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Ozone weekend effect in cities: Deep insights for urban air pollution control

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\textbf{A R T I C L E   I N F O}

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\textbf{A B S T R A C T}

Studying weekend-weekday variation in ground-level ozone (O\textsubscript{3}) allows one to better understand O\textsubscript{3} formation conditions, with a potential for developing effective strategies for O\textsubscript{3} control. Reducing inappropriately the O\textsubscript{3} precursors emissions can either produce no reduction or increase surface O\textsubscript{3} concentrations. This paper analyzes the weekend-weekday differences of O\textsubscript{3} at 300 rural and 808 urban background stations worldwide from 2005 to 2014, in order to investigate the O\textsubscript{3} weekend effect over time and assess the effectiveness of the precursors emissions control policies for reducing O\textsubscript{3} levels. Data were analyzed with the non-parametric Mann-Kendall test and Theil-Sen estimator. Rural sites typically did not experience a weekend-weekday effect. In all urban stations, the mean O\textsubscript{3} concentration on the weekend was 12% higher than on weekdays. Between 2005 and 2014, the annual mean of daily O\textsubscript{3} concentrations increased at 74% of urban sites worldwide (+ 0.41 ppb year\textsuperscript{-1}) and decreased in the United Kingdom (- 0.18 ppb year\textsuperscript{-1}). Over this time period, emissions of O\textsubscript{3} precursors declined significantly. However, a greater decline in nitrogen oxides (NO\textsubscript{x}) emissions caused an increase in Volatile Organic Compounds (VOCs) to NO\textsubscript{x} ratios leading to O\textsubscript{3} formation. In France, South Korea and the United Kingdom, most urban stations showed a significant upward trend (+ 1.15% per year) for O\textsubscript{3} weekend effect. Conversely, in Canada, Germany, Japan, Italy and the United States, the O\textsubscript{3} weekend effect showed a significant downward trend (- 0.26% per year). Further or inappropriate control of anthropogenic emissions in Canada, Southern Europe, Japan, South Korea and the United States might result in increased daily O\textsubscript{3} levels in urban areas.

\section{1. Introduction}

In cities, particulate matter with an aerodynamic diameter lower than 2.5 \textmu m and 10 \textmu m (PM\textsubscript{2.5} and PM\textsubscript{10}), nitrogen dioxide (NO\textsubscript{2}) and tropospheric ozone (O\textsubscript{3}) are among the most threatening air pollutants in terms of harmful effects on human health related to respiratory and cardiovascular diseases (Weinmayr et al., 2010; Pascal et al., 2013; WHO, 2013; Cohen et al., 2017; Nuvolone et al., 2018; Sicard et al., 2019). Tropospheric O\textsubscript{3} formation occurs when nitrogen oxides (NO\textsubscript{x}) and carbon monoxide (CO) react in the atmosphere in presence of sunlight (Seinfeld and Pandis, 1998). Recent epidemiological studies showed that O\textsubscript{3} causes harmful effects on human health, independently of other air pollutants (Cohen et al., 2017). In 2010, the number of premature deaths due to a long-term O\textsubscript{3} exposure was estimated at 1.1 million per year due to respiratory diseases, in particular asthma, across the world, with approximately 400, 000 and 270,000 deaths in India and China, and 50,000–60,000 deaths in Africa, Europe and North America (Malley et al., 2017). The short-term exposure was associated with 17,700 O\textsubscript{3}-related premature deaths in Europe in 2015 (EEA, 2018) and 74,000 in China in 2015 (Feng et al., 2019). Furthermore, ground-level O\textsubscript{3} is considered as the most detrimental air pollutant in terms of effects on vegetation (Sicard et al., 2016b,c; Agathokleous et al., 2020).

Lower O\textsubscript{3} mean concentrations are observed in urban areas (Sicard et al., 2019). In 2019, annual mean O\textsubscript{3} concentrations were 12% higher on the weekend than on weekdays. The weekend-weekday differences of O\textsubscript{3} concentrations are significant in urban stations worldwide. In France, South Korea and the United Kingdom, O\textsubscript{3} concentrations increased at 74% of urban stations worldwide (+ 0.41 ppb year\textsuperscript{-1}) and decreased in the United Kingdom (- 0.18 ppb year\textsuperscript{-1}). Over this time period, emissions of O\textsubscript{3} precursors declined significantly. However, a greater decline in nitrogen oxides (NO\textsubscript{x}) emissions caused an increase in Volatile Organic Compounds (VOCs) to NO\textsubscript{x} ratios leading to O\textsubscript{3} formation. In France, South Korea and the United Kingdom, most urban stations showed a significant upward trend (+ 1.15% per year) for O\textsubscript{3} weekend effect. Conversely, in Canada, Germany, Japan, Italy and the United States, the O\textsubscript{3} weekend effect showed a significant downward trend (- 0.26% per year). Further or inappropriate control of anthropogenic emissions in Canada, Southern Europe, Japan, South Korea and the United States might result in increased daily O\textsubscript{3} levels in urban areas.

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et al., 2013; Paoletti et al., 2014) where freshly emitted NO, in particular from road traffic, can deplete O3 locally (Solberg et al., 2005; Molina et al., 2009). The highest O3 mean concentrations are observed at rural and remote areas (Guerreiro et al., 2014; Monks et al., 2015) and high-elevation stations (Sicard et al., 2016a) due to higher biogenic VOCs emission, lower O3 titration by NO, and O3 and/or precursors transport from urban areas (e.g. Monks et al., 2015; Sicard et al., 2016a). The O3 concentrations tend to be higher on the weekends (Saturday and Sunday) compared to the weekdays (Monday to Friday) at urban sites worldwide, despite lower VOCs and NOx emissions. This “ozone weekend effect” was first reported in New York City (Cleveland et al., 1974), and was widely studied using in-situ measurements, modelling and satellite data in North America (e.g. Blanchard et al., 2008; Pierce et al., 2010; Koo et al., 2012; Wolf et al., 2013), Europe (e.g. Schipa et al., 2009; Castell-Balaguer et al., 2012), South America (e.g. Seguel et al., 2012; Martins et al., 2015), China (e.g. Tang et al., 2008; Wang et al., 2014; Zou et al., 2019), Taiwan and Japan (Tasi, 2005; Sadanaga et al., 2012).

The legislated ambient air quality standards and emissions control policies of O3 precursors around the world (e.g. European Council Directive 2008/50/EC; Ministry of Environmental Protection, 2012; US Federal Register, 2015; National Environmental Emissions Directive (2016/2284/EU); Convention on Long-range Transboundary Air Pollution, 2017) were effective in rural and remote areas (Sicard et al., 2013; Paoletti et al., 2014). However, O3 concentrations have increased in cities, by on average 0.16 ppb per year, across the globe over the time period 1995–2014 (Sicard et al., 2018). Hence, O3 pollution becomes a major air quality issue in cities (EEA, 2018; Sicard et al., 2018).

