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Ozone Trends in the United Kingdom over the Last 30 Years

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Received: 22 April 2020; Accepted: 19 May 2020; Published: 21 May 2020

Abstract: Previous work regarding the behaviour of ozone surface concentrations over many years in the United Kingdom had predicted that the frequency and severity of ozone episodes would become less marked in the future as a response to environmental regulations. The aim of this study is to extend these studies and compare the results with their predictions. The ozone data of 13 rural and six urban sites in the UK collected from the Department for Environment, Food and Rural Affairs over a period from 1992 to mid-2019 were used to investigate this behaviour. The yearly ozone exceedances (the number of hours that the ozone concentration exceeded the 50 ppbv limit) in the United Kingdom were found to have decreased over the last 30 years regardless of the type of site (rural or urban), showing that the adopted emission controls have so far been successful in the abatement of pollutant emissions. In the past three decades, the highest numbers of exceedances were reached in May regardless of the type of site. Furthermore, these episodes have become less frequent and less severe in recent years. In fact, the number of hours of exceedance is lower than that in previous decades, and it is almost constant throughout the week.

Keywords: ozone exceedance; urban site; rural site; human health

1. Introduction

There is an increasing interest in the study of the behaviour of tropospheric ozone concentrations over the past 30 years due to its role as a greenhouse gas with an estimated globally averaged radiative forcing of $0.4 \pm 0.2\ Wm^{-2}$, as a component of smog and as a primary tropospheric source of the hydroxyl radical (OH), which is a dominant tropospheric oxidant determining the lifetime of trace gases [1,2]. As a pollutant, ozone is corrosive and severely damaging to plants, trees and even buildings [3–5]. It has also been shown to have serious health effects on humans, particularly affecting the respiratory, cardiovascular and central nervous systems [6,7]. For example, it can cause irritation; it reduces the function of the lungs and promotes susceptibility to respiratory infections [8].

Tropospheric ozone is not directly emitted; it is formed as a secondary pollutant in the boundary layer by the reaction of primary pollutants (e.g., nitrogen dioxide and hydrocarbons) in the presence of sunlight. Because of this, its abatement depends on various parameters related to the emissions of these pollutants. Furthermore, ozone is transboundary [9], i.e., emissions from distant locations can contribute to its formation at a specific site; regulating the concentration of this pollutant requires international efforts. Ozone formation depends on the VOC–NO_X ratio [10]. In urban areas, ozone

concentrations are expected to rise due to its formation through NO_X photochemistry, which originates from road traffic exhaust, particularly primary diesel-fuelled vehicles at low speeds [11]. Ozone extremes have been found to have decreased during the last decade due to the substantial reduction of NO_X emissions in response to protocols [12–14]. Rural background ozone concentrations have been found to be higher than those in urban backgrounds [15] due to two well established reasons, one being the (northern hemispheric) ozone baseline and the second being the presence of more NO_X in urban sites actively scavenging ozone. A decrease in these pollutants would then lead urban sites to start behaving like their rural counterparts, and ozone concentrations would increase over the years as was found in [16].

Given that the formation of ozone depends on the concentration of the primary pollutants, a decrease in the concentration of pollutants like NO_X causes ozone to decrease under the NO_X-limited regime, while in cities (under the VOC-limited regime), a decrease in NO_X leads to an increase in ozone levels. The Tropospheric Ozone Assessment Report (TOAR) showed that there is no clear global pattern for surface ozone changes since 2000, with increasing and decreasing trends in both polluted and remote sites [17]. Environmental policies have already been established to decrease the emissions of these pollutants. In Europe, for example, the Directive on Ambient Air Quality and Cleaner Air (2008/50/EC), adopted in 2008, aims to assess and manage the concentration thresholds of pollutants by setting limits [18]. If these limits are exceeded then authorities are required to implement plans to decrease these concentrations, as well as establish sanctions. These limits have also been observed by individual countries, and local objectives have been established. In the case of ozone, the objective limit in Europe is an 8 h mean of 60 ppbv (not to be exceeded more than 25 times a year, averaged over three years) [19], whereas in the United Kingdom, this limit is 50 ppbv (not to be exceeded more than 10 times a year) [20].

