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Atlas of ozone chemical regimes in Europe

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HIGHLIGHTS

- An atlas of ozone chemical regimes has been constructed for 22 European cities.
- O_3 sensitivity to road transport and industrial emissions differ when considering different ozone metrics and different periods of the year.
- Counterproductive effects of precursors emission reductions on ozone are a concern where and when ozone concentrations are low.
- On the contrary, significant reductions of precursor emissions are found to reduce the number of exceedances of the EU target limit value.
- In most cities, mitigation of road transport yields larger benefit to ozone air pollution than mitigation of the industrial sector.

ABSTRACT

While concentrations of most air pollutants have been decreasing in Europe over the last 20 years, O_3 is showing variable trends, with increasing average and decreasing peak concentrations. The complexity of O_3 chemistry adds to the difficulty of understanding both the trends observed and how concentrations can be mitigated. This paper tries to answer the following questions: which emission sectors should be targeted and what levels of reduction could be achieved? To address these reflections, an Atlas of O_3 chemical regimes has been constructed. For this Atlas, 22 European cities were selected and the surrogate model Air Control Toolbox (ACT) was used to evaluate the simulated changes in several ozone metrics as a result of reductions in road transport and industrial emissions. O_3 chemical regimes have been classified and put in perspective with meteorological and emission data at each city location and around. The O_3 sensitivity to road transport and industrial emissions differ from one city to another, but also for the same city when considering different ozone metrics and seasons (e.g., annual means versus SOMO35 or summer peaks). Counterproductive impacts yielding O_3 increase when emissions are reduced are mainly encountered in regions or periods where O_3 concentration are relatively low. In terms of meteorological factors, O_3 chemical regimes are mostly impacted by the amount of solar radiation received but wind speed also has a considerable impact. Most cases show a higher sensitivity to emission reductions from road transport or equal sensitivity to emission reductions from road transport and industry. Very few cases are more sensitive to emissions from the industrial sector. However, the response of annual or seasonal average O_3 metrics to industrial and road transport emissions can be considered relatively low with a maximum reduction of 33% for a 100% reduction of both industrial and road transport emissions. This is because anthropogenic emission can only mitigate ozone above a substantial natural tropospheric background. It is precisely this incremental anthropogenic ozone, which should be targeted by efficient policies as we also demonstrate that none of the cities studied would exceed the European target value with a 100% reduction in emissions.

1. Introduction

Ground level ozone (O_3) is a harmful air pollutant known to affect morbidity and acute mortality in the population (WHO publications 2013) and to damage vegetation, affecting crops and forestry. Ozone is a secondary pollutant meaning that it is not emitted directly into the air. It occurs naturally in the earth's upper atmosphere and concentrations in the lower troposphere result from the balance between mixing from above, chemical production, destruction, and deposition at the earth's surface. Its chemical production results from chemical reactions between nitrogen oxides (NOx) and volatile organic compounds (VOCs) in the presence of sunlight. Concentrations are most likely to reach values harmful to health on hot sunny days, but can still reach high daytime values during colder months. Nitrogen dioxide (NO_2) is a precursor of O_3 but, O_3 is consumed by reaction with nitrogen monoxide (NO). In the presence of high NO concentrations, O_3 concentration values can become very low. The removal of O_3 by reaction with NO to form NO_2 is called titration in this article. In the absence of NO, ozone has a long lifetime and can be transported over long distances in the atmosphere, affecting the air quality of areas far from the source of emissions. Because of the long-range transport impact and the highly non-linear O_3 chemistry which differ depending on emissions, meteorological

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conditions and therefore geographic areas, it is particularly complicated to understand, simulate and predict O_3 concentrations. All these factors constitute a challenge to identify relevant mitigation options, as ozone precursor reductions can lead to different response in terms of ozone concentration changes.

The European Union (EU) has defined several standards, e.g. to characterise pollution episodes caused by ozone (information and alert threshold), to protect human health (long-term objective (LTO), and target value for human health) and to protect the vegetation (AOT40[1] and target value for vegetation) (Directive, 2008/50/EC). In addition, a specific metric is calculated to evaluate O_3 impact on health (SOMO35[2]).

There have been several studies devoted to the analysis of long-term trends in air quality. At a global scale, pollutant precursor emissions are decreasing since 2000 in North America and Europe when increasing in India and Africa whereas in Asia, these emissions rose sharply before starting to fall in 2012 (Soulie et al., 2023). As a results, ozone global burden increases (Gaudel et al., 2018; Wang et al., 2022) supported by equatorward redistribution of surface emissions and the rapid increases in aircraft emissions (Wang et al., 2022). Ground ozone concentrations trends are more disparate and if the heavily polluted regions of East Asia show ozone increases since 2000, many others show decreases and no clear global pattern for surface ozone changes can be found since 2000 (Gaudel et al., 2018). Focusing on Europe and on air pollutant at the surface, we refer to a report of the European Topic Centre on Air Pollution (Solberg et al., 2022) for a recent assessment for the period 2005–2019. Following strong reductions in primary pollutants emissions (NO_x, VOCs, primary particles, sulfur oxides), substantial decreases were found in Europe for sulfur dioxide (SO_2), NO_2 and particles concentrations with significant downward trends of about 65%, 30%, and 35%, respectively. The observed changes in ozone were however less straightforward and the nature of the trend depends on the ozone metric considered as well as the typology of sites:

- During the period 2005–2019 the annual mean ozone concentration has increased slightly while the high peaks have been reduced. This increase is substantial at traffic sites reaching almost 20% in Europe while the trend is almost nil for the rural sites. The increase in mean level can be explained by hemispheric transport of O_3 and reduced titration by NO as a result of reduced NOx levels in the atmosphere. The clear difference between rural sites and other typologies indicates that the decreased titration has more impact on the recent trends in Europe than hemispheric transport.
- Ozone peaks, estimated from the 4MDA8 metric (yearly 4th highest daily maximum 8-h ozone), decrease over the period, of about 2–5% at background sites, but the trend of the European composite is not significant. The reduction in high ozone peaks is expected when the general NOx level in Europe is reduced.

This contradiction is clearly visible when the trends are calculated by quantiles with downward trend for high O_3 values, and quantiles with upward trend for low O_3 values, upward trend that is particularly marked in urban areas. The trends in ozone metrics representaive of health and ecosystem exposure (SOMO35 and AOT40) are influenced by both high and low percentiles of ozone distributions. These trends are generally negative in rural areas and positives for traffic stations. But the interannual variability is so large that none of these trends is really significant.

The response of ozone to precursor changes was formalized in atmospheric chemistry using the framework of chemical regimes. The atmospheric chemistry of ozone production is complex and effective management of O_3 requires that the dependence on precursor emissions is understood. Particular attention has been given to the relative effectiveness of NOx or VOC emission reductions, either individually or together in reducing ozone pollution (e.g. Sillman, 1999; Milford et al., 1994). Chemical regimes have been identified which relate ozone concentrations to upwind precursor emissions. In the "NO_x sensitive chemical regime", anthropogenic NO_x emission reductions are more efficient in reducing ozone concentrations than anthropogenic VOC emission reductions (Sillman, 1999). The reverse occurs in the "VOC sensitive chemical regime". In several studies, North-West Europe is often found to be a VOC sensitive regime and Southern Europe to be rather a NO_x sensitive regime. Beekmann and Vautard (2010), analyzed the variability of chemical regimes in Europe. They found that some areas were consistently either VOC sensitive or NO_x sensitive. They found other areas, which they called transition regions, where O_3 production could be limited by either NO_x or VOC availability on a month-to-month and even day-to-day basis. Major parts of Germany were found to be a transitional region for example. They also found that emission trends in Europe expected as a result of current legislation might lead to an increase in the number of NO_x sensitive areas. They also noted that their conclusions might be affected by the spatial resolution of the modelling, for example that finer urban scale features may also play a role.

The present study aims to provide new insights in the sensitivity of ozone concentration changes to incremental reduction of anthropogenic emissions by focusing on road transport and industrial emissions. To achieve this, we rely on a meta-modelling approach, where a full Chemistry-Transport model is approximated with machine learning techniques. The surrogate model ACT (Colette et al., 2021), based on full Chemistry Transport Model (CTM) CHIMERE runs, is used to assess the comparative effect of emission reductions across two emission sectors: industry and road transport. By analogy with the classical ozone production isopleths of Sillman, 1999), where ozone concentration resulting from incremental changes in NO_x or VOC emissions are presented, here the results are presented as isopleths of O_3 metric change on 2D charts of industrial (IND) versus road transport (TRA) emission reductions. The use of a surrogate model allows to explore the full range of road transport or industrial emission reductions (from 0% to 100%) instead of having to perform full Chemistry-Transport simulations which would be prohibitive in terms of computing demand. It is only because the very design of the ACT model is specifically tailored to represent non-linear responses and interactions, that it can be used to infer chemical regimes along the whole range of both road and industrial emission reductions.

This methodology allows producing an Atlas of ozone chemical regimes accounting for all non-linear processes and covering 22 European cities for a range of ozone metrics. The methodology is presented in detail in Section 2. The synthetic results are presented in Section 3 accompanied with a supplementary material document including all the results for individual cities. A discussion is given in Section 4.

2. Methodology

2.1. The CHIMERE model

The air quality simulations used for both the design and the everyday training of the ACT tool are performed with the CHIMERE Chemistry-Transport Model (Mailler et al., 2017; Menut et al., 2013). The model is widely used for air quality research and application ranging from short term forecasting (Marécal et al., 2015) to projection

[1] AOT 40 (Accumulated Ozone exposure over a Threshold of 40 ppb, expressed in μg.m^{-3}.hr) is the sum of differences between hourly concentrations greater than 80 μg m^{-3} (=40 ppb) and 80 μg m^{-3} for a given period using the 1 h values measured daily between 8 a.m. and 8 p.m.

[2] SOMO35 (Sum Of Means Over 35 ppb, expressed in ppb.days) is the sum of max daily 8-h averages over 35 ppb (=70 μg/m^3) calculated for all days in a year.

at climate scale (Colette et al., 2015). We use a simulation setup similar to the operational regional forecast performed under the Copernicus Atmosphere Monitoring Service[3], albeit with a lower spatial resolution: 0.25° instead of 0.1°. The CHIMERE model version is chimere2016a using MELCHIOR gas phase chemistry, a two-product organic aerosol scheme and ISORROPIA thermodynamics. Meteorological data are operational analyses of the IFS[4] (Integrated Forecasting System) model of the European Centre for Medium Range Weather Forecasts[5] (ECMWF) at a temporal resolution of 3 h. While the spatial resolution of the IFS evolves in time with the subsequent upgrades of the operational production, it has always been higher than 0.25 since 2018, so that the spatial resolution of the meteorological driver is degraded prior to be used as a forcing to CHIMERE. The chemical boundary conditions are obtained from ECMWF, also with the IFS model.

2.2. Emissions

The anthropogenic emissions in the reference simulations are CAMS-REG v3.1 (Granier et al., 2019) for the year 2016. These emissions are based on the country report emissions required from the Convention for Long-Range Transboundary Air Pollution and collected by the Centre for Emission Inventories and Projections (http://www.ceip.at/) and made available online. Emissions at the SNAP (Selected Nomenclature for Air Pollution) level 1 are used as input to CHIMERE. When no emissions where available for a specific SNAP or a country, GAINS emissions were used (http://gains.iiasa.ac.at/models/gains_models.html). Improvements were also made to enhance consistency between countries, specifically on shipping emissions and agricultural waste burning. The final step in the inventory was the distribution of the complete emission data set across the European emission domain at 0.125° × 0.0625° longitude–latitude resolution using proxies and specific database as the E-PRTR database (http://prtr.ec.europa.eu/) which provides information on the location (longitude, latitude) and emissions of major facilities in Europe. Temporal emissions profiles are taken from the GENEMIS project (Friedrich and Reis, 2004), and are available as data files from the EMEP model website[6] www.emep.int. For road transport emissions, the temporal profiles of Menut et al. (2012) are also used. NMVOC speciation is based on Passant (2002) and GENEMIS recommendations are used for NO_x and SO_x speciation. The vertical distribution profiles that are used for each SNAP sector are constant profiles depending only on the SNAP sector and are presented in Terrenoire et al. (2015). Biogenic emissions are calculated on-line with CHIMERE using the MEGAN model (Guenther et al., 2006).