Observation of how weekend-weekday O3 production and O3 weekend effect respond to emissions reduction strategies may provide an insight into the effectiveness of policies to plan future suitable strategies for reducing emissions of O3 precursors (Karl et al., 2017). Previous analyses of the O3 weekend effect, usually for a single urban area, make use of various statistical methods, including quantile-quantile plot, non-parametric statistics and calculation of daily mean O3 concentrations. Such a trends analysis can provide information on how O3 control strategies may have affected the weekend-weekday effect over the last decade. The Tropospheric Ozone Assessment Report (TOAR), initiated by the International Global Atmospheric Chemistry Project, established an up-to-date database of global surface O3 observations (Schultz et al., 2017). Due to the spatial representativeness of O3 monitoring stations and the length of time series, the world’s largest TOAR database offers an unprecedented and effective way to analyse trends in surface O3 concentrations.

For the first time, a spatiotemporal analysis of short-term annual trends was performed at 300 rural and 808 urban background stations over the time period 2005–2014. This study aims to i) quantify the trends in weekend-weekday surface O3 concentrations, ii) investigate the O3 weekend effect over time, and iii) assess the effectiveness of the precursors emissions control policies for reducing O3 levels and their impacts on the O3 weekend effect. We hypothesized that in urban areas O3 concentrations are higher on weekends than on weekdays and that a 10-year time-series of O3 data is considered long enough to detect short-term trends, likely due to NOx and VOCs emissions changes.

2. Materials and methods

2.1. Stations and data selection

The TOAR database (https://join.fz-juelich.de) gathers surface O3 observations, including daily O3 concentrations, for almost 10,000 stations around the world from 1970 (Schultz et al., 2017). The classification and typology of stations follows the European Environment Agency guidelines, i.e. the ratio NO/NO2 was used to classify stations as rural or urban background stations (Snel et al., 2004). A rural station is located outside a city, far from city sources of air pollution (Snel et al., 2004). For the robustness of the study, we applied criteria in selecting stations and countries. We selected the stations with more than 90% of validated daily data per year for a minimum 10-year time period from 2005, as well as the countries with at least 20 stations available to have a good spatial representativeness of results. Finally, 300 rural and 808 urban stations were selected worldwide over the time period 2005–2014 for seven countries (Canada, France, Italy, Japan, South Korea, Spain and the United Kingdom) and 2005–2018 for two countries (Germany and the United States). The number of monitoring stations did not change from year to year. The national emissions of main O3 precursors (NOx, VOCs and CO) were provided by the European Monitoring and Evaluation Program (EMEP) and by the Organization for Economic Co-operation and Development (OECD) for on-road transport emissions. The emissions data were examined over different time periods, 1990–2005 and 2005–2014 (and 2005–2018).

In this study, the 24-h O3 mean concentrations is investigated over time to: i) represent the background O3 concentrations in cities; ii) account for low O3 exposure levels; iii) take into account the increasing hourly O3 levels; iv) consider the changes in the timing of transport emissions, shifted later on weekends; v) take into account the diurnal profile of O3 including the rush hours on weekdays in order to have a full overview of impacts of NOx emissions from road transport on weekend effect.

2.2. Estimation of the weekend effect

The differences between weekend (Saturday and Sunday) and weekday (Monday to Friday) ambient O3 concentrations were characterized (expressed as weekend-weekday O3 difference in %). For every week of the year and station, we calculated the average O3 concentration for the weekend and the average for the weekdays (523 weeks, 808 urban stations between 2005 and 2014) to compute the weekend-weekday O3 difference. Then, the seasonal averages of weekend and weekdays O3 concentrations were computed for different seasons during the study period: winter (January–March), spring (April–June), summer (July–September) and autumn (October–December). The non-parametric Mann-Whitney U test was used to test the statistical significance of the weekend-weekday differences at each site. The test is robust for non-normally distributed data and the presence of correlation among O3 values on adjacent days (Blanchard and Tanenbaum, 2003). We arbitrarily divided the urban stations into three types: no or low O3 weekend effect (weekend-weekday difference < 5% i.e. less than 1 ppb), moderate O3 weekend effect (5% < weekend-weekday difference < 15%) and high O3 weekend effect (weekend-weekday difference > 15%, i.e. more than 3 ppb). No categorization was performed for rural stations due to the low weekend-weekday O3 difference (less than 3%, on average).

2.3. Estimation of annual trends

A 10-year time-series of O3 data is considered long enough to assess short-term changes (Monks et al., 2015). To detect changes within O3 time-series and estimate the magnitude of trends at individual stations, the non-parametric Mann-Kendall test coupled with the non-parametric Sen’s slope estimator were used (Sicard et al., 2013; Guerreiro et al., 2014). The non-parametric tests are robust and suitable for non-normally distributed data with missing and extreme values (Sicard et al., 2016a). Both tests were applied for daily O3 mean concentrations, weekend-weekday O3 difference and annual national emissions of O3 precursors. Results were considered significant at p < 0.05 and presented here. All results are detailed in Supplementary Material.
3. Results

3.1. Weekly variations of ozone concentrations and trends at rural stations

At rural stations, the annual daily mean O₃ concentrations ranged from 28.5 ppb in the United Kingdom to 36.8 ppb in Japan over the time period 2005–2014 (Fig. 1, Tab. S1). The annual daily mean O₃ concentration was typically lower on Wednesday (e.g. 28.2 ppb in Germany) and higher on Sunday (e.g. 30.4 ppb in Germany). The weekend-weekday difference was less than 1 ppb at all stations (Tab. S1).

Between 2005 and 2014, the magnitude trends of annual O₃ mean concentrations, ranged from -0.09 (Spain) to -0.73 ppb year⁻¹ (Italy), while an increase was observed only in South Korea (+ 0.40 ppb year⁻¹) (Fig. 1). The annual O₃ mean concentrations decreased on average by 0.34 ppb year⁻¹ in Germany and by 0.33 ppb year⁻¹ in the United States over the time period 2005–2014, while a decreasing trend of 0.08 ppb year⁻¹ and 0.28 ppb year⁻¹ was observed over the time period 2005–2018 (Tab. S1). No significant differences in trends magnitude on weekdays compared to the weekend were observed (in Italy, South Korea, United Kingdom, United States), while the highest decreases were observed on Sunday in Spain (-0.27 ppb year⁻¹) and Japan (-0.46 ppb year⁻¹). In France, higher decreases were found on Wednesday (-0.22 ppb year⁻¹) and Sunday (-0.18 ppb year⁻¹), while a slight increase was observed on Saturday (+ 0.02 ppb year⁻¹). For annual mean concentrations, between 57% (France) and 87% (Germany) of rural stations showed a decrease from 2005 to 2014 with no weekend effect, and most of South Korean rural stations (75%) showed positive trends (Tab. S2).

About 52% and 89% of stations in Germany and the United States, respectively, showed a decline over the time period 2005–2018 (Tab. S2).