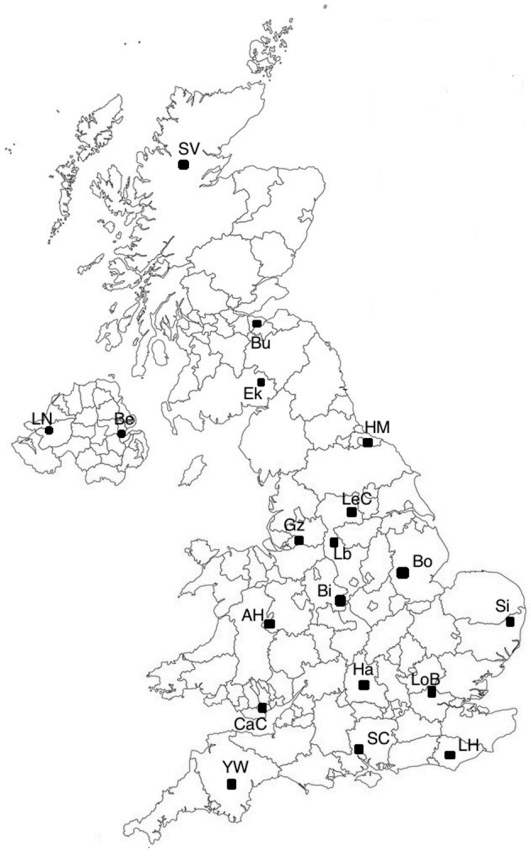
In order to understand what these policies have achieved in the reduction of the levels of the primary pollutants over the years, studies on ozone concentration trends in the United Kingdom have already been made [16,21–24]. This study is an update to these previous studies, addressing a more recent period and focusing on specific measuring sites throughout the UK. This study uses the freely available air quality data from the Department for Environment, Food and Rural Affairs (Defra) on selected rural and urban sites to address ozone exposure and understand its impact on human health. The aim of this study is to compare the results obtained in this work with the predictions made by the previous studies and determine if the implemented policies have succeeded or need to be amended. This study is thus a benchmark to indicate whether these policies have accomplished their objectives to date, or if pollution in the UK has worsened over the past three decades. Therefore, we analysed the ozone exceedances over the time period of 1992 to 2019 at 13 rural and six urban sites in the United Kingdom using the Defra ozone archive data. The decadal, yearly, monthly, daily and hourly variations of ozone exceedances are discussed in the study. We also analysed the magnitude and frequency of the most severe ozone episodes in rural and urban sites over the last 30 years.

2. Methodology

The source of the data for several measurement sites distributed throughout the UK was the Department for Environment, Food and Rural Affairs' (Defra's) Automatic Urban and Rural Network (AURN) data archive [25]. AURN is the UK's largest monitoring network comprising 150 sites and reporting hourly measurements of NO_X, SO_2, ozone, CO and particulate matter. We selected 13 rural and six urban sites in this study, which was based on the availability of the ozone data covering the last three decades (Figure 1). All these selected sites have an annual coverage of > 80% validated hourly data for ozone over the period from January 1992 to June 2019.

Ozone and NO_X measurements were carried out by UV photometry and chemiluminescence, respectively, following the guidelines of the European Committee for Standardisation [26]. Data were validated on an ongoing basis by manual review to exclude any errors due to instrument malfunctions or faulty calibrations [27]. The ozone and NO_X data (in $\mu g/m^3$ at 20 °C and 101.3 kPa) for each site

were archived at the National Air Quality Information Archive [25]. The uncertainty (expressed as a 95% confidence level) of the measurement datasets and sites was around 15% [28]. The analysis was centred around finding the number of hours the ozone concentration exceeded the 50 ppbv limit (also known as an exceedance) in every selected site for a period from January 1992 to June 2019. These dates were chosen based on the date when urban sites began reporting ozone concentrations (rural reports go back as far as 1986) and the date when this study was first started. A linear regression method was used to estimate the trends in magnitude. Statistical significance is based on a $p < 0.001$ and the trends are reported with 95% confidence internals. Data are then analysed by type of site in order to find the frequency and magnitude of ozone episodes, as well as how trends have changed over the past three decades. Furthermore, in order to establish the causes for these pollution episodes, a meteorological back-trajectory model derived from the NOAA on-line trajectory service was used [29].



Rural	Urban
Aston Hill (AH)	Belfast Centre (Be)
Bottesford (Bo)	Birmingham Centre (Bi)
Bush Estate (Bu)	Cardiff Centre (CaC)
Eskdatemuir (Ek)	Leeds Centre (LeC)
Glazebury (Gz)	London Bloomsbury (LoB)
Harwell (Ha)	Southampton Centre (SC)
High Muffles (HM)	
Ladybower (Lb)	
Lough Navar (LN)	
Lullington Heath (LH)	
Sibton (Si)	
Strathvaich (SV)	
Yaner Wood (YW)	

Figure 1. Distribution of the measurement sites (both rural and urban) in the UK.