2.3. The ACT model

Chemistry-transport models are needed in order to forecast air pollution episodes and, through sensitivity studies, to assess the benefits expected from mitigation strategies. However, they are complex, take time to run and therefore the number of scenarios they can compute is limited. As part of the Copernicus Atmosphere Monitoring Service (CAMS) dedicated to policymakers, INERIS has developed the Air Control Toolbox (ACT[7]) to extend the number of scenarios that can be considered. ACT is a surrogate model based on a polynomial function and trained on a dozen CTM sensitivity scenarios in which primary pollutant emissions are reduced. It is designed to be updated on a daily basis, i.e. the fitting of the parameters of the polynomial function are recalculated every day based on the scenario CTM runs. ACT is able to reproduce the non-linearity in CTM response to changes in NOx and VOC emissions that are important for O_3. In the present study where annual metrics are considered, we therefore use 365 individual ACT response model calculations to compute annual O_3 metrics. ACT is made available through a web-interface[8] and is able to produce daily metrics for defined areas within the underlying CTM model domain. The model is also designed to capture the daily means of both the PM_{10} and $PM_{2.5}$ fractions of particulate pollution and nitrogen dioxide (NO_2). The spatial coverage is the greater European continent.

The only two simplifications limiting the range of application of ACT are that emission reductions are assumed to apply (i) over the long term (so that it is not possible to investigate emergency mitigation measures, where emission reduction would only apply for a few days) and (ii) uniformly over the whole modelling domain (here Europe).

A full description of the ACT surrogate model design is given in Colette et al. (2021). Since ACT falls in the category of surrogate models, or “models of models”, it has the same inputs and outputs of the CHIMERE. As any offline Chemistry-Transport Model, CHIMERE requires as main inputs: meteorological data, anthropogenic and primary biogenic emission, land use information, and the main output is atmospheric concentration and deposition fluxes. Since it had been demonstrated in Colette et al. (2021) that a quadrivariate second order polynomial would capture the main response to uniform and constant emission reduction of four activity sectors, a dozen CHIMERE scenarios are required to train ACT. This training has to be updated every day and is performed in an operational forecasting system over Europe, so that the surrogate models does not need to consider the meteorological local or synoptic situation as an input variable. In terms of performances, it has been demonstrated that ACT shows relative errors below 1% at 75% of the grid points and days, below 2% at 95% of the grid points and days, and below 10% for any grid points and days. This error regards the ability of ACT to reproduce the behaviour of CHIMERE, whereas CHIMERE itself may exhibit errors when compared to in-situ observations (see for instance the Evaluation and Quality Control routinely monitored as part of CAMS[9]).

ACT is configured to accept parametric emission changes in four activity sectors based loosely on the SNAP categorization. These are:

- AGR: Agriculture (SNAP sector 10: including both crops and livestock)
- IND: Industry (SNAP sectors 1, 3, 4: Combustion in energy and transformation industries, combustion in manufacturing industry, Production processes)
- RH: Residential Heating (SNAP sector 2: non-industrial combustion plants)
- TRA: Road transport (SNAP sector 7: urban and non-urban roads and motorways)

The surrogate ACT model trained on CHIMERE sensitivity simulations also allows exploring the chemical sensitivity (or regimes) within the parameter space of sectoral emission reductions. ACT is a quadrivariate second order polynomial with interactions using as predictors the four sectors considered. By plotting the surface response to two of these four sectors in a 2D parameter space, it is possible to assess chemical regimes for a given day, location and pollutant. In doing so, we perform an analogy with the classical ozone production isopleths of Sillman (1999), by substituting the NOx and VOC emissions in the x and y axes by different activity sectors. Here, the focus is on the industrial (IND: as SNAP 01, 03, and 04) and road transport (TRA: as SNAP 07) activity sectors.

3 http://regional.atmosphere.copernicus.eu.
4 https://www.ecmwf.int/en/publications/ifs-documentation.
5 www.ecmwf.int.
6 www.emep.int
7 https://policy.atmosphere.copernicus.eu/CAMS_ACT.php.
8 https://policy.atmosphere.copernicus.eu/CAMS_ACT.php.
9 https://atmosphere.copernicus.eu/regional-services.

2.4. Choice of the cities

Twenty-two (22) European cities were chosen to be representative of different meteorological conditions (ranging from southern to northern Europe), different O_3 regimes and different emission profiles. The set of selected cities is shown in Fig. 1. The situation of the cities relative to the target value for human health (the maximum daily 8-h mean may not exceed 120 μg per cubic metre (μg/m^3) on more than 25 days) and vegetation (AOT may not exceed 18000 μg m^{-3}.h) for the year 2019 is represented by coloured circles, with red colour for annual exceedances and green one to indicate respect of the target values. The cities mainly exposed to exceedances of the EU target values are mainly Mediterranean cities that receive large amounts of solar radiation.

2.5. Metrics, period and classification

The ACT tool explores the response in terms of ozone metric to emission reductions ranging from 0 to 100%. The model can consider emission reductions for four sectors, but in this study, we focus on reduction emissions from the industrial and the road transport sectors. Emissions from agriculture and residential heating are held constant. For each city, we establish isopleths for the change in ozone metric drawn on charts whose axes represent emission reductions applied to the TRA and IND sectors. Calculations were made for 4 different periods in order to test the sensitivity of the O_3 regimes to the period studied. For the year 2019, 3 yearly ozone metrics were calculated: SOMO35, annual averaged of the daily max hourly O_3 and the 93.15 percentile of the daily maximum O_3 concentrations, corresponding to the 26th highest O_3 concentration. This last metric allows to verify the current EU target value: a 93.15 percentile higher than 120 μg m^{-3} means that the EU target value is not reached. In addition to annual indicators, daily max hourly O_3 were also averaged over:

- the winter 2019 (DJF),
- the summer 2019 (JJA),
- the summer 2018 (data are only available from 12 July to 31 August),

These periods were chosen based on data availability (the CAMS ACT tool was implemented in mid-2018 in the CAMS European forecast daily production and was not available before).

3. Results

3.1. Model scores

The model is evaluated by calculating the performance at capturing in-situ concentration as reported from air quality monitoring networks (Root Mean Score Errors – RMSE -, the bias and the correlation coefficient) for the summer 2019 (JJA) over all the domain. The simulated daily maximum O_3 concentrations are compared to measurements for all background stations (rural and urban) in Table 1. The model underestimates summer daily maximum by 9.26 μg m^{-3} on average. Correlation is relatively good (0.73) and the RMSE of 20.2 μg/m^3 correspond to a relative RMSE of 19.8%. This can be put in context with results from Sharma et al., 2017 on about 50 scientific papers that modelled O_3 concentration. The comparison is not direct because Sharma et al., 2017 only compiles score on daily mean ozone for which they find average R^2 of 0.62 and RMSE of 29 μg m^{-3}. The performances of the ACT surrogate in the present study can therefore be considered as better than average.

Specifically at the selected cities, the simulated situation with regard to the human health target value is also compared to measurements. The model simulated well observed exceedances for all cities except Berlin and Prague (see Table 2: Percentile 93.15 calculated by the model at the city location with no emission reduction (initial value) and with 100% reduction of trafic and industrial emissions). On the other hand, the model simulates an exceedance of the target value for Seville, whereas the observations show a percentile 93.15 slightly below the limit value of 120 μg/m^3 for all urban stations of Seville.

3.2. Examples of O_3 regimes and isopleths

For producing isopleths, emissions from traffic and industry are each reduced from 0 to 100% (with a 1% reduction step, this amounts to studying the distribution of indicators according to 10,000 reduction scenarios) and resulting change in O_3 is calculated. All the produced isopleths for the different O_3 metrics, seasons and cities are shown in the supplementary material document ("City Fiches"). They all represent the difference between the value of the metric after the application of an emission reduction and that without any reduction. This difference, referred to as ΔO_3 hereafter, is negative (in blue) if the metric has decreased as a result of emission reductions, and positive (in red) if the metric has increased. Below are a couple of typical examples of O_3

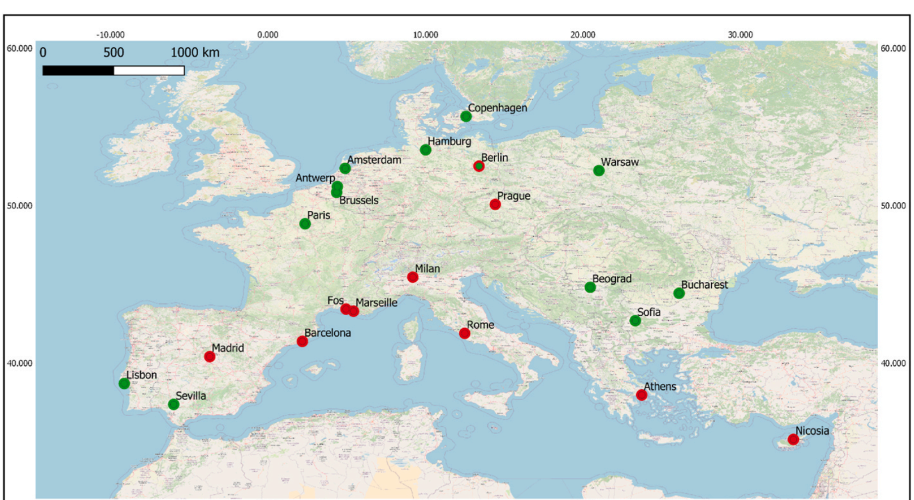


Fig. 1. Selected cities for the Atlas of ozone chemical regimes. For each city, respect of the human health target value for the year 2019 is represented by a large green circle and respect of the target value for vegetation by a small green circle. In contrast, a large red circle is used when the target value for health is not met, and a smaller red circle for the target value for vegetation. Data taken from the EEA AQ e-Reporting for 2019 (https://www.eea.europa.eu/data-and-maps/dashboards/air-quality-statistics). See also the city characteristics in the city-fiches (supplementary material).