3.2. Weekly variations of ozone concentrations and trends at urban stations

In cities, the annual mean of daily O₃ concentrations ranged from 19.5 ppb in the United Kingdom to 27.2 ppb in the United States over the time period 2005–2014, with annual daily mean O₃ concentrations in Italy, France and Spain around 24 ppb (Fig. 2, Tab. S3). At the urban stations, the weekly variation of O₃ showed the obvious characteristics of the O₃ weekend effect. In all stations, the lower O₃ concentrations occurred on Tuesday, Wednesday or Thursday while the higher O₃ concentrations occurred on Sunday. During the weekdays, the difference of daily mean O₃ concentrations was lower than 0.5 ppb on average; however, the O₃ concentrations were 1.4–3.8% higher on Monday than on other weekdays (Tuesday-Friday).

Between 2005 and 2014, the annual mean of daily O₃ concentrations increased from 0.09 (Germany) to 0.80 ppb year⁻¹ (South Korea), while a decrease was observed in the United Kingdom (-0.18 ppb year⁻¹) (Tab. S3). Interestingly, in Germany, Italy and the United States, the O₃ concentrations increased during the weekdays and decreased during the weekend with higher decline on Sunday (Fig. 2). For instance in the United States, the daily O₃ mean concentrations increased by 0.22–0.31 ppb year⁻¹ during the weekdays and decreased by 0.08 ppb year⁻¹ on Saturday and by 0.15 ppb year⁻¹ on Sunday over the time period 2005–2014. Similarly, in Germany, the O₃ concentrations increased by 0.01–0.15 ppb year⁻¹ during the weekdays and decreased by 0.16 ppb year⁻¹ on Saturday and by 0.22 ppb year⁻¹ on Sunday. In Italy, higher O₃ increases were obtained from Monday to Friday (0.54–0.89 ppb year⁻¹) while a decline (-0.12 ppb year⁻¹) was observed during the weekend. The O₃ concentrations decreased in the United Kingdom, similarly during the weekdays (from -0.11 to -0.22 ppb year⁻¹) and weekend (from -0.10 to -0.25 ppb year⁻¹), i.e. with no weekend effect. A significant increase was observed on all days of the week in South Korea (+0.73–0.91 ppb year⁻¹) and France (+0.33–0.44 ppb year⁻¹) except on Wednesday (+0.04 ppb year⁻¹). In Canada, Japan and Spain, the O₃ levels increased on all days but the trend magnitude was lower during the weekend (+0.34–0.40 ppb year⁻¹ in Canada; +0.08–0.13 ppb year⁻¹ in Japan; +0.28–0.39 ppb year⁻¹ in Spain) than on weekdays (+0.44–0.57 ppb year⁻¹ in Canada; +0.48–0.73 ppb year⁻¹ in Japan; +0.47–0.81 ppb year⁻¹ in Spain). In France, Spain and Italy, the trends magnitude on Wednesday was lower (by 55% on average) than the other days of the week. Globally, we observed O₃ increases during the weekdays and either a decline (Germany, Italy and United States) or a lower increase (Canada, Spain and Japan) during the weekend. In line with the above trend magnitude, between 46.8% (Germany) and 94.3% (Canada) of urban stations showed an increase of daily O₃ concentrations from 2005 to 2014 (Tab. S4). In the United Kingdom, 65.5% of

![Fig. 1. Averaged daily ozone mean concentrations (ppb) and annual significant trends (ppb per year, at p < 0.05) calculated by joining daily data from rural monitoring stations over the time period 2005–2014. The striped histograms represent the trends during weekends (Saturday and Sunday). No rural station in Canada met the selection criteria at p < 0.05.](image-url)
stations showed a decrease of O\(_3\) mean concentrations. Overall, we observed a higher number of stations showing an O\(_3\) increase during the weekdays than on weekends e.g. in Germany, Spain and Japan.

Similar findings were observed in Germany and the United States over the time period 2005–2018 (Tab. S3). The daily O\(_3\) concentrations increased, on average by 0.18 ppb year\(^{-1}\) in Germany and by 0.21 ppb year\(^{-1}\) in the United States. About 87% and 71% of urban stations in Germany and the United States, respectively, showed an increase of daily O\(_3\) mean concentrations (Tab. S4), with a lower number of stations showing an increase of O\(_3\) levels during the weekend (e.g. 48% on Sunday in Germany) than in the weekdays (e.g. 85–94% in Germany). In Germany, a change in trends in daily O\(_3\) concentrations was reported in 2010: the daily O\(_3\) concentrations decreased by 0.10 ppb year\(^{-1}\) between 2005 and 2010 and increased by 0.27 ppb year\(^{-1}\) from 2010 (p < 0.05, data not shown).

3.3. The ozone weekend effect

The average O\(_3\) difference of the weekends relative to the weekdays was about 12% over the period 2005–2014, ranging from 8.1% in the United States to 16.6% in the United Kingdom (Table 1). In all urban stations, the highest mean O\(_3\) concentrations occurred on Sunday, i.e. on average 13.1% higher than on weekdays (ranging from 9.5% in Italy and the United States to 19.1% in Germany); the daily O\(_3\) concentrations were on average 10.5% higher on Saturday than on weekdays. On average 26% of urban stations experienced mean O\(_3\) concentrations on weekends that were less than 5% higher than on weekdays, and 31% of urban stations had O\(_3\) concentrations on weekends more than 15% higher than on weekdays. Only 3% of monitoring stations in Germany had mean O\(_3\) concentrations on weekends less than 5% higher than on weekdays. In Japan, the United Kingdom, France and Canada, 20–30% of stations had no or low weekend effect over the time period 2005–2014. In Italy, Spain, Japan and Canada, 35–40% of stations showed a moderate weekend effect. In France, only 2% of stations had a high weekend effect, while this percentage was as large as 44–47% in Germany, Japan and United Kingdom. In the United States and Germany, 53–56% of stations showed a weekend-weekday O\(_3\) difference in the range of 5–15%, i.e. with a moderate weekend effect between 2005 and 2018.

The stronger seasonality for the O\(_3\) weekend effect occurred in Germany with weekend-weekday O\(_3\) difference ranging from 7.9% in summer to 28.9% in winter (Fig. 3). In all stations, the maximum O\(_3\) weekend effect was observed in winter (18.1% difference, on average) and autumn (14.5% difference), i.e. the cold period in the Northern hemisphere, compared to low or moderate O\(_3\) weekend effect in spring (7.6% difference) and summer (7.4% difference).

3.4. The ozone weekend effect over time

By joining all urban stations over the period 2005–2014, the weekend-weekday O\(_3\) difference increased at about 52% of stations by 0.24% per year, on average (Table 1). The majority of urban stations showed positive trends, i.e. the O\(_3\) weekend effect increased by 1.15% per year on average at 81% of urban stations in France, South Korea and the United Kingdom; e.g. about 87% of stations in France (+ 0.90% year\(^{-1}\)) and 93% of stations in the United Kingdom showed a pronounced upward trend (+ 2.10% year\(^{-1}\)). The O\(_3\) weekend effect declined by 0.26% per year at 66% of urban stations in Canada, Germany, Italy, Japan and the United States. A slight decline was found in Canada (- 0.09% year\(^{-1}\)) and Italy (- 0.10% year\(^{-1}\)) at about 51% and 53% of urban stations, respectively, while a null trend was observed in Spain. Between 2005 and 2014, the weekend-weekday O\(_3\) difference decreased by 0.45% and 0.50% per year in Germany and the United Kingdom, with about 86% and 84% of stations showing a weakening of the O\(_3\) weekend effect. The O\(_3\) weekend effect weakened 0.65% and 0.55% per year in Germany and the United States, with about 97% and 89% of stations showing a weakening over the time period 2005–2018.