3. Results and Discussion

3.1. Three-Decadal Trend of Ozone Mixing Ratios

The yearly averaged maximum ozone mixing ratios for 13 rural sites and six urban sites were found to have decreased gradually over the last 30 years (Figure 2) at rates of 1.0 ppbv/y (1.2%/y, $p < 0.001$) and 0.68 ppbv/y (0.9%/y, $p = 0.002$), respectively (the individual sites' maximum ozone and average ozone trends can be found in Table S1). The year-to-year ozone exceedance variability is highly dependent on meteorology, which makes it hard to separate the trends caused by any other effects (e.g., reduced precursor emissions) [30,31]. However, an increasing trend in yearly average ozone was found at a rate of 0.13 ppb/y (0.5%/y, $p < 0.001$) for rural sites and 0.20 ppb/y (1.1%/y, $p < 0.001$) for urban sites (Figure 2). The increases in yearly average ozone can be explained by a

decreasing trend in average NO_X mixing ratios at a rate of 0.22 ppb/y (3.7%/y, $p < 0.001$) for rural sites and 1.2 ppb/y (3.3%/y, $p < 0.001$) for urban sites, resulting in less NO_X scavenging [14,32,33], but the magnitude of the increasing trend at rural sites is smaller than those obtained at urban sites, due to the strong dependency of the concentrations of ozone on the northern hemispheric ozone baseline in rural areas [16]. Similar results for the decrease in maximum ozone concentration and increase in background ozone concentration are found in European sites for the period of 1995 to 2014 [34].

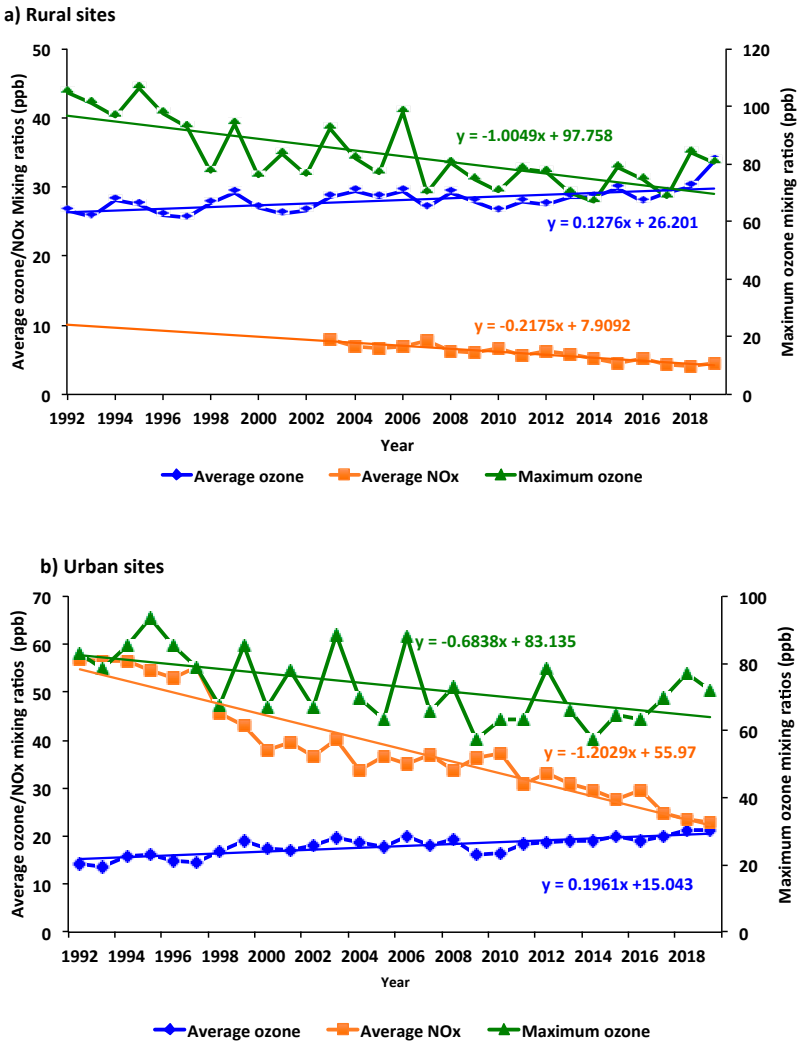


Figure 2. The mixing ratios of yearly average ozone, average NO_X and maximum ozone for (**a**) rural and (**b**) urban sites over the last 30 years. Note: The data points indicate the averages of all rural sites (**a**) and urban sites (**b**) of the yearly averaged data for the indicated time period. No available data for rural NO_X from 1992 to 2002. Trends are based on linear regression fitting with 95% confidence intervals and *p* values.

