ.*, **33**, 1821-1845, 1999.
- Simpson, D., Anderson-Skoeld, Y. and M.E. Jenkin, Updating the chemical scheme for the EMEP MSC-W oxidant model: Current status, *EMEP MSC-W Note 2/93*, The Norwegian Meteorological Institute, Oslo, 1993.
- Simpson, D., Guenther, A., Hewitt, C.N. and R. Steinbrecher, Biogenic emissions in Europe, 1, Estimates and uncertainties, *J. Geophys. Res.*, **100**, 22875-22890, 1995.
- Stewart, R.W., Multiple steady states in atmospheric chemistry, *J. Geophys. Res.*, **98**, 20601-20611, 1993.
- Stewart, R.W., Dynamics of the low to high NO_x transition in a simplified tropospheric photochemical model, *J. Geophys. Res.*, **100**, 8929-8943, 1995.
- Trainer M. *et al.*, Regional ozone and urban plumes in the southeastern United States: Birmingham, a case study, *J. Geophys. Res.*, **100**, 18823-18834, 1995.
- White, W.H. and D. Dietz, Does the photochemistry of the troposphere admit more than one steady state? *Nature* **309**, 242-244, 1984.

C. Honoré and R. Vautard, Laboratoire de Météorologie Dynamique, Ecole Normale Supérieure, 24, rue Lhomond, 75231 Paris Cedex 05, France.

M. Beekmann, Service d'Aéronomie, Université Pierre et Marie Curie, 4, place Jussieu, 75252 Paris Cedex 05, France.

(Received September 3, 1999; revised April 3, 2000; accepted May 5, 2000.)