From 2005 to 2014 by joining all stations, the number of stations with a weekend-weekday O\(_3\) difference lower than 5% decreased by 0.65% year\(^{-1}\) on average, while the number of stations with a weekend-weekday O\(_3\) difference higher than 15% increased by 0.11% year\(^{-1}\), with a maximum upward trend (+ 6.46% year\(^{-1}\)) observed in the United Kingdom (Table 1). A substantial year-to-year variability in the weekend-weekday O\(_3\) difference was observed over time. For instance, the presence of a significant weekend effect for O\(_3\), with consistently higher concentrations (more than 15%) on weekends and a strong weekly cycle, increased from 60 to 70% of stations before 2008 to around 30% from 2011 in Germany (data not shown). In the United States, the presence of a significant O\(_3\) weekend effect has spread from ~15% of sites in 2005–2009 to ~7% of sites in 2010–2015. The number of stations with a weekend-weekday O\(_3\) difference lower than 5% spread from ~22% in 2005–2009 to ~44% in 2010–2015 (data not shown).
Table 1

Averaged weekend-weekday ozone (O\textsubscript{3}) difference (expressed in %), annual trends for ozone weekend effect (OWE, expressed in % per year), and percentage of urban stations per trend category (decrease and increase) and per range of weekend-weekday ozone difference over the time period 2005–2014 (as well as 2005–2018 for Germany and United States) ± standard deviation (N: number of stations). We divided the urban stations into three types: no or low O\textsubscript{3} weekend effect (weekend-weekday difference < 5%), moderate O\textsubscript{3} weekend effect (5% < weekend-weekday difference < 15%) and high O\textsubscript{3} weekend effect (weekend-weekday difference > 15%).

| Countries | Time period | N  | Weekend-weekday O\textsubscript{3} difference | Saturday-weekday O\textsubscript{3} difference | Sunday-weekday O\textsubscript{3} difference | OWE trends | Increasing trend | Decreasing trend | Percentage of monitoring stations per range of weekend-weekday O\textsubscript{3} difference | Trends per range (% year\textsuperscript{-1}) |
|-----------|-------------|----|---------------------------------------------|-----------------------------------------|---------------------------------------------|------------|-----------------|-----------------|-------------------------------------------------|-------------------|
| Canada    | 2005–2014   | 35 | 11.7 ± 3.1                                   | 11.4 ± 3.4                              | 12.0 ± 4.6                                  | 0.09 ± 0.56 | 48.6            | 51.4            | 0.95 ± 2.86                                                | -1.43 ± 0.56       |
| France    | 2005–2014   | 136| 10.9 ± 5.4                                   | 9.3 ± 5.1                               | 12.6 ± 6.1                                  | +0.90 ± 0.75 | 87.5            | 12.5            | 2.81 ± 4.68                                                | 0 ± 3.80 ± 4.12    |
| Germany   | 2005–2014   | 79 | 14.8 ± 3.5                                   | 10.6 ± 4.2                              | 19.1 ± 3.4                                  | -0.45 ± 0.31 | 13.9            | 86.1            | +0.90 ± 0.75                                                | 0 ± 3.0 ± 3.80     |
| Italy     | 2005–2014   | 50 | 9.0 ± 4.1                                    | 8.6 ± 4.1                               | 9.5 ± 5.1                                   | -0.10 ± 0.94 | 46.9            | 53.1            | 0.85 ± 1.29                                                | -0.41 ± 1.06       |
| Japan     | 2005–2014   | 55 | 14.3 ± 5.6                                   | 12.7 ± 6.8                              | 15.9 ± 6.5                                  | -0.17 ± 0.67 | 44.4            | 55.6            | 0.15 ± 0.64                                                | -0.16 ± 0.10       |
| South Korea | 2005–2014   | 200| 9.9 ± 4.8                                   | 9.5 ± 6.6                               | 10.3 ± 6.0                                  | +0.46 ± 1.10 | 64.0            | 36.0            | 1.79 ± 0.70                                                | +0.43 ± 0.46       |
| Spain     | 2005–2014   | 77 | 12.3 ± 7.0                                   | 11.3 ± 7.1                              | 13.2 ± 7.2                                  | 0.01 ± 1.94  | 55.8            | 44.2            | 0.15 ± 0.98                                                | +1.08 ± 1.29       |
| United Kingdom | 2005–2014 | 29 | 16.6 ± 12.2                                 | 16.6 ± 14.1                             | 17.2 ± 14.5                                 | +2.10 ± 1.62 | 93.1            | 6.9             | 3.01 ± 1.59                                                | +6.46 ± 2.14       |
| United States | 2005–2014 | 147| 8.1 ± 6.4                                    | 6.7 ± 6.0                               | 9.5 ± 7.8                                   | -0.50 ± 0.55 | 15.6            | 84.4            | 3.43 ± 2.04                                                | -1.15 ± 0.64       |
| All stations | 2005–2014 | 808| 11.8 ± 5.9                                   | 10.5 ± 6.5                              | 13.1 ± 6.9                                  | +0.24 ± 0.80 | 52.4            | 47.6            | -0.65 ± 1.10                                                | +0.11 ± 0.26       |
| Germany   | 2005–2018   | 79 | 13.4 ± 4.2                                   | 9.2 ± 4.6                               | 17.7 ± 4.3                                  | -0.65 ± 0.30 | 2.5             | 97.5            | +0.89 ± 2.25                                                | -4.43 ± 3.74       |
| United States | 2005–2018 | 147| 6.9 ± 5.8                                    | 5.6 ± 4.2                               | 8.1 ± 7.0                                   | -0.55 ± 0.53 | 11.6            | 89.4            | +2.23 ± 1.74                                                | -1.75 ± 0.12       |
3.5. Trends in ozone precursors emissions

In the 28 European Union countries (EU-28), significant reductions, particularly from the late 1990s, were observed, i.e. -3.2% year\(^{-1}\) for NMVOCs, -2.3% year\(^{-1}\) for NO\(_x\) and -3.9% year\(^{-1}\) for CO over the time period 1990–2005 (Table 2). An increase in NO\(_x\) emissions (+1.2% year\(^{-1}\)) was observed in Canada and a null trend was observed in Japan. In Canada, the NO\(_x\) emissions started to decrease from 1999; i.e. increased by 3.5% year\(^{-1}\) between 1990 and 1999 and decreased by 2.1% year\(^{-1}\) from 2000 to 2005 (data not shown). Between 1999 and 2005, significant increases in NMVOCs (+3.6% year\(^{-1}\)) and NO\(_x\) (+9.1% year\(^{-1}\)) emissions were observed in South Korea. Across the EU-28 countries, significant decreasing trends were observed over the time period 2005–2014, e.g. -3.2% year\(^{-1}\), -3.8% year\(^{-1}\) and -3.7% year\(^{-1}\), respectively for NMVOCs, NO\(_x\) and CO (Table 2). For NMVOCs, between 2005 and 2014, the highest decrease was found in France (-4.9% year\(^{-1}\)), while an increase was observed in South Korea (+2.1% year\(^{-1}\)). A slight decrease was observed in the United States (-1.1% year\(^{-1}\)). For NO\(_x\) the decrease ranged from -5.2% year\(^{-1}\) (Spain) to -1.6% year\(^{-1}\) (South Korea) over the time period 2005–2014. In South Korea, a change in trends in NO\(_x\) emissions was reported: the NO\(_x\) emissions decreased by 6.4% year\(^{-1}\) between 2005 and 2009 and increased by 2.2% year\(^{-1}\) from 2010 to 2014 (data not shown).