3.2. Yearly Variation of Ozone Exceedances over the Three Decades

The yearly total ozone exceedances for all rural sites show an overall decrease in the past three decades with the exceptions of the years 1992, 1995, 1999, 2003, 2006, 2008 and 2018 (Figure 3a). The weather conditions in the UK in the years 2003 [35,36] and 2006 [37] were particularly extreme, leading to a dramatic increase in summer pollution exceedances. The same applies for 1992 [38], 1995 [39] and 2018 [40], although the conditions were not as extreme in these years. This can be observed in Figure 3 where a high number of exceedances was reported for all these years. However, the high exceedances for 1999 and 2008 were not characterized by extreme weather conditions. The high

exceedances in 1999 are due to a particularly long episode at the end of July, explained by the persistent anticyclonic conditions during this period preventing the bad air conditions from dissipating [23]. The high exceedances in 2008 were mainly a result of the influence of the site Strathvaich, which reached 1000 h of exceedance in 2008 (Figure 3a), a quarter of the overall hours of exceedance from every site for this year. Most of these exceedances were reported in the spring months (e.g., March, April and May) rather than summer months (e.g., June, July and August) when ozone episodes are expected to happen (see Figure S1b). There is a typical spring-time ozone maximum characteristic of the northern hemispheric baseline air [41]. This cycle, shown to achieve a maximum between March and April, is also found in Strathvaich, which is due to an unclassical behavior of the baseline cycle. This means that the high number of exceedances in 2008 is due to this baseline cycle rather than any influence from ozone precursor emissions, and thus, the maximum achieved in 2008 in rural sites is not due to any severe pollution episodes.

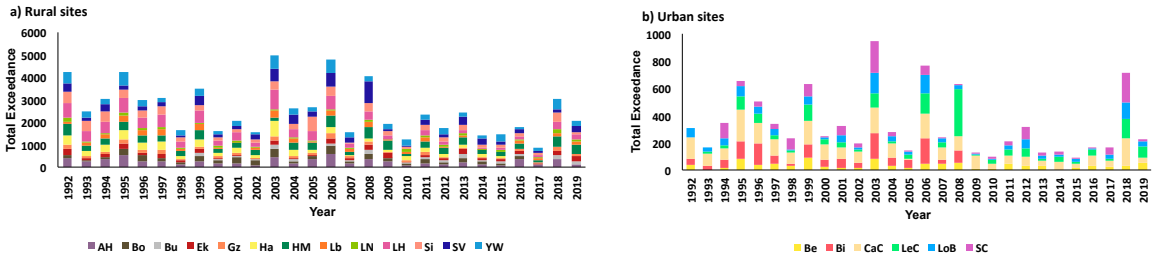


Figure 3. Yearly total exceedances of ozone in (**a**) rural and (**b**) urban sites over the last 30 years. Note that the total exceedance is the total number of hours the ozone concentration exceeded the 50 ppbv limit for (**a**) rural sites and (**b**) urban sites.

Similarly, for urban sites, the years with the highest exceedances were found to be 1995, 1999, 2003, 2006, 2008 and 2018 (see Figure 3b). In 1992, "peak years" were identified at rural sites, which had very few hours of exceedance at urban sites compared with the other years. The 2008 maximum in urban sites was also influenced by only one site, Leeds Centre, with over 350 h of exceedance (Figure 3b), more than half of the overall hours from each site for this particular year. In 2008, most of the total hours of exceedance in Leeds Centre were reported in May (see Figure S2b). During this month, two episodes took place, one lasting for 14 days, starting on the 5th and ending on the 18th, and another lasting for 8 days from the 20th to the 27th. The highest ozone mixing ratio was recorded on the 11th, reaching 86.6 ppbv. Both episodes were only seen at Cardiff Centre, but their durations were shorter, one lasting for 6 days and the other lasting for 3 days. Birmingham Centre also reported one of these episodes, one starting on the 5th and lasting for 6 days. The rest of the sites did not report either of the episodes; in fact, Belfast Centre, London Bloomsbury and Southampton Centre showed no consecutive exceedances in May. The high number of exceedances during this year is attributed to the episode that took place earlier in the month. A backward trajectory analysis was performed for the Birmingham Centre, Cardiff Centre and Leeds Centre sites in order to deduce the cause of this episode. The trajectories (see Figure S3), following a 96 h span on the day the highest mixing ratios were reached, pass through continental Europe prior to their arrival in the UK at 4 p.m. local time. Since the highest mixing ratio was recorded at Cardiff Centre, it can be assumed that this magnitude is due to the air parcel passing directly over London and transporting with it a high concentration of ozone precursors. It is likely that during this episode, there was an anticyclonic weather event and easterly flows, which transport pollution from continental Europe to the UK, favouring considerable ozone production [42].

The number of exceedances for the urban sites is much lower than that for the rural sites (Table 1) because in urban sites, NO_X emissions are more prevalent, which cause ozone scavenging, resulting in lower ozone mixing ratios. From the 1990s to the 2000s, the ozone exceedances increased. A decrease in NO_X from the 1990s to the 2000s (Figure 2) is likely to have led to less NO scavenging, and ozone is then

supposed to have accumulated, increasing the number of hours of exceedance. However, from the 2000s to the 2010s, the ozone exceedances decreased, possibly because of the reduction in ozone precursor emissions (e.g., anthropogenic VOCs) caused by the 1999 Gothenburg protocol, which reduced VOC emissions in the UK by ~40% from the 2000s to the 2010s [43]. Overall, the exceedances for both urban and rural sites were decreased by 27% and 30%, respectively, from the 1990s to the 2010s.