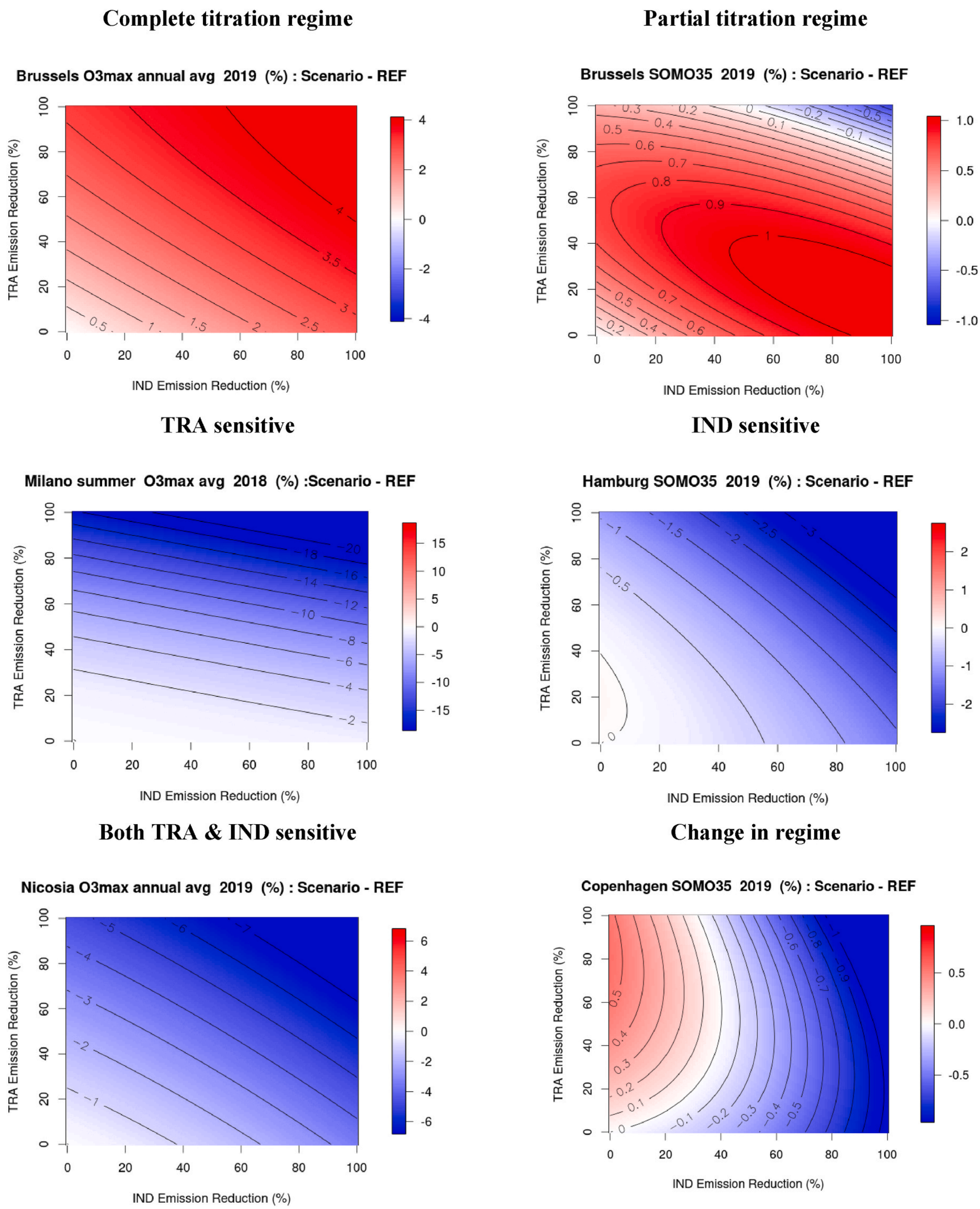


Fig. 2. Examples of O_3 isopleths and O_3 regimes for different cities, O_3 metrics and periods.

Table 1
Model performance calculated on ozone daily maximum for the period JJA over Europe.

	Bias (μg/m^3)	R^2	RMSE (μg/m^3)	RRMSE (%)
O_3 daily max	−9.26	0.73	20.20	19.8

regimes and the associated isopleths for illustration purposes (the full set of results being provided in the supplementary material document “City Fiches”):

When the isopleths are completely red, it means that, whatever the reduction of emissions from road transport and industry is, the ozone metric values are increasing rather than decreasing: this is a case of O_3 titration. On the contrary, a blue isopleth means that the emission reductions are indeed reducing ozone. The importance of this reduction can be read directly on the isopleths, here in % reduction of ozone metric. These isopleths also allow to assess if industrial emission reductions allow a greater reduction of ozone than road transport emission reductions, and vice versa, depending on the slope of the isopleths. We will see in section 3.3 that we can classify the set of isopleths into 6 different classes in terms of chemical regimes.

Table 2
Percentile 93.15 calculated by the model at the city location with no emission reduction (initial value) and with 100% reduction of trafic and industrial emissions.

Percentile 93.15	Milan	Rom	Madrid	Barcelona	Athens	Fos-sur-Mer	Marseille	Sevilla	Nicosia	Beograd	Sofia	Prague
Initial value (no emission reduction)	162	141	136	136	135	133	130	125	123	120	117	116
With 100% reduction	94	94	101	112	114	102	109	103	105	80	93	91

Percentile 93.15	Lisbon	Bucharest	Berlin	Paris	Hamburg	Brussels	Antwerp	Amsterdam	Warsaw	Copenhagen
Initial value (no emission reduction)	115	114	112	112	110	109	107	106	104	103
With 100% reduction	96	90	88	88	91	87	85	87	85	94

3.3. Overall impact of emission reductions

In this section we examine the magnitude of the change in ΔO_3 across the emission reduction scenarios by presenting results in boxplot format. In practice, these boxplots include all the data of the traffic and industry isopleths presented in section 3.2: the simulated ozone changes resulting from the 10,000 combinations of industrial and road emission reduction scenarios from 0 to 100% by increments of 1%. Figs. 3 to 8 comprises boxplots showing the distribution of those ΔO_3values obtained for each city. Each box shows the median, min, max as lines and a box between the 25% and 75% quantiles Each plot is organized in order of metric median value and the cities, shown on the x-axis, change place from figure to figure.

The sensitivity of O_3 to the different periods can be clearly seen from Figs. 3 to 8. In winter (Fig. 5), a complete titration regime is found for all cities except Nicosia. Indeed, in winter, solar radiation is much lower at the zenith than in summer and the nights are longer. O_3 production is therefore low and O_3 is mainly consumed by its reaction with NO. A decrease in NO emissions (from IND or TRA) will therefore lead to less O_3 destruction and in most cities effectively result in an increase in O_3. The largest wintertime O_3 increase is simulated for Milan, with a median daily max O_3 increase of 26% (i.e. 9 μg m^{-3}), and a maximum of 66% (for 100% reduction of IND&TRA emissions). However, this increase in O_3 is tempered by the fact that O_3 values in Europe are low in winter with very few exceedances of the 120 μg m^{-3} threshold. Some cities are not only in titration regime in winter, but show titration or very low reduction of O_3 also for summer average of the daily maximum and SOMO35 indicator. These are Paris, Antwerp, Brussels, Amsterdam and Copenhagen. However, here too, the failure or ineffectiveness of emission reductions on ozone levels must be put into perspective, as target values for health and vegetation are not exceeded in these cities.

For the annual average O_3 daily max metric (Fig. 6), only Beograd, Nicosia, Bucharest, Sofia, Sevilla and Rome show O_3 reductions whatever the emission reductions are. But for those cities, the reduction in O_3 metric is limited to 4% for the median reduction and 13% for the maximum. Emissions reductions are slightly more efficient when considering the annual metric SOMO35 (Fig. 7) that do not take into account O_3 concentrations lower than 70 μg m^{-3}. In particular, for the cities of Barcelona, Milan, Copenhagen, Berlin and Hamburg, emission reductions do lower SOMO35 in most cases, while their annual average ozone levels tend to rise as a result of these emission reductions.

Summer (Figs. 3 and 4) is the period for which O_3 reductions associated with emission reductions are greatest, due to the large amount of O_3 production at this time. The largest reductions are found in Rome, Milan, Madrid, Prague, Bucharest, Fos-sur-Mer, Sofia and Sevilla, with for example, a median reduction of 11% (-16 μg m^{-3}) in Milan in summer 2019. For the large majority of summer isopleths, this median level is obtained for TRA and IND emissions reductions larger than 50% (see city fiches). When TRA and IND emissions are reduced by 100%, the highest summer reductions occur in Milan and reach -32% (50 μg m^{-3}) during summer 2019. In the majority of the cities examined though, the highest reductions do not exceed 20%. O_3 reductions associated to the annual metric SOMO35 are halfway between those simulated for summer average of the daily max O_3 and for its annual average, with O_3 reduction for the majority of cities but limited to 5% for the median reduction and 15% for the maximum.

For the 93.15 percentile of the daily maximum (for the year 2019), an indicator that is representative of the most significant ozone peaks over the year, the emissions reductions are predicted to have the most efficient impact, with median reductions ranging from 3% to 13% and maximum reduction up to 37% for Milan (67 μg m^{-3}). Moreover, emission reductions are never counterproductive for that indicator,

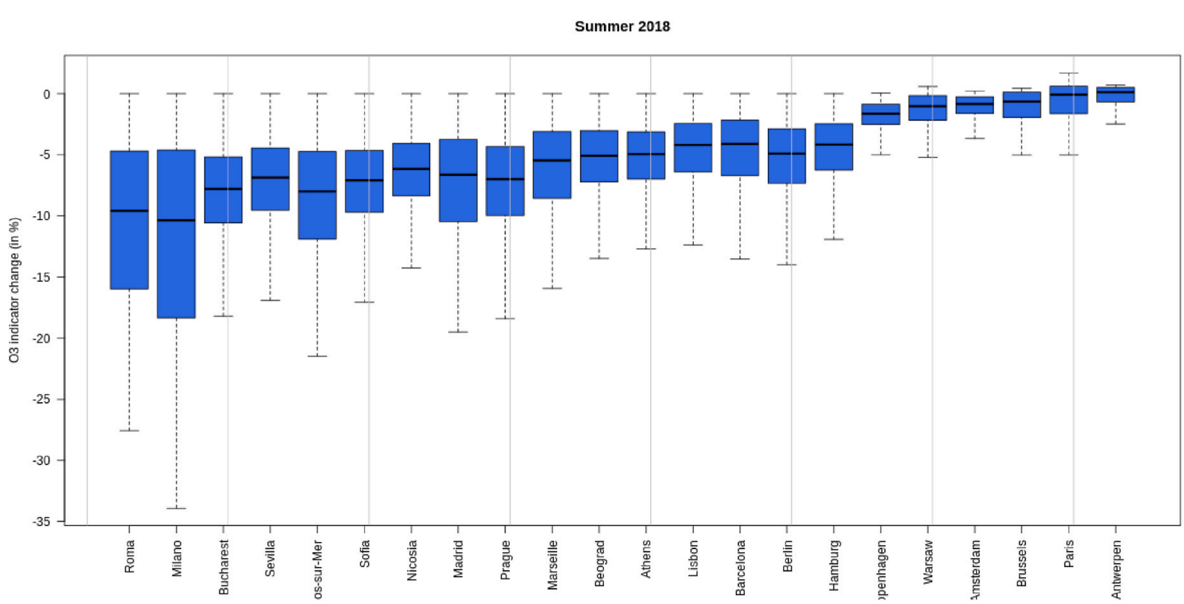


Fig. 3. hourly O_3 daily max - 2018 SUMMER average distribution of O_3 reduction per city for reductions from 0 to 100% for both the industrial and the road transport sectors. Negative values mean reduction in O_3 consecutive to emission reductions.

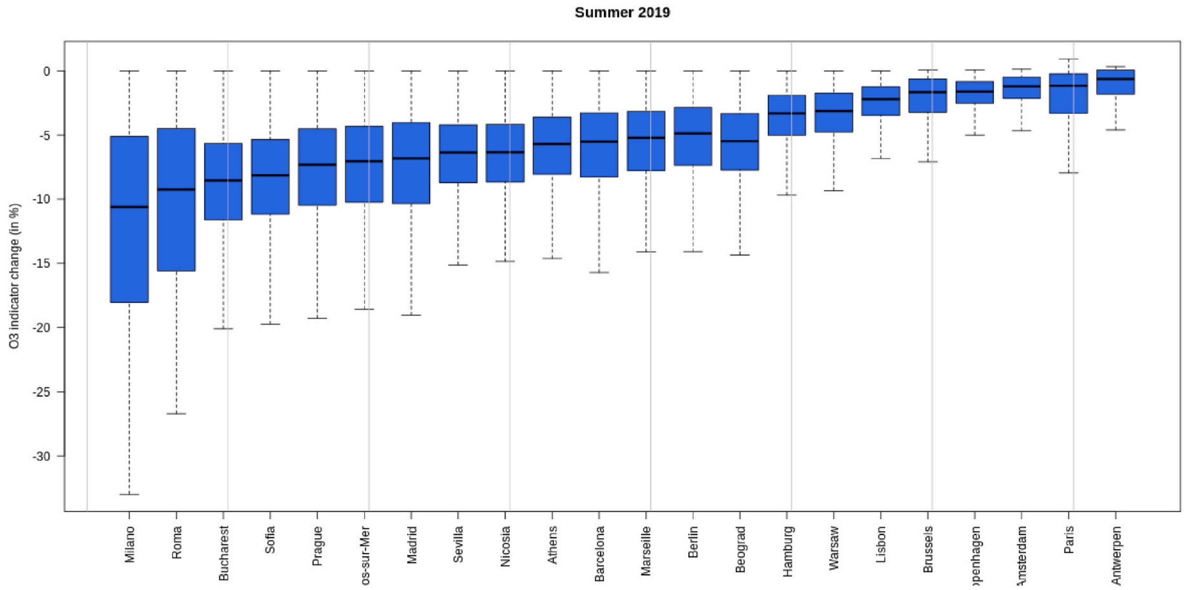


Fig. 4. hourly O_3 daily max - 2019 SUMMER average: distribution of O_3 reduction per city for reductions from 0 to 100% for both the industrial and the road transport sectors. Negative values mean reduction in O_3 consecutive to emission reductions.