At national level, emissions of NO\(_x\) and VOCs from on-road transport decreased (Table 3) in Canada (40.0% and 41.1%), France (33.6% and 69.7%), Germany (36.9% and 46.9%), Italy (38.9% and 62.7%) and Spain (47.6% and 79.4%) between 2005 and 2014, and by 40.7% and 48.8% in Germany over the time period 2005–2018. In the United States, NO\(_x\) and VOCs emissions from road transport declined by 42.2% and 32.9% from 2005 to 2014, respectively, and have strongly dropped between 2005 and 2018 (55.0% and 47.0%). In the United Kingdom, the NO\(_x\) and VOCs emissions from road transport have fallen by 42.4% and 88.5%, respectively between 2005 and 2014. During 2005–2014, the NO\(_x\) and VOCs emissions from on-road transport decreased in Japan (43.7% and 45.2%) and South Korea (30.6% and 48.3%).

4. Discussion

The local \(O_3\) formation depends on the ratio of VOCs to NO\(_x\) (Beckman and Vautard, 2010; Markakis et al., 2014). In areas with a high ratio, i.e. under “NO\(_x\)-limited” conditions (e.g. remote areas, ratio >15–20 ppb/ppb), a decrease of NO\(_x\) burden reduces \(O_3\) production, while a rise of VOCs burden has no or small effect on \(O_3\) production (Pusede and Cohen, 2012; Xue et al., 2014). In areas under “VOC-limited” conditions (e.g. urban areas, ratio <4–8 ppb/ppb), a reduction in NO\(_x\) enhances the \(O_3\) formation, while a reduction in VOCs diminishes the \(O_3\) formation (Kang et al., 2004; Tang et al., 2012; Markakis et al., 2014; Xue et al., 2014). A better understanding of weekend-weekday ozone changes allows to gain insight into changing NO\(_x\) and VOCs emissions on \(O_3\) formation (Karl et al., 2017) to understand whether an area is under NO\(_x\)-limited or VOC-limited conditions in order to develop effective strategies for ground-level \(O_3\) control (Seguel et al., 2012). The local and synoptic meteorology affects the daily variation of surface \(O_3\) (Sicard et al., 2009; Han et al., 2020). The 10-year trends are unlikely due to meteorological variations but are likely due to short-term NO\(_x\) and VOCs emissions reduction (Pierce et al., 2018; Wolff et al., 2015).

4.1. The ozone trends in rural areas

At rural stations, representative of background levels, annual mean \(O_3\) concentrations ranged from 30 to 40 ppb, in agreement with the background \(O_3\) concentrations (35–50 ppb) observed at mid-latitudes in North Hemisphere (Lefohn et al., 2014; Sicard et al., 2017). In this study, the annual mean of daily \(O_3\) concentrations decreased by 0.36 ppb year\(^{-1}\) on average at 70% of 284 rural stations between 2005 and 2014, and increased by 0.40 ppb year\(^{-1}\) at 75% of 16 rural stations in South
Previous studies reported decreases of O\textsubscript{3} levels at most rural stations in Europe, Japan and the United States from the 2000s (Paoletti et al., 2014; Simon et al., 2015; Sicard et al., 2016a; Lefohn et al., 2018; Seo et al., 2018), for instance the background O\textsubscript{3} concentrations decreased by 0.05 ppb year\textsuperscript{-1} at rural stations globally over the time period 1995–2014 (Sicard et al., 2018). The reduction in annual O\textsubscript{3} mean concentrations at rural stations, representative of background levels, can be attributed to the reduction in NMVOCs and NO\textsubscript{x} emissions mainly due to the implementation of stringent vehicle emission standards, the use of flue-gas abatement techniques and the progress in the storage and distribution of solvents (Monks et al., 2015; Lefohn et al., 2018; Seo et al., 2018; Winkler et al., 2018; EEA, 2019). The majority of countries in the European Union (EU-28) and North America reduced emissions of O\textsubscript{3} precursors in line with stringent Directives implemented in the late 1990s, e.g. Gothenburg Protocol (1999), National Emission Ceilings Directives (2001, 2016), United States Federal Register (2015) and the Convention on Long-Range Transboundary Air Pollution (2017). In Germany, a slighter decrease of mean O\textsubscript{3} concentrations was observed within 2005–2018 (- 0.08 ppb year\textsuperscript{-1}) due to higher O\textsubscript{3} concentrations in 2015 (+5%) and 2018 (+10%) than the 10-year average (2005–2014).

Significant positive trends were previously reported at many sites in South Korea (Kim et al., 2013; Fleming et al., 2018). The observed increase of daily O\textsubscript{3} mean concentrations at 75% of rural stations in this country is mainly attributed to the increase of NMVOCs emissions between 2005 and 2014 as well as the rising of NO\textsubscript{x} emissions from 2010. In South Korea, despite the enhancement of vehicle emission standards, the NMVOCs emissions from solvent use rapidly increased in recent years (Kim and Lee, 2018; Seo et al., 2018). Furthermore, South Korea is located in the downwind area of China where increasing NO\textsubscript{x} (~+30%) and NMVOCs (~+20%) emissions were reported over the time period 2005–2014 (Akimoto et al., 2015; Xing et al., 2015; Miyazaki et al., 2017; Liu et al., 2017; Zheng et al., 2018). Emissions of NO\textsubscript{x} and NMVOCs in China can contribute up to 90% to the daily maximum 8-h average O\textsubscript{3} concentration observed in monitoring stations in South Korea (Choi et al., 2014; Kim and Lee, 2018).