Table 1. The average exceedances over the last three decades.

Type of Site	1990s	2000s	2010s	Overall
Rural	1941	2141	1412	5494
Urban	532	647	376	1554

Note: Average values accounting for the number of sites of each type.

3.3. Seasonal Trend Variation of Ozone Exceedances over the Three Decades

The rural and urban sites follow a seasonal exceedances trend, with a summer high and winter low throughout the three decades (Figure 4). The ozone episodes depend on the weather conditions and, above all else, sunlight, since its formation is led by photolysis. It is then logical to assume that in a period in which sunlight is constant and its duration is long, a larger amount of ozone would be formed and accumulated, increasing its concentration. Furthermore, ozone episodes are linked with summer anticyclonic weather, leading to warm and sunny conditions with low wind speeds, lowering the dissipation rate of pollutants. However, this trend is not the same for each decade. The seasonal exceedances have all tended to peak in May, but the way in which the trend emerges is different throughout the years. For example, in the 1990s and 2000s, the exceedances dropped gradually after reaching the May maximum, but in the 2010s, the exceedances dropped to a minimum in June, increased in July and dropped again in August (Figure 4). These discrepancies can be explained by the variable weather conditions from year to year. For example, the June minimum in the 2010s decade is solely explained by the different weather conditions; among the summer months, June is characterized by lower pressure and temperature, and higher rainfall in the UK [44]. From 2011 to 2016, the weather was consistent, with frequent rain and low temperatures [45–50]. However, in 2017, a hot spell was recorded in mid-June, with temperatures reaching up to 28 °C towards the south east of England [51]. In 2018, a particularly heavy rainfall event was recorded resulting from Storm Hector [52], and in 2019, rainfall, around 2.5 times heavier than average, was recorded towards the East Midlands [53]. It is well established that rainfall and elevated wind speeds have a cleaning effect on pollution emissions [54], and thus, heavy rainfall would result in fewer ozone exceedances.

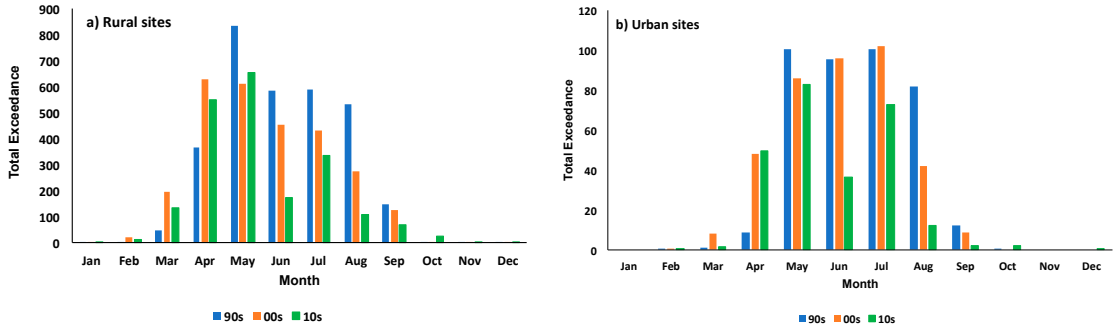


Figure 4. Seasonal total ozone exceedances in (**a**) rural and (**b**) urban sites averaged for the decades of the 1990s, 2000s and 2010s. Total exceedance is calculated as the total number of hours at an ozone concentration ≥ 50 ppbv for each month in a year, yearly averaged for each decade.

3.4. Daily Variations of Ozone Exceedances over the Three Decades

The diurnal plots for rural and urban sites (Figure 5) show that the highest ozone exceedances are found to have been reached at around 4 p.m. local time (mid-afternoon) throughout the three decades, and the lowest ozone exceedances were reported in the early mornings at around 7 a.m. to 8 a.m.; the cycle is very consistent with that in the similar study of Garland and Derwent [55]. This daily maximum is related to the influence of photochemical reactions with air pollutants, whereas the daily minimum is related to both ozone sinking by reaction with NO_2 [56] and ground deposition [57]. The night decadal exceedances up to 80 h for rural sites and up to 8 h for urban sites (Figure 5) can be explained by meteorological factors, i.e., the formation of an inversion layer at night trapping the ozone formed during the day or the wind speed and direction either facilitating the transport of ozone precursors or dispersing NO_2 and impeding its reaction with ozone. The decreased night-time exceedances for urban sites compared with rural sites can be explained by the sink reaction with NO_2, since this pollutant is more readily available in an urban background compared with in a rural background.