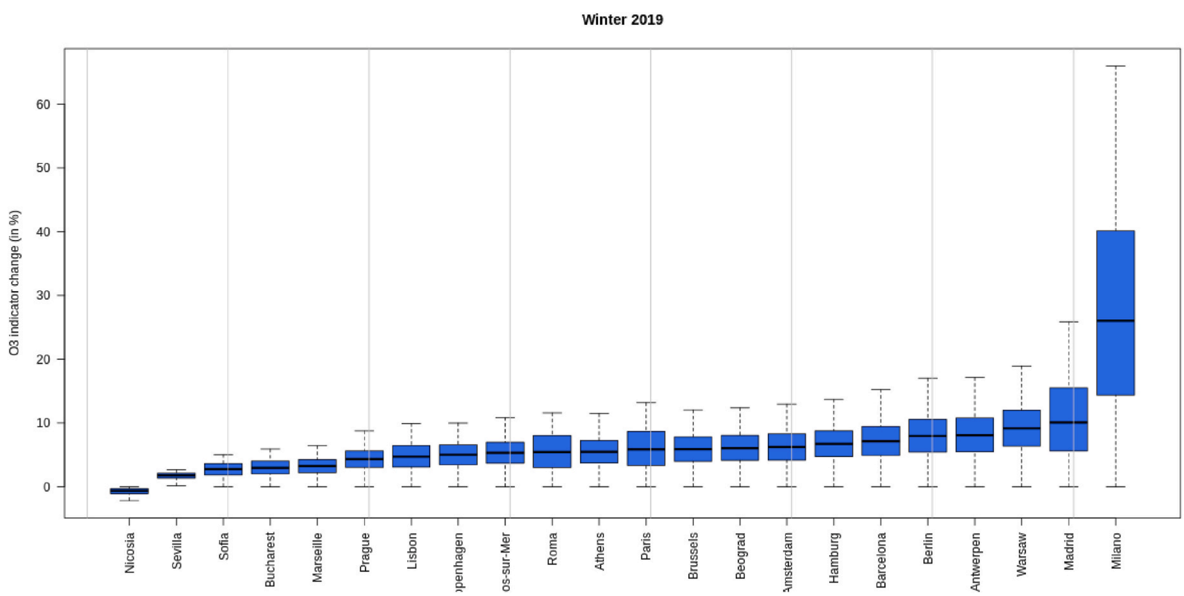


Fig. 5. hourly O_3 daily max - 2019 WINTER average: Distribution of O_3 reduction per city for reductions from 0 to 100% for both the industrial and the road transport sector. Negative values mean reduction in O_3 consecutive to emission reductions.

except for only one exception: Paris for NOx and NMVOC reduction lower than 20% and 10% respectively (see the Paris isopleths in city fiches).

For this 93.15 percentile, it is also interesting to compare the initial indicator (without emissions reduction) with its value when traffic and industrial emissions are reduced by 100% (Table 2). Thus, while the model initially simulates 9 cities exceeding the EU target value, no city exceeds this limit value with a 100% reduction in emissions. Overall, the more we focus on summertime months, and on yearly indicators with high threshold, the more effective emission reductions can be, and the fewer cases of titration there are. This is because emission reductions mainly reduce high ozone peak when daily averaged O_3 can increased due to a lower impact of titration. Ozone high peaks aside, limited impact of emission reductions from road transport and industry (even for a 100% reduction across Europe) suggests the importance of long-distance (inter-continental) transport, biogenic emissions and emissions from other sectors on O_3 formation. It is also interesting to note that summers 2018 and 2019 (Figs. 3 and 4) show different behaviors for some cities, which has to be associated mainly to the fact that the considered period for these two summers is different and which will be further analyzed in the following sections.

3.4. *Ozone regimes*

The set of isopleths, for all ozone metrics, cities and periods studied have been classified into 6 different O_3 classes in terms of chemical regimes:

1) Titration regime (complete or partial): reductions in emissions (IND or TRA or both) lead to an increase in the O_3 metrics (positive ΔO_3).

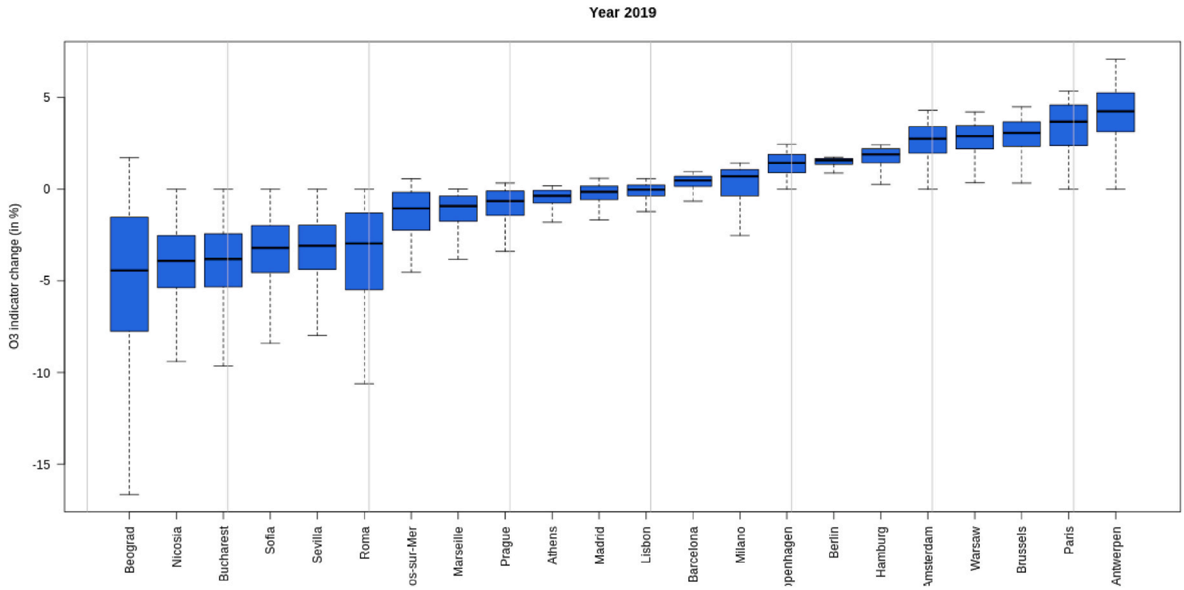


Fig. 6. hourly O_3 daily max - 2019 ANNUAL average: Distribution of O_3 reduction per city for reductions from 0 to 100% for both the industrial and the road transport sector. Negative values mean reduction in O_3 consecutive to emission reductions.

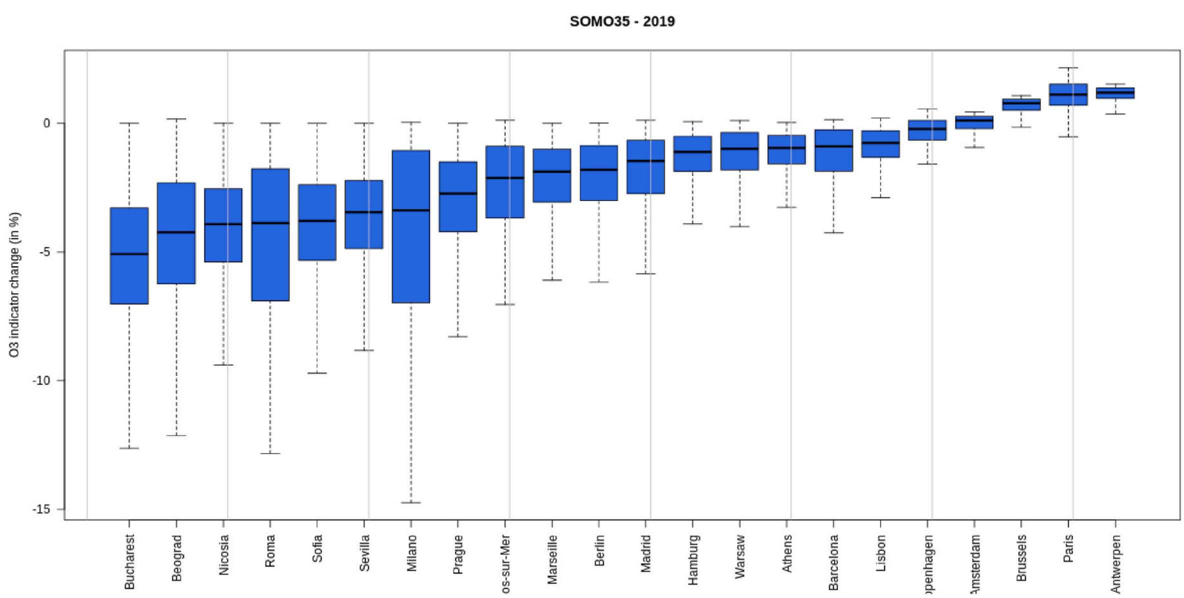


Fig. 7. hourly O_3 daily max - 2019 SOMO35 – Distribution of O_3 reduction per city for reductions from 0 to 100% for both the industrial and the road transport sector. Negative values mean reduction in O_3 consecutive to emission reductions.

This can be the case for any reduction (complete titration regime) or only for some part of the IND:TRA reduction space (partial titration regime);

2) TRA sensitive: reductions in road transport emissions produce a greater reduction in the considered O_3 metric than reductions in industrial emissions do;
3) IND sensitive: reductions in industrial emissions produce a greater reduction in the considered O_3 metric than reductions in road transport emissions do;
4) TRA & IND sensitive: road transport and industrial emission reductions have a similar impact on the considered O_3 metric;
5) Change in regime: An increase in the O_3 metric occurs in a part of the IND:TRA reduction space, and a decrease in the O_3 metric occurs elsewhere;
6) Change in sensitivity: there is a clear shift from a regime sensitive to road transport emissions reductions to a regime sensitive to industrial emissions reductions (or the reverse). This case was not encountered in the cities and over the period selected.

An example of each of the first 5 ozone regimes encountered is given in Fig. 2. The procedure used to classify O_3 regime results for each city is described below and shown as a flow-chart in Fig. 9.

A value of the median $\Delta O_3 > 0$ indicates a titration regime. This is classified as a:

- complete titration regime if the minimum ΔO_3 value is $= 0$ and
- partial titration regime if this minimum value is < 0.