### Table 3

| Countries                  | 2005–2014 (and 2005–2018**) Mean (Gg) | Trend (%) | 2005–2014 (and 2005–2018**) Mean (Gg) | Trend (%) | 2005–2014 (and 2005–2018**) Mean (Gg) | Trend (%) |
|----------------------------|--------------------------------------|-----------|--------------------------------------|-----------|--------------------------------------|-----------|
| NMVOCs                     |                                      |           | NO\textsubscript{x}                   |           | CO                                  |           |
| Canada                     | 207 ± 38                             | - 41.1    | 570 ± 97                             | - 40.0    | 2303 ± 447                           | - 45.3    |
| France                     | 128 ± 53                             | - 69.7    | 609 ± 81                             | - 33.6    | 733 ± 274                            | - 73.7    |
| Germany                    | 129 ± 28 (121 ± 29) **               | -46.9 (- 48.8) | 574 ± 98 (540 ± 107) **               | -36.9 (- 40.7) | 955 ± 157 (896 ± 171) **            | -44.2 (- 47.0) |
| Italy                      | 214 ± 75                             | - 62.7    | 480 ± 79                             | - 38.9    | 883 ± 289                            | - 68.0    |
| Japan                      | 101 ± 20                             | - 45.2    | 404 ± 75                             | - 43.7    | 847 ± 142                            | - 7.6     |
| South Korea                | 80 ± 18                              | - 48.3    | 394 ± 59                             | - 36.6    | 493 ± 100                            | - 40.6    |
| Spain                      | 56 ± 28                              | - 79.4    | 381 ± 80                             | - 47.6    | 349 ± 193                            | - 73.5    |
| United Kingdom             | 100 ± 58                             | - 88.5    | 447 ± 104                            | - 42.4    | 879 ± 416                            | - 82.4    |
| United States              | 2673 ± 362 (2476 ± 494) **           | -32.9 (- 47.0) | 5835 ± 1107 (5342 ± 1348) **         | -42.2 (- 55.0) | 27,189 ± 5025 (25,154 ± 5716) **    | -44.8 (- 53.8) |

Significant positive trends were previously reported at many sites in South Korea (Kim et al., 2013; Fleming et al., 2018). The observed increase of daily O\textsubscript{3} mean concentrations at 75% of rural stations in this country is mainly attributed to the increase of NMVOCs emissions between 2005 and 2014 as well as the rising of NO\textsubscript{x} emissions from 2010. In South Korea, despite the enhancement of vehicle emission standards, the NMVOCs emissions from solvent use rapidly increased in recent years (Kim and Lee, 2018; Seo et al., 2018). Furthermore, South Korea is located in the downwind area of China where increasing NO\textsubscript{x} (~+30%) and NMVOCs (~+20%) emissions were reported over the time period 2005–2014 (Akimoto et al., 2015; Xing et al., 2015; Miyazaki et al., 2017; Liu et al., 2017; Zheng et al., 2018). Emissions of NO\textsubscript{x} and NMVOCs in China can contribute up to 90% to the daily maximum 8-h average O\textsubscript{3} concentration observed in monitoring stations in South Korea (Choi et al., 2014; Kim and Lee, 2018).
4.2. The vehicle emission regulations

In the United States, the most recent emission standards for light-duty vehicles are the Tier 3 standards (2017–2025), which are revisions of the earlier Tier 2 (2004–2009) and Tier 1 (1994–1997) federal emission regulations. Tier 2 standard fully taken effect in 2004 and when it was fully implemented in 2009, the average NO\textsubscript{X} emissions of the entire light-duty vehicle fleet sold by each manufacturer met the average standard of 0.07 g NO\textsubscript{X}/mile; 0.09 g VOCS/mile and 0.01 g PM/mm. Looking at Tier 3, the fleet average NO\textsubscript{X} + VOCS limit is phased-in starting from 2017 with 0.086 g/mile (0.079 g/mile in 2018) to reach 0.030 g/mile in 2025. In the European Union, Euro 3-4-5 standards were put into effect in 2001, 2006 and 2011, respectively. For diesel cars, the average NO\textsubscript{X} + VOCS limit ranged from 0.560 g/km (Euro 3) to 0.230 g/km (Euro 5). The current Euro 6 standard for light-duty vehicles (NO\textsubscript{X} + VOCS = 0.170 g/km) went into effect in 2015. For gasoline cars, the average standards are 0.150 g NO\textsubscript{X}/km (Euro 3) and 0.060 g NO\textsubscript{X}/km (Euro 6–5).

In the United States, the successive Tier standards have lowered the NO\textsubscript{X} (50%) and VOCS (44%) emission intensity between 2004 and 2017. Similarly in Canada, the on-road vehicles aligned emission certification requirements for light-duty vehicles with those of the US EPA Tier 2 from 1st January 2004. In the European Union, the successive Euro 3–5 standards have lowered the NO\textsubscript{X} (64%) and VOCS (17%) emission intensity in the EU between 2005 and 2015. In Japan, the emission standards are among the most stringent in the world (Wang et al., 2014), and the successive standards for diesel and gasoline cars, comparable to Tier 2 and Euro 5, have lowered the NO\textsubscript{X} (71%) and VOCS (80%) emission intensity between 2005 and 2015 (Wang et al., 2014). Japan was also the first country in the world to implement fuel efficiency standards for heavy-duty vehicles. South Korea has gradually intensified its vehicle emission standards to the level of the United States and the European Union. South Korea adopted Low Emission Vehicle standards (LEV II, 2004–2015) for gasoline-fueled vehicles, similar to the federal light duty vehicle Tier 2 criteria. For diesel vehicles, Euro 4-5-6 regulations were introduced starting in 2007, 2009 and 2014, respectively, while emissions standards were equivalent with Euro 3 in 2004 (Wang et al., 2014).

In 2014, diesel-powered cars accounted for about 3% of total auto sales in the United States, which is considerably lower than the 50% in Europe (US-EPA, 2015). In the United States, on-road transport contributes to 41% and 19% of total NO\textsubscript{X} and VOCS emissions between 2004 and 2015. Diesel-powered motor vehicles account for about 3% of the fleet, but they account for about 50% of NO\textsubscript{X} emissions from road transport, and gasoline-powered motor vehicles contribute to 32% (US-EPA, 2015). McDonald et al. (2018) also found that VOCS from vehicles accounted for 20% of freshly emitted VOCS in urban areas (gasoline exhaust: 19%; diesel exhaust: 1%). In Canada, on-road transport contributes to 27% and 10% of total NO\textsubscript{X} and VOCS emissions. In the four European countries (France, Germany, Italy and Spain), the on-road transport sector is the largest contributor to NO\textsubscript{X} emissions (40–55%) and represents 8–15% of VOCS emissions. In the United Kingdom, road transport accounted for 33% and 11% of NO\textsubscript{X} and VOCS emissions, and diesel vehicles contribute to 35% of NO\textsubscript{X} from transport (DEFRA, 2020). At urban stations, 80% of the NO\textsubscript{2} concentration originated as NO\textsubscript{X} emissions from road transport (DEFRA, 2020). In Japan and South Korea, road transport contributes to 25–35% of total NO\textsubscript{X} and 9–10% of VOCS emissions, respectively between 2005 and 2014. In South Korea, despite diesel motor vehicles represent 26% of total vehicles, they account for 75% of NO\textsubscript{X} emissions from on-road transport (Kim and Lee, 2011). Therefore, to reduce the emissions from motor vehicles, Natural Gas Vehicles are being introduced to replace diesel vehicles. Compared to diesel-powered motor vehicles, the Compressed Natural Gas vehicles reduce by 62% and 35% the NO\textsubscript{X} and VOCS emissions (Kim and Lee, 2011).