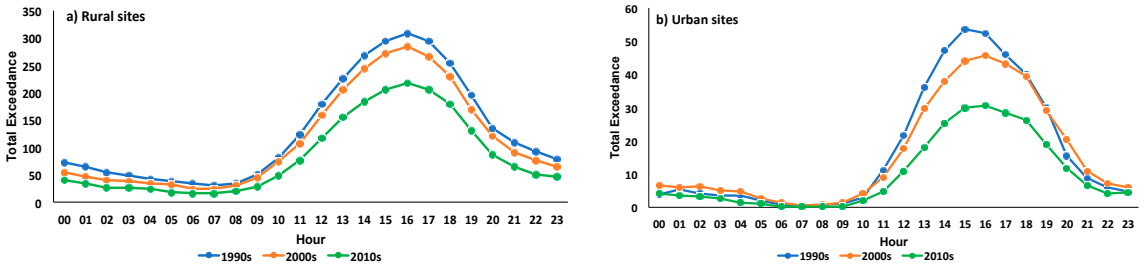


Figure 5. Hourly total ozone exceedances in (**a**) rural and (**b**) urban sites averaged for the decades of the 1990s, 2000s and 2010s. Total exceedance is calculated as the total number of hours at an ozone concentration ≥ 50 ppbv for each hour in a day, yearly averaged for each decade.

3.5. Weekly Variations of Ozone Exceedances over the Three Decades

Ozone exceedances for urban and rural sites follow a weekly pattern (Figure 6) since ozone formation depends on the temporal variations in precursor emissions. The trend is much the same as in previous studies [15,23], with the highest exceedances on weekends (e.g., on Saturday and Sunday) throughout the three decades. For the rural sites, there was a less marked variation in the exceedances, which remained constant throughout the whole week. However, for urban sites, the weekly variation is significant because of the strong variability in the emissions of precursors between the weekend and weekdays. The lower weekend NO_X concentrations due to lower traffic emissions reduce ozone scavenging, resulting in significantly higher weekend ozone concentrations than those on weekdays for urban sites [58].

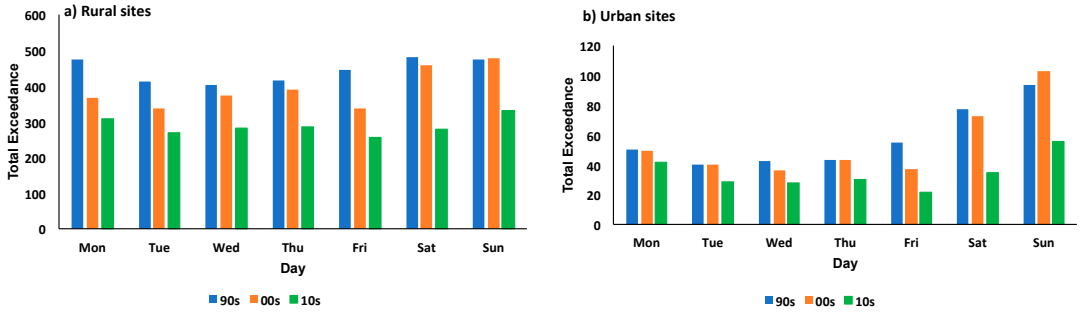


Figure 6. Daily total ozone exceedances in (**a**) rural and (**b**) urban sites averaged for the decades of the 1990s, 2000s and 2010s. Total exceedance is calculated as the total number of hours at an ozone concentration ≥ 50 ppbv for each day in a week, yearly averaged for each decade.

3.6. Frequency and Magnitude of Ozone Episodes

In order to determine the magnitude and frequency of the most severe ozone episodes in rural and urban sites, data were analysed for the years 1992, 1995, 1999, 2003, 2006, 2008, 2018 and 2019, years in which the numbers of exceedances were extremely high compared with those in other years. Exceedances were then considered for each summer month to determine the number of consecutive days ozone concentrations reached the limit of 50 ppbv.

The most severe ozone episodes in the rural and urban sites data (Table 2) show that the ozone concentrations with the greatest exceedances in May decreased over the years. For the urban sites, the number of consecutive days when exceedances were achieved were much lower compared with those for the rural sites. It is difficult to determine a single month and duration of episodes in this type of site due to the variable number of exceedances from one site to the other. After comparing the days in which each site reached a maximum ozone concentration for the longest period, it is deduced that three severe ozone episodes occurred in 2003, 2006 and 2019. This is because the highest concentrations reached in these years were far greater than those of previous years in every single site regardless of type. These events, defined as Case Studies 1–3, were evaluated for each site to assess their origin and magnitude (Table 3).

Table 2. Duration and magnitude of most severe episodes in rural and urban sites.