A value of the median $\Delta O_3 < 0$ indicates that reducing IND or TRA

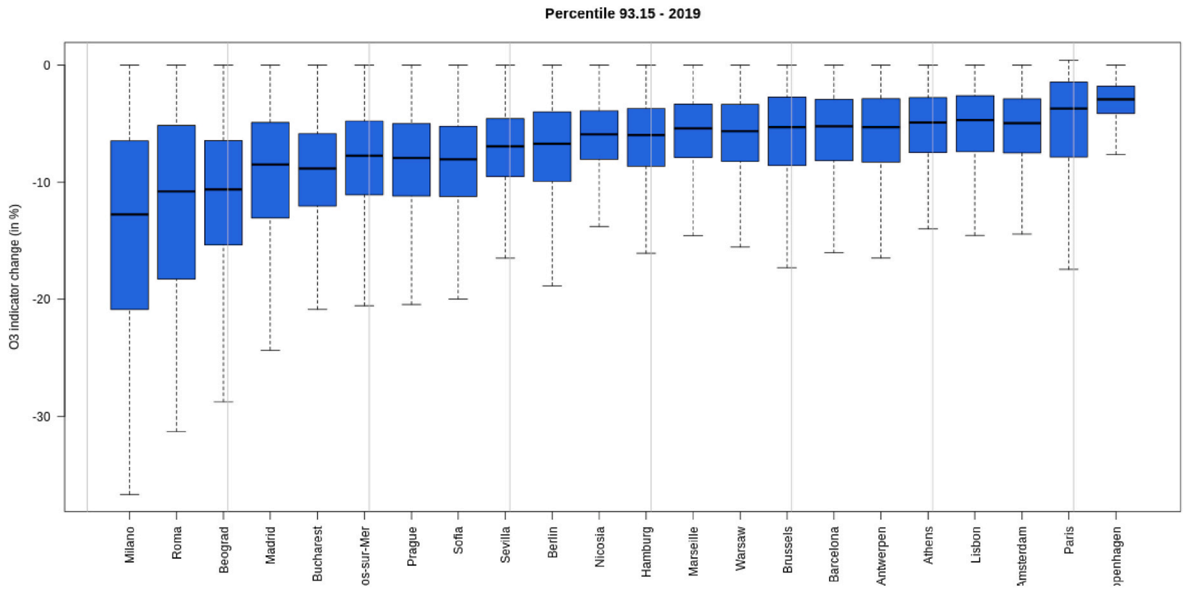


Fig. 8. 93.15 percentiles of the O_3 daily maximum in 2019 – Distribution of O_3 reduction per city for reductions from 0 to 100% for both the industrial and the road transport sector. Negative values mean reduction in O_3 consecutive to emission reductions.

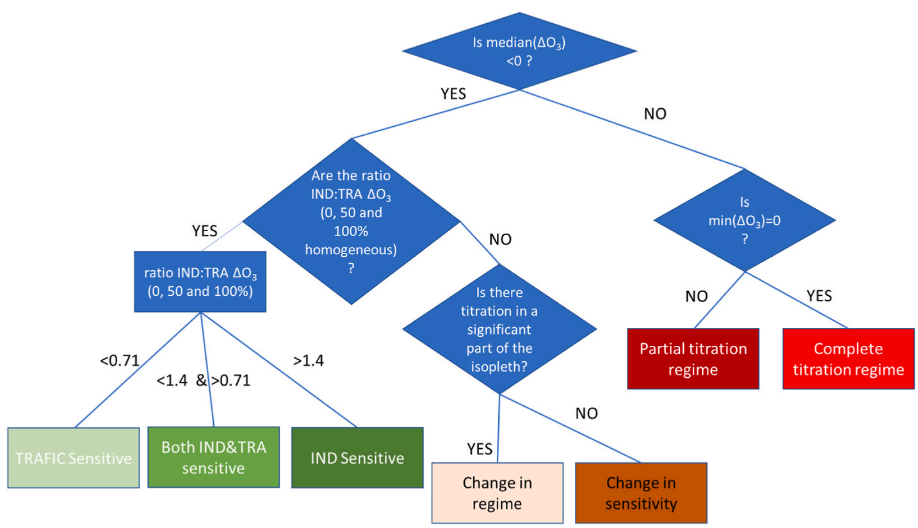


Fig. 9. Representative flowchart of the regime classification based on median, min ΔO_3 and ratio between O_3 responses to road transport and industrial emissions reductions.

emissions yields some benefit in reducing ozone concentrations. The response can however be quite different depending on targeted cities, ozone metrics, or selected year/period. This response was therefore subsequently classified to explicit if the sensitivity was mainly attributed to IND, TRA, both IND and TRA, if it changes from sensitivity regime, or if some part of that response still exhibited a titration regime. This additional step of classification has been (or is) based on an indicator designed to separate the different cases. This indicator is based on a ratio that allows the comparison between the reduction in O_3 simulated for the same relative reduction of emissions (from 0 to 100%) from the industrial sector and from road transport. As this indicator can be different depending on where you are in the IND:TRA emissions reduction space, it has been calculated at 3 levels, as shown in the example of Fig. 10:

- The ratio between ΔO_3 obtained when reducing 100% IND at 0% TRA reduction compared to ΔO_3 obtained when reducing 100% TRA at 0% IND reduction, noted as [IND:TRA $\Delta O_3]^0$. It is symbolised by the red arrows in Fig. 10.
- The ratio between ΔO_3 obtained when reducing 100% IND at 50% TRA reduction compared to ΔO_3 obtained when reducing 100% TRA at 50% IND reduction, noted as [IND:TRA $\Delta O_3]^{50}$. It is symbolised by the green arrows in Fig. 10.
- The ratio between ΔO_3 obtained when reducing 100% IND at 100% TRA reduction compared to ΔO_3 obtained when reducing 100% TRA at 100% IND reduction, noted as [IND:TRA $\Delta O_3]^{100}$. It is symbolised by the yellow arrows in Fig. 10.

When all 3 indicators are >1.4, the case will classify as “IND sensitive” (reductions in industrial emissions have at least 40% more impact than reductions in road transport emissions). All 3 indicators <0.71 will classify the case as “TRA sensitive” (reductions in road transport emissions have at least 40% more impact than reductions in industrial emissions). This is the case for the example of Fig. 10. In between (i.e. all 3 indicators >0.71 and < 1.4), the case is classified as “Both TRA&IND

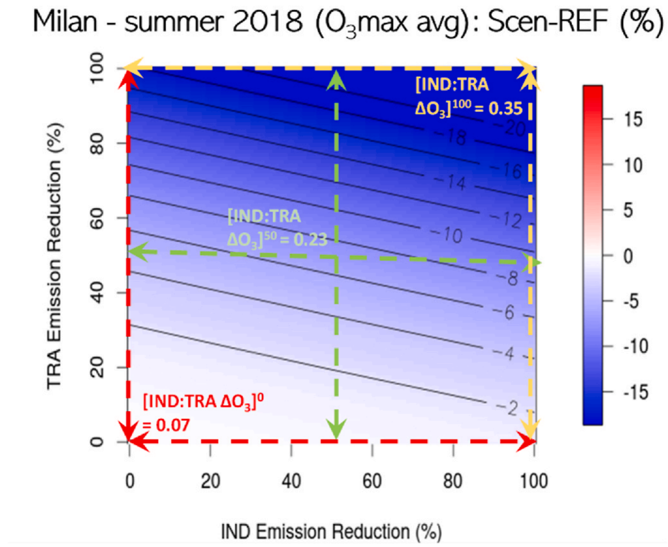


Fig. 10. Diagram of the calculation of the indicator [IND:TRA $\Delta O_3]^X$ for X = 0 (red arrows), X = 50 (green arrows) and X = 100 (yellow arrows). The ratio is obtained by first calculating the difference between the ΔO_3 values at both ends of the arrows, and then dividing the value obtained for the horizontal arrow by the value obtained for the vertical arrow.

sensitive". If the indicators at 0, 50 and 100% ([IND:TRA $\Delta O_3]^0$, [IND: TRA $\Delta O_3]^{50}$ and [IND:TRA $\Delta O_3]^{100}$) are not all in the same category (i.e. non-homogeneous), 3 possibilities are considered:

- 2 indicators fall into the same category and the third is close to one of these limit values: the case is classified in the category of the 2 indicators;
- there is titration in a significant part of the isopleth: the case is classified as "Change in regime"
- the 3 indicators fall into different categories, or 2 fall in the same, but the third value is clearly far from the limit of this category: the case is classified as "Change in sensitivity";

At this stage, we can recall an important strength of the approach implemented here. It is only because the ACT surrogate modelling approach is specifically designed to capture non-linearities as well as interactions between emission changes applied to either TRA or IND emissions that we can propose such a classification. Using more classical "brute force" sensitivity analyses investigating only emission reductions of, say, 15% would not allow an extrapolation over the range 0–100% in the context of non-linear chemistry. Such an exploration based on a single emission reduction would for instance clearly not allow identifying "changes in regime" over the full range of reductions. The frequency distribution of city results obtained using this classification procedure is summarized in Fig. 11.

These figures clearly show the differences between the periods (summer, winter, yearly average) and the O_3 metrics in terms of classification of ozone regimes. In summer (Fig. 11a), the titration regime is marginal as it occurs only in 11% of the target cities. For 43% of the target cities, the average summertime daily maximum O_3 is more reduced by road transport emissions reduction than by industrial emissions reduction compared to 5% having a higher sensitivity to industrial emissions reduction. A large fraction (41%) is sensitive to emissions reductions in both industrial and road transport sector. In winter (Fig. 11b), almost all target cities show a complete titration regime and daily maximum O_3 concentrations increased for all emission reductions. The annual average of O_3 daily max shows a behavior between these two extremes for either summer or winter. 45% of the target cities are in a titration regime (partial or complete), 23% are road transport sensitive, 5% IND sensitive and 18% both TRA and IND sensitive. 9% of the target cities classify as "change in regime", meaning that titration is observed for a significant part of the IND:TRA emissions reduction space, but the regime changes to O_3 net decrease when emission reductions reach a higher level. For SOMO35 (Fig. 11d), the number of cities displaying a titration regime is logically lower than for the annual mean because of the definition of the SOMO35 metric. Indeed, the effect of the titration is the consumption of O_3, resulting in lower O_3 concentrations. For SOMO35, being the sum of the maximums of O_3 on 8 h higher than 70 μg m^{-3}, the days of strong titration are not counted in the calculation of the SOMO35. The proportion of cities that show greater sensitivity to IND than TRA reductions for SOMO35 is slightly greater (at 9%) than for the other metrics. 41% of the target cities are road transport sensitive and 27% both road transport and industrial sensitive. The last indicator studied is the percentile 93.15. On this high ozone peak indicators, the majority of the cities are both TRA and IND sensitive (62%). Around 24% of the cities are TRA sensitive and 9% are IND sensitive.

Overall, partial or complete titration regime aside, most indicators are either equally sensitive to trafic and industrial emission reduction, or more sensitive to trafic emission reduction. Some cities are more sensitive to reductions in industrial emissions, but not necessarily on all indicators (e.g.: on SOMO35 but not on percentile 91.3): Madrid, Hamburg, Copenhagen, Lisbon, Warsaw and Beograd.

3.5. Factors influencing the differences in O_3 regimes between cities

Some cities have been identified in section 3.2 as being in titration regime or showing very low O_3 reductions when reducing road transport and industrial emissions and this for all O_3 metrics. These are Paris, Antwerp, Brussels, Amsterdam and Copenhagen. When only considering the annual average O_3 max metric, we can add to this list the cities of Berlin, Warsaw, Hamburg, Barcelona and Milan. The cities showing the largest relative reduction in annual average O_3 max metric when reducing road transport and industrial emissions are Bucharest, Belgrade, Nicosia, Rome, Sofia and Sevilla. Milan shows a very different behavior depending on which O_3 metric is considered: it is one of the cities showing the largest relative reduction for SOMO35 but, when looking at annual average O_3 max, it shows a titration regime. For the summer O_3 metrics, Milan and Rome are clearly the cities with the largest relative reduction, followed by Bucharest, Sevilla, Fos-sur-mer, Sofia, Nicosia, Madrid and Prague. In the following section, we try to identify the parameters which may explain the differences between cities, season and metrics.