4.3. The ozone trends in cities

The annual mean of background O\textsubscript{3} ranged from 20 to 30 ppb, typical of concentrations recorded in cities e.g. over the United States and Europe (Sicard et al., 2013; Jaffe et al., 2018). In this study, the annual mean of daily O\textsubscript{3} concentrations increased by 0.41 ppb year\textsuperscript{-1} on average at 74% of 779 urban stations between 2005 and 2014, and decreased by 0.18 ppb year\textsuperscript{-1} at 65% of 29 urban stations in the United Kingdom. The O\textsubscript{3} baseline level is rising in the cities in Europe, United States, Japan and South Korea from 2000 (Paoletti et al., 2014; Simon et al., 2015; Sicard et al., 2016a; Fleming et al., 2018; Lefohn et al., 2018). Between 1995 and 2014, the background O\textsubscript{3} levels increased by on average 0.31 ppb year\textsuperscript{-1} in cities in Canada, Germany, Japan and Spain while a slight increase (+0.09 ppb year\textsuperscript{-1}) was observed in the United States (Sicard et al., 2018). In Japan, the surface O\textsubscript{3} concentrations increased by 0.31 ppb year\textsuperscript{-1} in Tokyo; 0.22 ppb year\textsuperscript{-1} in Nagoya and 0.37 ppb year\textsuperscript{-1} in Osaka between 1990 and 2010 (Akimoto et al., 2015), and by 0.68 ppb year\textsuperscript{-1} in Seoul (South Korea) from 2005 to 2014 (Jung et al., 2018; Seo et al., 2018). Kim and Lee (2018) confirmed the surface O\textsubscript{3} increase by 0.65 ppb per year in Seoul metropolitan area from 2000 to 2016.

As the mean O\textsubscript{3} concentrations are driven by the NO titration effect in urban areas (Vestreng et al., 2008; Colette et al., 2011; Escudero et al., 2014), the significant upward O\textsubscript{3} trends observed at most urban stations can be attributed to a reduced titration of O\textsubscript{3} by NO (Colette et al., 2011; Huszar et al., 2015; Sicard et al., 2018). In European cities, the relative contribution of on-road transport emissions to O\textsubscript{3} levels is 8–10% during winter and up to 15–24% during summer (Karamchandani et al., 2017; Mertens et al., 2019). The air pollution in the cities is mainly due to local urban emissions (Huszar et al., 2015). NO\textsubscript{X} originates mainly from motor vehicle traffic and the dominant anthropogenic sources of VOCS are vehicle exhaust, gasoline evaporation, and emissions from liquefied petroleum gas (Fanizza et al., 2014). Since the 2000s, the NO\textsubscript{X} and VOCS emissions from road transport have declined rapidly, mainly due to the implementation of stringent vehicle emission standards in Japan (Wang et al., 2014), the United States (Simon et al., 2015; Winkler et al., 2018), Canada (ECCC, 2016) and South Korea (Seo et al., 2018) as well as across the EU-28 (Winkler et al., 2018; EEA, 2019). Here, we investigated the effects of emissions changes from road transport, due to successive vehicles standards, on VOCS to NO\textsubscript{X} ratio between 2005 and 2014. Based on emissions data over the time period 2005–2014, the VOCS to NO\textsubscript{X} ratio increased by 16% in the United States and decreased by 2–3% in Canada and Japan, 20–25% in Germany and South Korea, 39% in Italy, 55–60% in France and Spain and by 80% in the United Kingdom. Such changes caused a shift towards VOC-limited regime for O\textsubscript{3} formation (Marr and Harley, 2002). Over the last decade, the reduction of anthropogenic emissions was insufficient to shift the chemical regimes from VOC-limited to NO\textsubscript{X}-limited conditions, leading to a predominant role of reduced O\textsubscript{3} titration by NO\textsubscript{X}. Indeed, the emission control strategy established by governments or local authorities relied more on NO\textsubscript{X} than on VOCS.

Inversely to other countries, the annual mean of daily O\textsubscript{3} concentrations decreased in the United Kingdom, associated to a significant ratio decrease. The significant decrease of NO\textsubscript{X} during the 2010s is so significant (DEFRA, 2020) that the conditions for O\textsubscript{3} formation can be considered as NO\textsubscript{X}-limited (Beckmann and Vautard, 2010). In cities, despite an increasing fleet size the vehicle emission regulations are able to reduce O\textsubscript{3} fluxes while background O\textsubscript{3} levels are increasing. An effective strategy to decrease current urban O\textsubscript{3} levels is to combine significant reductions in VOCS emissions with slight changes in NO\textsubscript{X} emissions (Im et al., 2011; Huszar et al., 2015). As the VOCS emissions from road transport are reduced over time, from 16% in 2005 to 8% in 2014, other VOCS sources become more important such as use of solvents. Effective control strategies targeting multiple VOCS sources are needed in cities (McDonald et al., 2018).

In this study we observed a change in the trends of daily O\textsubscript{3}
concentrations in Germany in 2010, with a decrease over 2005–2010 and an increase over 2010–2018, suggesting that O₃ production has recently transitioned or is transitioning from NOₓ-limited to VOC-limited chemistry. As a result, the reduction of anthropogenic emissions was effective in Germany until 2010, and continued NOₓ controls are increasing O₃ levels in cities. Between 2001 and 2014, Anav et al. (2019) showed that central-northern Europe (e.g. Northern Germany) and the United Kingdom were under a NOₓ-limited regime. On the weekends, O₃ showed positive sensitivity to NOₓ emissions in most areas (Fleming et al., 2018). The United Kingdom was under NOₓ-limited conditions for O₃ formation all days of the week, while in Germany, Italy and the United States, we observed VOC-limited conditions during weekdays and NOₓ-limited conditions on the weekend. In Canada, Japan and Spain, weekend O₃ increases could turn to O₃ decreases as the chemical regime changed from VOC-limited to NOₓ-limited O₃ formation. Several studies reported that higher NOₓ reductions relative to VOCs on the weekends led to O₃ enhancement (Duncan et al., 2010; Pierce et al., 2010; Huryn and Gough, 2014; Fleming et al., 2018). For most sites in France and South Korea, the weekend O₃ concentrations did not decrease despite the NOₓ emissions reductions. Hence, the area is largely sensitive to VOCs emissions (Jin et al., 2012; Kim et al., 2013; Choi et al., 2014), and surface O₃ remediation efforts will have to focus on reducing VOCs relative to NOₓ (Huryn and Gough, 2014).