Year	Month	Duration (days)	Highest Mixing Ratios (ppb)	Site Type	Location
1992	May and June	16 and 9 + 9 [a]	125 and 125	Rural	Ha and Si
1995	August	17	133	Rural	YW
1995	May and August	6 and 3 + 4 [d]	104 and 102	Urban	LoB and CaC
1999	July	4	94	Urban	CaC
2003	August	8	108	Rural	Ha and LH
2003	August	7	116	Urban	SC
2006	July	4 + 7 [b]	114	Rural	LH
2006	July	4	101	Urban	CaC
2008	May	26 or 8 + 9 [c]	89	Rural	AH and YW
2008	May	27 or 9 + 10 [e]	90	Urban	CaC
2018	May	11	89	Rural	YW
2018	May	8	89	Urban	SC
2019	April	13	87	Rural	HM
2019	April	5	79	Urban	LeC

Note: [a] Two episodes in June lasting for 9 days each; [b] Two episodes in July lasting for 4 days and 7 days, respectively; [c] In some sites, a single long episode lasting for 26 days and in all other sites, two episodes lasting for 8 days and 9 days, respectively; [d] Two episodes in August lasting for 3 days and 4 days, respectively; [e] In some sites, a single long episode lasting for 27 days and in all other sites, two episodes lasting for 9 days and 10 days, respectively.

Case Study 1

The earliest weeks of August 2003 were particularly problematic in several European countries. A heat wave caused temperature records to be broken in France, Germany, Italy, Spain, the Netherlands and the UK. During August 9th and 10th, both England and Scotland broke their previous temperature records: 38.3 °C in England and 32.9 °C in Scotland [36]. This hot spell was characterized by anticyclonic conditions, where a high-pressure system moving around western Europe brought a hot, dry tropical continental air mass to the UK. This pattern occurred for much of the rest of the month [59]. Moderate to high concentrations of ozone were reported in most of the sites evaluated in this study. The highest concentrations were reported in Harwell (Ha), Lullington Heath (LH) and Southampton Centre (SC),

with mixing ratios of over 103 ppbv reached in the afternoon of August 9th on each site. The period for this episode spans 8 consecutive days on average, starting between the 3rd and 4th of August.

Table 3. Magnitude and duration of case studies.

Sites	Case Study 1 August 2003		Case Study 2 July 2006		Case Study 3 April 2019	
	Days	O_3 (ppbv)	Days	O_3 (ppbv)	Days	O_3 (ppbv)
AH	9	79.5	6	112	10	77.4
Bo	11	99.9	11	95.8	N/A	N/A
Bu	5	66.3	3	<50	6	74.1
Ek	5	74.4	5 + 5	89.7	16	78.2
Gz	6	88.7	5 + 7	95.8	6	73.5
Ha	14	108.0	5 + 8	105.0	N/A	N/A
HM	7	68.3	6 + 7	71.3	16	86.3
Lb	11	88.7	5 + 6	70.3	7	81.5
LN	5	55.0	2	86.6	16	78.2
LH	10	108.0	5 + 8	114.2	14	76.0
Si	11	79.5	6 + 14	89.7	5	77.9
SV	4	75.4	2 + 3	92.8	8	75.7
YW	10	89.7	2 + 7	99.9	8	70.4
Be	4	65.2	3	95.8	5	76.5
Bi	1	68.3	6	85.6	N/A	N/A
CaC	9	85.6	5	100.9	4	72.9
LeC	8	70.3	4	78.5	8	78.9
LoB	6	90.7	5	90.7	4	61.9
SC	10	116.2	3	76.4	3	54.6

Note: N/A—no available data.

Case Study 2

Another record-breaking heat wave struck the UK during the summer of 2006. It was found that July 2006 was the warmest month on record in the UK [60], which was characterized by warm, sunny days associated with high pressure systems over northern Europe. This month was at least 1 degree Celsius hotter than in the previous case study, and during the first four days of the month, temperatures exceeded 30 °C across England and Wales, with the next few days back to more normal conditions. On July 11th, temperatures increased again, and an anticyclonic weather system became established over the UK. This middle part of the month was at its warmest and sunniest [60]. During this period, the ozone mixing ratios were even higher than in the previous case study, with the highest mixing ratios recorded in Lullington Heath (LH) at 114.2 ppbv and very high concentrations recorded in Aston Hill (AH), Harwell (Ha) and Cardiff Centre (CaC), all above 100 ppbv. The analysis of Case Studies 1 and 2 suggests that ozone formation and accumulation are directly dependent on the weather conditions.

Case Study 3

This episode was not characterized by a heat wave, in contrast to the previous two case studies. Even though it was described as the hottest Easter Weekend in the UK according to the BBC [61], the temperatures hardly reached 25 °C all over the Kingdom, and by the 26th of April, storm Hannah

had already reached the UK and dissipated the bad weather conditions with winds of over 70 mph [62]. Moderate mixing ratios above 70 ppbv were recorded in all sites except for SC. The highest mixing ratio achieved was 86.3 ppbv in High Muffles (HM). It is evident that this case study also had the lowest recorded mixing ratios out of the three. However, the duration of this episode was much longer, lasting an average of 13 consecutive days on rural sites and 5 days on the urban ones.