3.5.1. Meteorological factors

O_3 is produced through the photolysis of NO_2. The solar radiation is therefore one of the meteorological factors having the largest influence on O_3 production. Low surface winds are a proxy for the persistence of cyclonic conditions which favor ozone production. For each city, solar radiation and surface winds are listed in the dedicated City Fiches (see supplementary material document). This analysis remains however very qualitative. We selected these two parameters known to influence ozone formation but the list could have been expanded further, for instance with planetary boundary layer depth or precipitation. Even then, the discussion would only focus on local factors (interpolated at the location of target cities), whereas ozone buildup also depends on more regional meteorological conditions such as weather regimes depicting the overall synoptic anticyclonic situation occurring at larger scale. Assessing in detail the differences in the main meteorological factors driving ozone formation for the selected cities would therefore require a dedicated methodological analysis which cannot be achieved with the ACT surrogate methodology. That is why the discussion in this section should only be considered as an illustration of meteorological factors which also play a role in addition to emission changes. This study is not attempting to be exhaustive or rank the relative importance of individual meteorological factors. Solar radiations taken from the IFS meteorological data

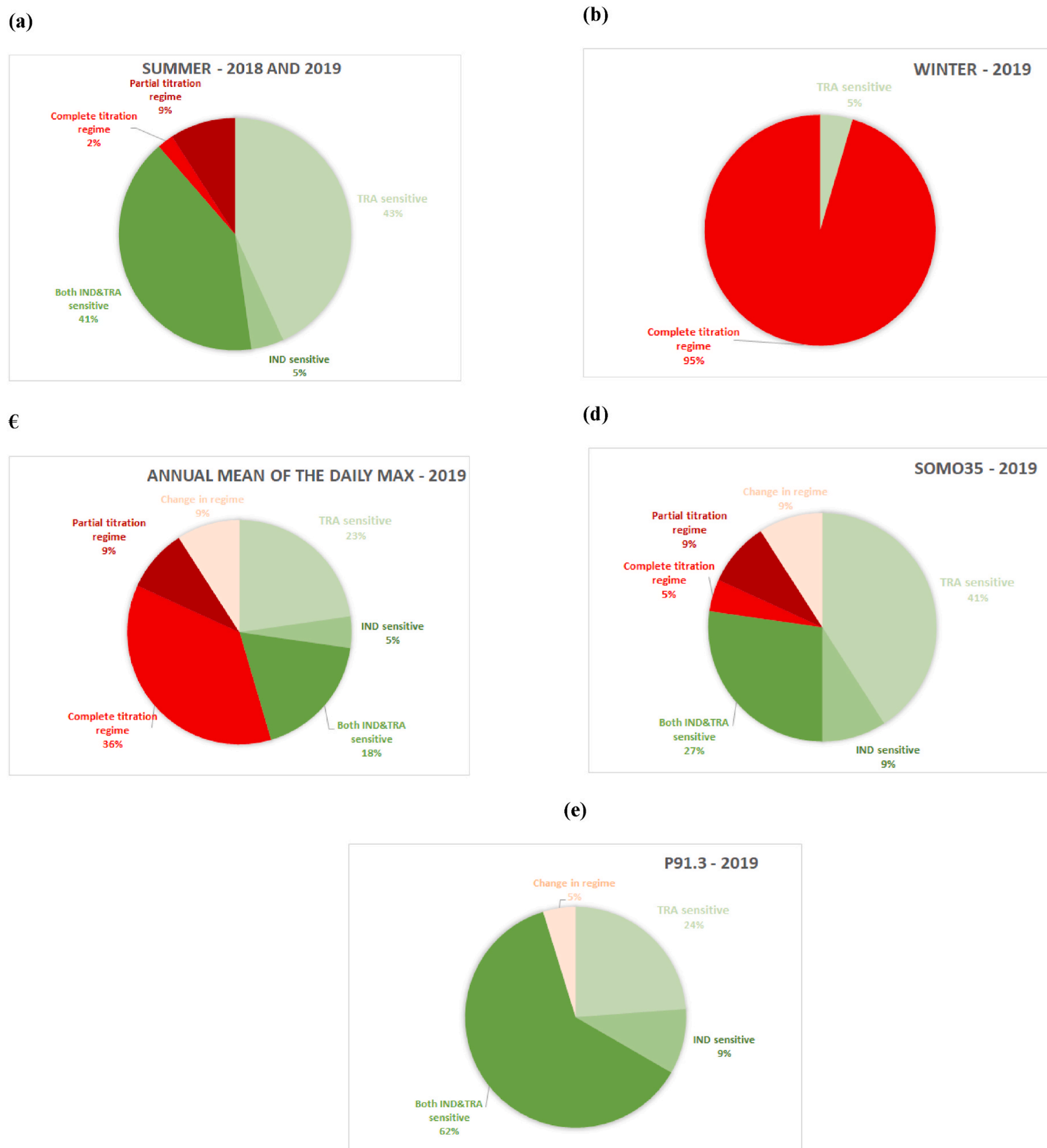


Fig. 11. Summary classification of ozone regimes for different ozone metrics over the 22 target cities. Each pie-chart sums up to the distribution of regimes across the 22 selected cities (TRA sensitive: light green, IND sensitive: mild green, both IND and TRA sensitive dark green, change in regime: light pink, partial titration dark red, and complete titration mild red). The list of selected ozone metrics is: (a) summer average of the daily max in 2018 and 2019, (b) winter mean of the daily max in 2019, (c) annual mean of the daily max in 2019, (d) SOMO35 for 2019, (e) percentile 93.15 of the daily maxima.

and used in the CHIMERE model have been interpolated over each of the cities and are shown in Fig. 12 for annual average and summer average respectively.

As expected, there is a gradient from the southern European cities having higher solar radiation to the northern ones. Part of the cities identified as in titration regime, or showing very low impact whatever the season and metrics are, received less solar radiation (Amsterdam, Antwerp, Copenhagen, Brussels, Berlin, Paris, Prague) which has the effect of limiting the production of O_3, and thus the impact of reducing emissions. On the contrary, the cities showing the largest O_3 reduction received more solar radiation than the above-mentioned cities, but they are not necessarily the sunniest. Another observation is the higher solar radiation value for the JJA summer period in 2019 than for the period from July 12 to August 31 for summer of 2018, regardless of the city. This may explain the higher O_3 reductions simulated for all cities: as the averaged O_3 production is higher in JJA 2019, emission reductions have more impact.

For some cities, the solar radiation alone cannot explain the simulated behavior. For example, Athens, Barcelona or Lisbon are cities exposed to high solar radiation but are not very sensitive to emissions reductions. Milan and Paris received more or less the same solar radiation but show very different behavior. Hamburg is the city with the lowest solar radiation but is more sensitive than Brussels for example. It is therefore necessary to also look at other parameters. Fig. 13 shows the values of the average wind speed for each city.

Lisbon experiences the highest wind speeds. This may explain why, despite strong sun exposure, emission reductions have little impact, since the polluted air masses do not stagnate in the city but are

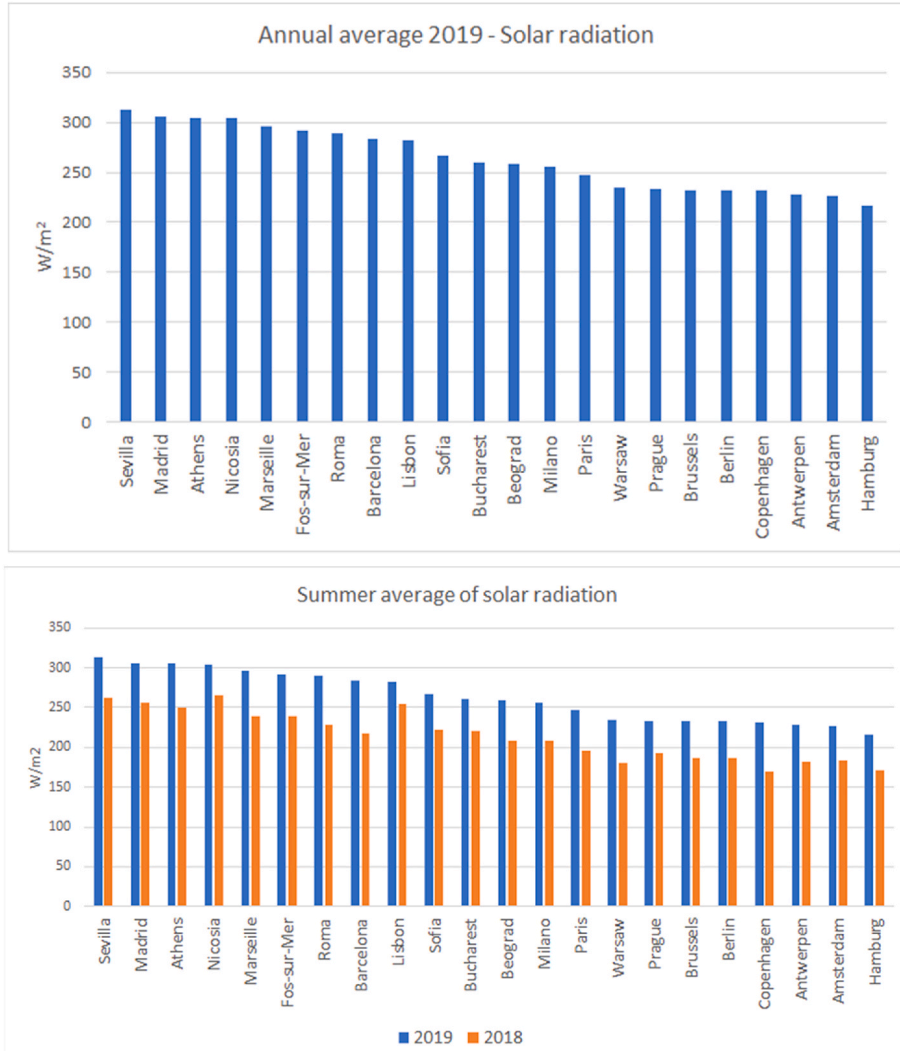


Fig. 12. Annual 2019 and Summer (from July 12 to August 31 for 2018, and from June 1 from August 31 for 2019) average of solar radiation (IFS model).

transported further away.

3.5.2. Emissions speciation factors

For this section we only focus on NO_x and NMVOC emissions which are the two main anthropogenic precursors of O_3. Particles and other gases can have an indirect impact on O_3 (by impacting the availability of NO_x and NMVOC), or a direct impact (heterogeneous reactions) but the sensitivity of O_3 to these species is much lower than to NO_x and NMVOC. We should also note that methane (CH_4) and carbon monoxide (CO) also play a role in ozone chemistry, but those species were not addressed in the present study. Emissions for all primary pollutants were interpolated for each city at the local level (i.e. at the scale of the grid covering the official city boundaries), within a 50 × 50 km grid centered on the city, a 100 × 100 km grid centered on the city, and at national level. Thus, emissions at the regional and country level include local emissions. This information is reported in the supplementary material document ("City Fiches") in the form of tables and radar plots.

It is well known that the NOx/NMVOC ratio has an importance in the ozone regime (Sillman, 1999). Before looking at the impact on ozone reductions, it is interesting to assess the initial situation (without emission reductions) of each city in terms of the total amount (i.e. emissions from all sectors: industrial, road, agricultural, residential-tertiary, air, maritime, solvent and waste) of NOx and NMVOC used in the model at local and regional level. Figs. 14 and 15 show for each city the modelled SOMO35 indicator for the year 2019 as a function of total NMVOC emissions (x-axis) and total NOx emissions (y-axis) occurred within the city. The larger the circle, the higher the SOMO35 indicator.

Cities with the lowest SOMO35 levels are those with high NOx emissions and a high (>1.2) NOx/NMVOC ratio either at the local level (Warsaw, Paris) or at a regional level (Brussels, Antwerp, Amsterdam). The opposite is not true as Marseille and Fos-sur-Mer also show a high NOx/NMVOC ratio yet SOMO35 levels are high. This is because they are located more south than the other cities therefore they receive more solar radiations that favors ozone production. Hamburg and Berlin also show different behavior, with low SOMO35 despite a relatively low NOx/NMVOC ratio. Here again, the amount of solar radiation received probably plays a role, as Berlin and Hamburg are among the least sunny cities all year round. In Figs. 16 and 17, in addition to total emissions, industrial and road transport emissions are also plotted.

From Fig. 16 it can be seen that NO_x emissions at local level are not always dominated by the road transport sector (Warsaw, Fos-sur-mer or Berlin have higher NO_x emissions from industry than from the road transport sector).