Further or inappropriate anthropogenic emissions control in Canada, Southern Europe, Japan, South Korea and the United States might result in increased background O₃ levels in urban areas (Bach et al., 2014; Querol et al., 2014; Markakis et al., 2014; Sicard et al., 2018). To mitigate O₃ levels in cities, under VOC-limited chemistry, the VOCs emissions need to be significantly reduced with slight changes in NOₓ emissions (Calfapietra et al., 2009; Im et al., 2011; Huszar et al., 2015). Importantly, the substantial reduction in NOₓ and VOCs emissions since the early 1990s is accompanied by a high reduction in O₃ peaks and 98th percentiles (Sicard et al., 2013, 2018; de Foy et al., 2020). In the United States, hourly O₃ peaks declined by 1–13% from 2008 to 2018 (Collet et al., 2014). In Southern Europe, a significant reduction in the amplitude of peak O₃ concentrations (98th percentile, -7.4%; hourly peak, -12.5%) was found at 73 urban stations between 2000 and 2010 (Sicard et al., 2013).

4.4. The ozone weekend effect over time

The O₃ weekend effect was not observed at rural stations, as previously reported (Beany and Gough, 2002; Sadanaga et al., 2012; Huryn and Gough, 2014). In all urban stations, the mean O₃ concentration on the weekend was 12% higher than on weekdays. A maximum O₃ level during the weekend, in particular on Sunday, was previously observed in the United States (e.g. Atkinson-Palombo et al., 2006; Murphy et al., 2007; Blanchard et al., 2008; Wolff et al., 2013), Europe (e.g. Pont and Fontan, 2001; Schipa et al., 2009; Castell-Balaguer et al., 2012) and Asia (Tang et al., 2008; Sadanaga et al., 2012). A weekend-weekday O₃ difference of 8% was reported in Southern Italy in 2005 (Schipa et al., 2009), of 5–10% in a coastal town at the eastern coastline of Greece over 1996–2005 (Riga-Karandasios et al., 2006) and of 7–21% in Eastern Spain over 2005–2008 (Castell-Balaguer et al., 2012), which is consistent with our findings for the Mediterranean area (Italy: 5–13%; Spain: 5–19%). In Tokyo, an average weekend-weekday difference of 13–30% was found from 2005 to 2008 (Sadanaga et al., 2012). In California, the average weekday to weekend changes in O₃ were in the range of +10% between 2008 and 2010 (Wolff et al., 2013).

Based on the literature, the main causes of the higher O₃ concentrations in cities, under VOC-limited conditions, during the weekend are: 1) a reduction in NOₓ emissions from road traffic on weekends leading to a lower O₃ titration by NO (dominant cause); 2) a change in the timing of NOₓ emissions, emitted later in the day, allowing a more efficient O₃ formation; 3) as aerosol emissions are lower during weekends, the higher solar radiation favors O₃ formation; 4) an increase of O₃ precursors on the weekend from recreational, home and garden activities (Fujita et al., 2003; Heus et al., 2003; Jiménez et al., 2005; Atkinson-Palombo et al., 2006; Murphy et al., 2007; Tang et al., 2009; Sadanaga et al., 2012; Wolff et al., 2013). The NOₓ reduction during the weekend is higher than the VOCs reduction (Koo et al., 2012; Wolff et al., 2013). For example, Koo et al. (2012) reported a decline of NOₓ emissions by 24% on Saturdays and by 50% on Sundays, while the VOCs emissions decreased by 7% on Saturdays and by 20% on Sundays in Midwestern United States. The lowest levels of NO and NOₓ observed on late night of Sunday and early morning of Monday, due to reduced human activities, explain the higher O₃ concentrations on Monday compared to other weekdays (Fujita et al., 2003; Jiménez et al., 2005; Murphy et al., 2007; Tang et al., 2009; Wolff et al., 2013).

Ozone titration occurs under high NOₓ levels, in particular in winter (Sillman, 1999). The O₃ weekend effect is more pronounced during the cold period (VOC-limited regime) for most of the stations and is mainly attributed to the lower O₃ titration by NO as a consequence of the reduced local NOₓ emissions (Zou et al., 2019). In summer, moderate O₃ weekend effect occurred because O₃ formation is under NOₓ-limited conditions (Zou et al., 2019).

The weekend-weekday O₃ difference increased by on average 1.15% per year at urban stations in France, South Korea and the United Kingdom, where the number of urban stations that experienced no or low weekend effect declined over time, and decreased by on average 0.26% per year in Canada, Germany, Italy, Japan and the United States, with a lower number of stations reporting high weekend effect over time. Most of countries showed mixed upward and downward trends of the O₃ weekend effect depending on the O₃ formation regime and the extent to which the area is NOₓ-limited versus VOC-limited (Fleming et al., 2018). In France, South Korea and the United Kingdom, most urban stations showed a significant upward trend for O₃ weekend effect. In Spain, a slighter increase of the daily O₃ concentrations was observed during the weekend compared to weekdays, while in South Korea and France, the increase on Saturday and Sunday was higher than weekdays. In Canada, Germany, Italy, Japan and the United States, the daily O₃ concentrations increased during weekdays and decreased (or increased slighter than on weekdays) on Saturday and Sunday, therefore the O₃ weekend effect vanished, i.e. weekend-weekday O₃ difference decreased over time. The O₃ weekend effect mostly vanished in the United States as previously reported by Pierce et al. (2010) during an 18-year period (1988–2005) across the United States and by Wolff et al. (2013) comparing the two time periods 1997–1999 versus 2008–2010 in California.

Looking at the weekend-weekday O₃ difference, we did not find a significant difference among Europe (on av. 9–15%), the United States (on av. 8%) and Canada (on av. 12%). The O₃ weekend effect is similar in the United States and Italy (on av. 8–9%). Regarding the effects on O₃ weekend effect, it seems that the most important factor is not the size and composition of the vehicle fleet (diesel vs. gasoline) but the legislative emission standards for light-duty vehicles.

5. Conclusions

The analysis indicates that all urban stations showed higher O₃ concentrations on weekends than on weekdays while rural sites typically did not experience a weekend-weekday effect. From rural to urban areas, the O₃ formation shifted from NOₓ-limited to VOC-limited conditions. A comprehensive understanding of weekend-weekday O₃ changes over time allows one to gain deep insights into the true effectiveness of current control strategies for NOₓ pollution in order to develop future effective strategies. The COVID-19 lockdown measures led to an O₃ increase in European cities (+17%), about 10% higher than O₃ weekend effect, mainly due to higher and longer NOₓ reduction from road transport (Sicard et al., 2020). In cities, despite an increasing fleet size the vehicle emission regulations are effective to reduce O₃ peaks over time. However, an inappropriate reduction of O₃ precursors can
either produce no reduction or increase surface O3 in cities.

To date, most O3 control strategies rely upon reductions of the major precursors, i.e. NOx. During the last decade, investigated urban areas shifted toward a VOC-limited O3 formation regime due to the higher reductions of NOx emissions than VOCs, which has reduced the O3 titration effect by NO leading to higher ground-level O3 concentrations in cities and increased population exposure to O3. Therefore, the findings indicate that the national O3 control strategies are pushing many urban areas into a regime of maximum O3 formation, except in the United Kingdom. An effective strategy to decrease current urban O3 levels is to combine significant reductions in VOCs emissions with slight changes in NOx emissions (Im et al., 2011; Huszár et al., 2015).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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Credit author statement

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