Study of spatial and temporal variability of production rates and composition of NO_x sources using in-situ measurements combined to a dynamic model of NO_x - O_3 system

P. Joassin[1,2], F. Lenartz[2] and M. Dury[2]

[1]Corresponding author, p.joassin@issep.be
[2]ISSeP : Institut Scientifique de Service Public, Wallonie, Belgique

Abstract

Hourly measurements of NO, NO_2 and O_3 from outdoor stations have been used to highlight spatial and temporal (seasons and week days) variability of NO_x-O_3 system features, i.e. the NO_x emission/dissipation rate and the equilibrium state reached by the global equation NO + O_3 → NO_2 + O_2. A dynamic model of the NO_x-O_3 system has been used to derive the fraction of NO_2 in total NO_x sources and the efficiency of NO oxidation due to VOCs.

Data sources

Outdoor concentrations of nitrogen oxide (NO), nitrogen dioxide (NO_2) and ozone (O_3) are measured using HORIBA devices deployed in 5 stations of the Wallonia telemetric monitoring network. Hourly (day and night) measurements have been continuously collected from all stations during a full year period and aggregated into 4 time periods corresponding to natural seasons and 2 categories of week days. A first category gathers working days i.e. Monday, Tuesday, Thursday and Friday (exception for Wednesday). A second category consists only in Sundays. Additional collocated and concomitant data are collected, directly for air temperature using stations sensors, or indirectly for solar UV irradiance and sky nebulosity using yearly climatology.

Station number	Colour in graphs	Lat. (°)	Lon. (°)	Alt. (m)	Name	Environment typology
1	Blue	50,5832	5,3974	135	Engis	Residential/near industry
2	Red	50,6288	6,0027	292	Eupen	Rural
3	Green	50,6584	5,6278	56	Herstal	Urban/near traffic ways
4	Brown	50,6134	5,5702	71	Val-Benoît	Urban
5	Yellow	50,3031	6,0017	492	Vielsalm	Forest

Season	from	to
Winter	01-01-2022	31-03-2022
Spring	01-04-2022	30-06-2022
Summer	01-07-2021	30-09-2021
Fall	01-10-2021	31-12-2021

Modelling approach

A 3 equations model represents NO_x- O_3 system with concentrations [NO] , [NO_2] , [O_3] as state variables. Model parameters are emission/dissipation rate of total NO_x (src_{NOx} derived from measurements), fraction of NO_2 in total NO_x ($NO2_{NOx}$ model output), kinetic frequency of NO_2 photo-dissociation due to solar UV (J_{NO2} calculated), kinetic coefficient of NO oxidation due to ozone ($K_{NO.NO3}$ calculated), and kinetic frequency of NO oxidation due to VOCs (F_{NO} model output). Parameters $NO2_{NOx}$ and F_{NO} are obtained by modelling approach through best adjustments of default values and optimization of the NO_x-O_3 system dynamics over periods of 2 hours from initial to final values of state variables. Results also consider evolution of ratio R between real time quotient Q_r of the synthetic reaction NO + O_3 → NO_2 + O_2 and its theoretical equilibrium constant K_{eq}.

$$\frac{dNO2}{dt} = src_{NOx} . NO2_{NOx} + [NO] . F_{NO} - [NO2] . J_{NO2} + K_{NO.O3} . [NO] . [O3]$$

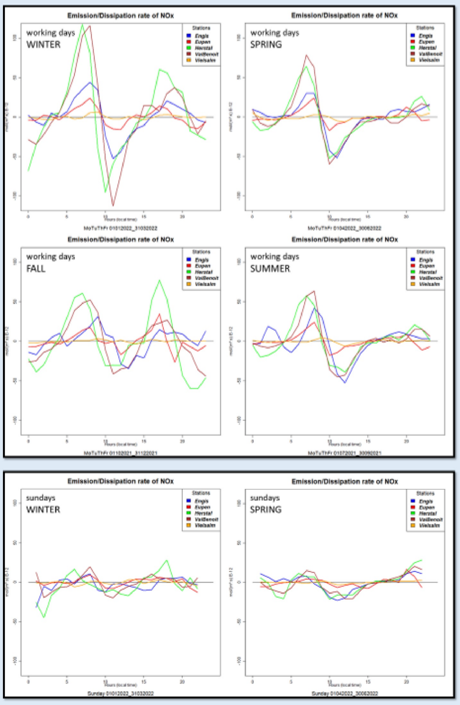
$$\frac{dNO}{dt} = src_{NOx} . (1 - NO2_{NOx}) - [NO] . F_{NO} + [NO2] . J_{NO2} - K_{NO.O3} . [NO] . [O3]$$

$$\frac{dO3}{dt} = [NO2] . J_{NO2} - K_{NO.O3} . [NO] . [O3]$$

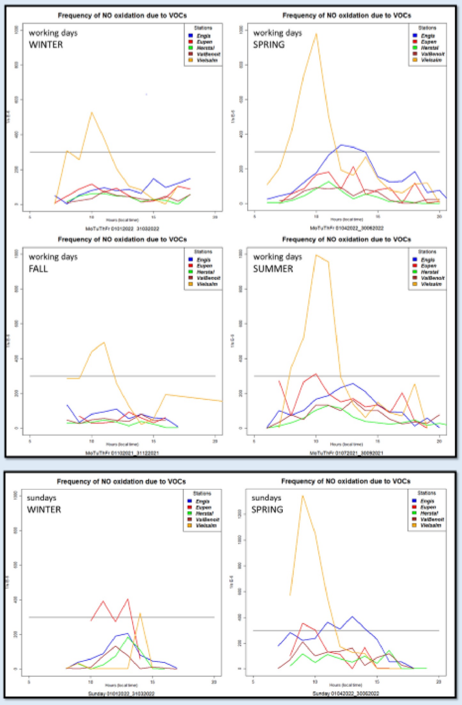
$$Keq = \frac{K_{NO.O3}}{J_{NO2}} \quad Qr = \frac{[NO2]}{[NO] . [O3]} \quad R = \frac{Qr}{Keq}$$

Results

rate src_{NOx} mol.m^{-3}.s^{-1}



frequency F_{NO} s^{-1}



ratio R (no dim.)