At local level, NMVOC emissions (Fig. 17) are rarely higher for the industrial sector than for the road transport sector, except in Hamburg, Barcelona and Fos-sur-mer. At the regional level, industrialized regions see their industrial emissions of NMVOC exceed those of the road

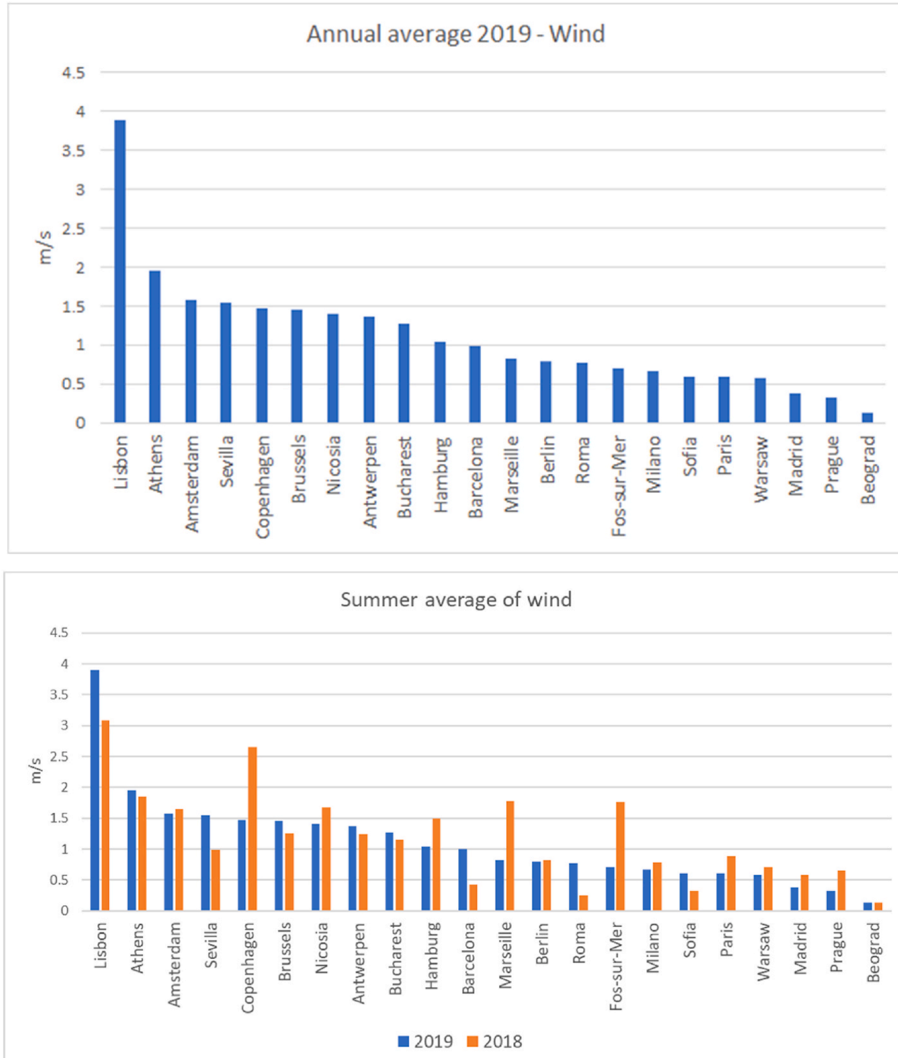


Fig. 13. Annual (2019) and summer (2018, 2019) average wind speed (IFS model).

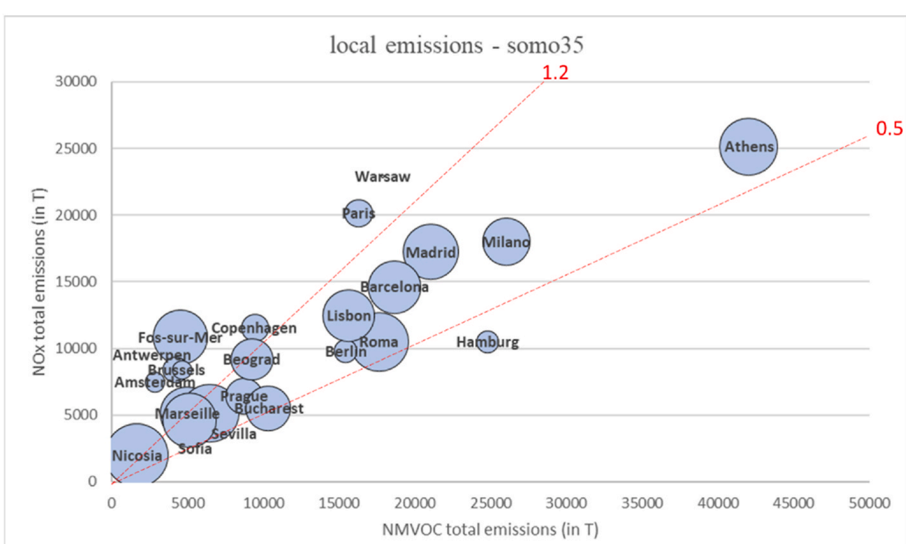


Fig. 14. Modelled SOMO35 indicator for the year 2019 in the reference simulation (i.e., without emission reductions) as a function of local (city) emissions of NOx (y-axis, tons) and NMVOC (x-axis, tons). The diameter of the circles is proportional to the value of the SOMO35 indicator. 2 dotted lines representing a NOx/NMVOC emissions ratio of 1.2 and 0.5 are drawn for indication purposes.

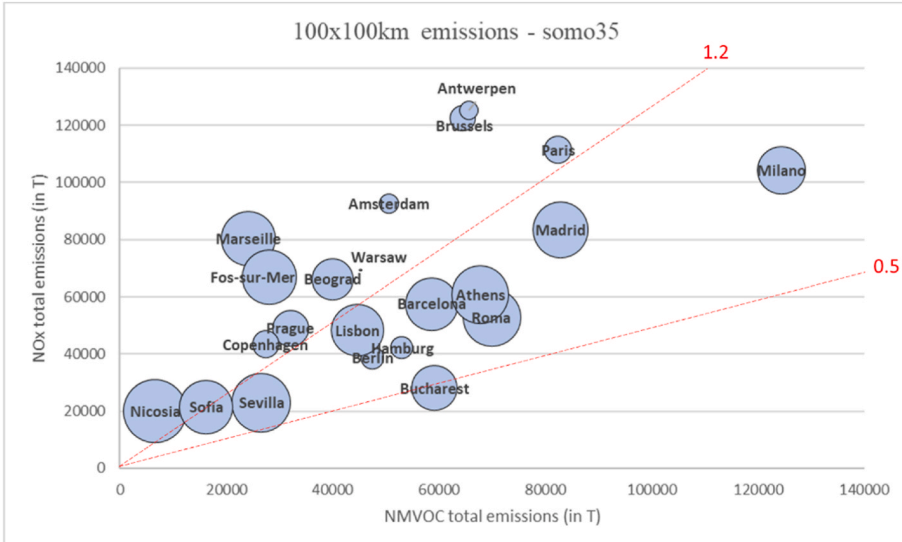


Fig. 15. Modelled SOMO35 indicators for the year 2019 in the reference simulation (i.e., without emission reductions) as a function of regional (100 × 100km around the city) emissions of NOx (y-axis, tons) and NMVOC (x-axis, tons). The diameter of the circles is proportional to the value of the SOMO35 indicator. 2 dotted lines representing a NOx/NMVOC emissions ratio of 1.2 and 0.5 are drawn for indication purposes.

transport sector (Madrid, Antwerp, Brussels, Marseille in addition to Hamburg, Barcelona and Fos-sur-Mer). However, it should be noted that NMVOC emissions from both IND and TRA account for only a portion of the total NMVOC emissions. This shows that in some cases, anthropogenic emissions from sectors other than industry or road transport may be important. In particular, one important source of NMVOC is SNAP6: "solvent and other produced use" for which the emissions have not been targeted in this study.

In Brussels, Antwerp and Amsterdam, that are in titration regime (according to our classification) or showing very small sensitivity to emissions reductions, NO_x emissions are not so high at local level, but when extended to the region, NO_x levels are very high. The entire corresponding regions (including all of Belgium and the Netherlands) is therefore in a titration regime due to high NO_x levels (which consume O_3) and low O_3 production due to low sunlight. Marseille is also characterized by limited local emissions compared to the surrounding region, but because the meteorological conditions are very different (much more solar radiation, exposed to high ozone over the Mediterranean Sea) compared to the Benelux area, this does not result in a titration regime but in limiting the efficiency of reducing ozone concentration. It is interesting to see that many of the cities with significant O_3 sensitivity to emission reductions are medium-sized cities with limited NO_x emission levels, located in southern Europe (Nicosia, Bucharest, Sevilla, Sofia). Athens shows the largest local NO_x emissions. Although there is a lot of solar radiation to produce O_3, the destruction of O_3 by reaction with NO is significant, hence limiting the impact of emission reductions. The comparison of Paris and Milan is also interesting. We have seen that the amount of solar radiation is equivalent for these two cities. The NO_x emissions at both local and regional level are also of the same order of magnitude. However, Milan shows a much larger O_3 sensitivity to emissions reductions in summer, whereas Paris shows a small reduction or even an increase in O_3. This difference is certainly partly due to differences in emissions of NMVOC (Fig. 17). At the local level, NMVOC emissions (from road transport in particular) are much higher in Milan than in Paris, thus greatly increasing the potential for O_3 production in the case of Milan. Climate conditions of the Po valley also play a role. Indeed, due to its location on the plain, partly surrounded by mountains, Milan is also known for its air mass stagnation effects, which leaves time for polluted air masses to produce ozone in the city of Milan, whereas ozone is often high downstream of polluted air masses in Paris.

The only cities for which at least one indicator is more sensitive to industrial emissions are those with high industrial emissions at the local or regional levels (Barcelona, Milan, Copenhagen, berlin, Hamburg and Amsterdam) but with a relatively low NOx/NMVOC ratio. As an example, Fos-sur-mer has high NOx industrial emissions which leads to a titration phenomenon when these emissions are reduced and a rise in ozone levels for certain indicators.

3.5.3. Discussions on uncertainties

The results obtained in this paper are of course highly dependent on the ACT model and the way in which emission reductions are transformed into ozone impact. ACT is a surrogate model of CHIMERE. It has been demonstrated that its ability to reproduce the behaviour of CHIMERE, and specifically its reaction to emission reductions, is very good, with less than 2% of errors for more than 95% of the day and location in Europe. The uncertainties for the CHIMERE model itself may come from chemical and physicals parametrisation, or from its horizontal resolution. With finer resolution, it is likely that titration phenomena would be amplified, and another chemical parametrisation may also change the results. The spatial resolution will also have an impact on the refinement of meteorological data, with a possibility to introduce additional biases. The performances of the model in capturing in situ observations for the reference simulation are quantified in Section 3.1. The modelling suite is also largely sensitive to the forcing data among which we find meteorology, boundary conditions, and most importantly emission fluxes. Emissions data, in particular the value and speciation of biogenic and anthropogenic NMVOCs, are known as one of the more uncertain data in air quality and will have a strong impact on the results of this study. It should be noted that the design of the present study relying on a surrogate model, allows for the first time to explore the whole range of emission reductions between 0 and 100% by increment of 1%. The coverage of emission uncertainties is therefore much more comprehensive than in sensitivity simulations, where only a couple of emission reduction levels are covered and non-linearity generally ignored. The good comparison of the model with observations and the fact that most exceedances are well reproduce gives certain guarantees on results, but it would be interesting to develop a broad study of the sensitivity of the results obtained here to the main sources of uncertainty.