We used the back-trajectories to determine from where the ozone precursors were coming and how they were affecting the sites in Case Study 3. The trajectories were followed by an incoming air parcel on a 96 h span towards three selected sites—Eskdatemuir (Ek), Lough Navar (LN) and Aston Hill (AH)—from April 17th to April 24th, arriving at 4 p.m. (local time), when the highest ozone mixing ratios were recorded for these sites. The sites chosen for this analysis were selected due to their location; an air parcel arriving in LN and AH (western sites) must travel through the south of the UK and possibly pass through other sites in this area. The same applies to Ek, since it is in the north of England. The trajectories for Ek and AH seem to have the same behaviour throughout the entire duration of the episode, passing through east Europe, the north of Germany and finally arriving in England, but on the 24th, the trajectory arriving in AH shifts suddenly from Europe to the Atlantic Ocean (see Figure S4). On the other hand, the trajectories arriving in LN change from day to day, coming in from France at the beginning of the episode, looping to the Atlantic Ocean on the 21st and then shifting again and arriving from central Europe on the day the highest ozone mixing ratios were reached and for the rest of the episode (see Figure S4). The highest ozone mixing ratio was recorded in HM on the 22nd at 8 p.m. local time. This site is on the Ek trajectory every single day of the episode. On the days prior to the 22nd, the trajectory loops over east and central Europe before arriving in Ek from a south-easterly direction (Figure S4). On the 22nd, the trajectories from both AH and Ek loop on each other from east Europe and separate over north Germany before arrival in the UK (see Figure S4). This means that the incoming air parcel on this day is the same for both sites, and when it finally arrives in HM, it has been carrying ozone precursors from four different countries. Two days later, the Ek trajectory changed its origin from east Europe to central Europe (Figure S4). It is then evident that the reason why this episode had such an effect on rural sites is purely the origin and transportation of ozone precursor emissions and not exclusively the weather conditions.

4. Conclusions

In this study, data from the Department of Environment, Food and Rural Affairs (Defra) was analysed in order to discuss the behaviour of ozone concentrations in the UK over a period from 1992 to mid-2019. This was done to explore how the frequency and magnitude of ozone episodes has changed over the years as a response to environmental policies to reduce pollutant emissions. It was found that maximum annual-mean ozone exceedances have decreased over the last three decades regardless of the type of site. The ozone exceedances in rural sites were found to be higher than those in the urban sites due to the lack of NO_X emissions to scavenge ozone. Ozone episodes have been shown to take place exclusively in the late spring and summer, when the sunlight is constant and the weather conditions prohibit pollution from dissipating. The diurnal variation of ozone exceedances shows a maximum during the mid-afternoon for both rural and urban sites. Additionally, ozone episodes usually are more frequent on the weekends due to a reduced removal effect of NO_X (emissions are lower on the weekends). It was also found that the day (in which ozone episodes are more frequent) has shifted from decade to decade due to the decrease in NO_X levels. In recent years, these episodes have become less marked, with exceedances remaining constant throughout the whole week regardless of the type of site. The adopted emission controls in both the UK and Europe have so far been successful in decreasing pollutant emissions. Ozone trends during the 2010s decade have become less visible, but further analyses must be carried out periodically with different methodologies in order to adopt and implement the policies to control the trend, be able to achieve the ozone objective limit of 50 ppbv and grant a better quality of life for both people and ecosystems.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4433/11/5/534/s1, Table S1: The annual average ozone maximum and the trend of maximum ozone and average ozone for the period of 1992–2019. Figure S1: Monthly ozone exceedances in rural sites for last three decades, (a) 1990s, (b) 2000s and (3) 2010s. Figure S2: Monthly ozone exceedances in urban sites for last three decades, (a) 1990s, (b) 2000s and (3) 2010s. Figure S3: Trajectories arriving in Birmingham Centre (Bi), Cardiff Centre (CaC) and Leeds Centre (LeC) at 4 pm (local time) on 11 May 2008. Figure S4: Trajectories arriving in Eskdatemuir (Ek), Aston Hill (AH) and Lough Navar (LN) at 4 pm (local time) for the period of 17 April to 24 April 2019.

Author Contributions: F.M.R.D. and M.A.H.K. analyzed the data and wrote the paper; U.V. and D.E.S. conceived and designed the project; B.M.A.S. and E.D.G.S. analyzed the data. All authors have read and agreed to the published version of the manuscript.

Funding: DES and MAHK thank Natural Environment Research Council (NERC), Bristol ChemLabS and Primary Science Teaching Trust under whose auspices various aspects of this work were funded.

Acknowledgments: We thank the Department for Environment, Food and Rural Affairs (Defra) for supporting UK monitoring network data and National Oceanic and Atmospheric Administration (NOAA) on-line trajectory service for providing meteorological back trajectories.

Conflicts of Interest: The authors declare no conflict of interest.

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