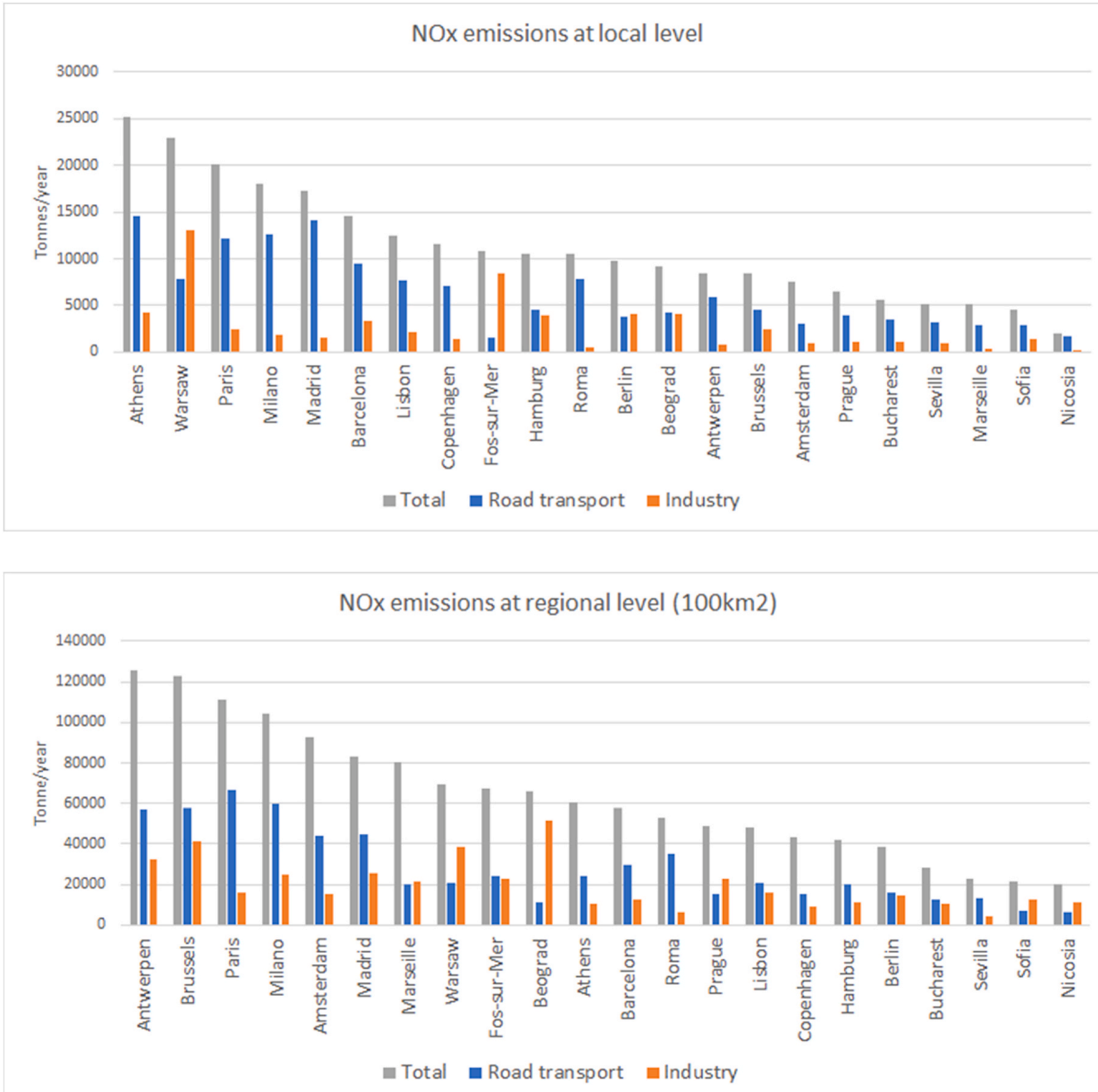


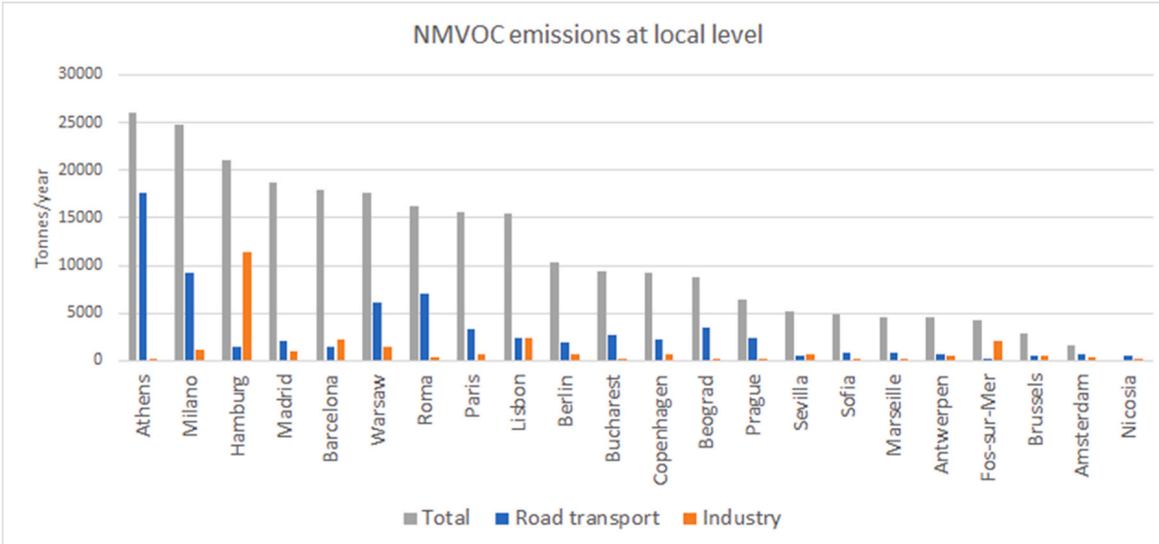
Fig. 16. NO_x emissions at local level (top) and within a 100 × 100 km grid centered on the city (bottom), for total anthropogenic, road transport and industrial sources.

4. Conclusions

In this study the surrogate model ACT was used to examine the change in surface ozone that might be brought about through reductions in emissions from road transport (TRA) and a combination of industry sources (IND). The results of these calculations have been presented as an Atlas of 2-dimensional emission reduction charts showing ozone metric changes (ΔO_3) as isopleths. A total of 22 target cities across Europe were selected and O_3 changes analyzed for the years 2018/2019. Results have been supplemented with information on O_3 regime, meteorological parameters and emissions information. Focus was on three metrics for O_3: the daily 1 h maximum averaged over a season, SOMO35, a health metric, and the 93.15 percentile of the daily maximum O_3 concentrations, corresponding to the 26th highest O_3 concentration (not to exceed 120 μg m^{-3} for EU target value). The results have been expressed as a change in O_3 metrics (ΔO_3) with change in emissions. Detailed results are available in the supplementary material document "City Fiches".

We have classified the shape of the ΔO_3 charts into five O_3 classes in terms of chemical regimes. The O_3 sensitivity to road transport and industrial emissions differ from one city to another, but also for the same city when considering the different ozone metrics and from one period of the year to another (winter vs summer), or even one year compared to another (2018 vs 2019). Five effective classes in terms of chemical regimes are considered in the analysis: either (i) Road transport (TRA) or (ii) Industry (IND) sensitive if emission reductions for one of those activity sectors is found to lead to ozone reductions. Sensitivity to both IND and TRA is considered as an individual class (iii). We also differentiate the cases where TRA and/or IND emission reduction yields a significant increase in ozone metrics (referred to as partial or complete titration regimes (iv)). A final class is where the model indicates both ozone increases and decreases occur over the range of emissions reduction ((referred to as change in regime (v)).

The proportion of cases (city/period/metrics) for which the O_3 regime is a titration regime is significant, especially in winter (96%) and for the annual average of O_3 daily maximum (45%). This is particularly the case for northern European countries with low solar radiation (and thus low O_3 production) but also for some countries further south but with high NO_x emissions at local and/or regional scale. In these cases, measures to reduce NO_x emissions are counterproductive for reducing



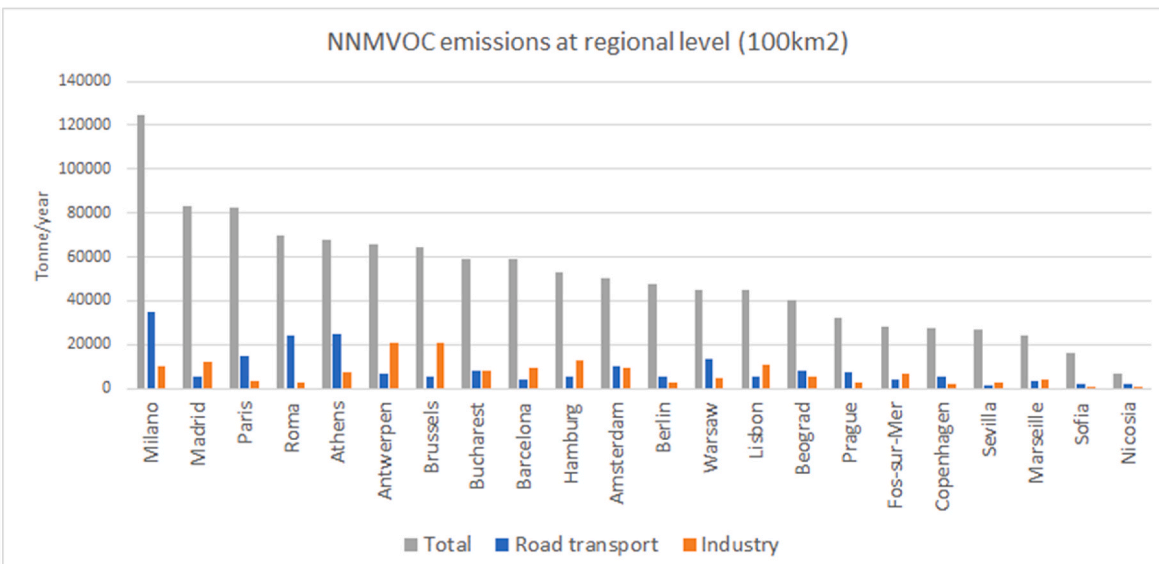


Fig. 17. NMVOC emissions at local level (top) and within a city-centered grid of 100 × 100 km (bottom), for total anthropogenic, road transport and industrial sources.

O_3. O_3 titration (i.e. counterproductivity of NO_x reduction measures) is not observed at very high O_3 levels, since the principle of titration is consumption of O_3 by its reaction with NO. That is why reduced titration, which leads to an increase of ozone, is essentially a concern where and when ozone concentrations are low in the reference case and EU target value are not reached.

The more we focus on summertime months, or on yearly indicators with high threshold (SOMO35, percentile 93.15), the more effective emission reductions can be, and the fewer cases of titration there are. The cases of complete titration decrease quite significantly to none, 2 and 4% respectively when considering percentile 93.15, summer period and SOMO35 compared to the winter case (96%). Partial titration regimes separately, for the remaining cases (more than 75% of the cities), the emission reductions from road transport and industry are expected to reduce O_3 metric values but this reduction is limited with a maximum reduction of 37% in Milan for the percentile 93.15 when both IND and TRA emissions are eliminated. This is a fairly limited O_3 reduction in comparison to the major reduction in emissions (100%). For other cities in summer (2019) O_3 maximum reductions are more in the range of 20–25%, so even less responsive to major reductions in road transport and industrial emissions. Moreover, it was shown that none of the cities studied would exceed the European target value with a 100% reduction in both TRA and IND emissions. This study thus suggests that reducing ozone precursor emissions from traffic and industrial sectors may have counterproductive effects on certain ozone indicators, but is unlikely to lead to exceedances of the target value; on the contrary, it may reduce the number of exceedances if the emissions reductions are significant.

The cities which show the largest relative O_3 reductions are southern European cities with either not too high NOx emissions or high NOx emissions but also high VOC emission levels. Climatic conditions favor O_3 production, particularly the amount of solar radiation received and the propensity for stagnation of air masses, for which annual average wind speed was used as a surrogate.

Outside the titration regime, most cases show a higher sensitivity to emission reductions from road transport or equal sensitivity to emission reductions from road transport and industry. Very few cases are most sensitive to emission reductions from the industrial sector.

CRediT authorship contribution statement

E. Real: Writing – review & editing, Writing – original draft, Validation, Software, Methodology, Conceptualization. **A. Megaritis:** Writing – review & editing, Supervision, Conceptualization. **A. Colette:** Writing – review & editing, Supervision, Conceptualization. **G. Valastro:** Project administration. **P. Messina:** Supervision.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Real reports financial support was provided by Concawe.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2023.120323.

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