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Houston's rapid ozone increases: preconditions and geographic origins

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Abstract

Many of Houston's highest 8-h ozone (O_3) peaks are characterised by increases in concentrations of at least 40 ppb in 1 h, or 60 ppb in 2 h. These rapid increases are called non-typical O_3 changes (NTOCs). In 2004, the Texas Commission on Environmental Quality (TCEQ) developed a novel emissions control strategy aimed at eliminating NTOCs. The strategy limited routine and short-term emissions of ethene, propene, 1,3-butadiene and butene isomers, collectively called highly reactive volatile organic compounds (HRVOCs), which are released from petrochemical facilities. HRVOCs have been associated with NTOCs through field campaigns and modelling studies. This study analysed wind measurements and O_3, formaldehyde (HCHO) and sulfur dioxide (SO_2) concentrations from 2000 to 2011 at 25 ground monitors in Houston. NTOCs almost always occurred when monitors were downwind of petrochemical facilities. Rapid O_3 increases were associated with low wind speeds; 75 % of NTOCs occurred when the 3-h average wind speed preceding the event was less than 6.5 km h^{-1}. Statistically significant differences in HCHO concentrations were seen between days with and without NTOCs. Early afternoon HCHO concentrations were greater on NTOC days. In the morning before an observed NTOC event, however, there were no significant differences in HCHO concentrations between days with and without NTOCs. Hourly SO_2 concentrations also increased rapidly, exhibiting behaviour similar to NTOCs. Oftentimes, the SO_2 increases preceded a NTOC. These findings show that, despite the apparent success of targeted HRVOC emission controls, further restrictions may be needed to eliminate the remaining O_3 events.

Introduction

In 2004, the Texas Commission on Environmental Quality (TCEQ) proposed a novel emissions control strategy to address ozone (O_3) pollution in Houston.[1] This strategy placed limits on emissions of ethene, propene, 1,3-butadiene and butene isomers, collectively called highly reactive volatile organic compounds (HRVOCs), which are released from petrochemical facilities in the industrial ship channel region. The TCEQ's analysis of Houston's O_3 problem – detailed in their 2004 State Implementation Plan (SIP) – showed that many of the highest O_3 peaks were measured following brief periods of concentration increases greater than 40 ppb h^{-1} and sometimes greater than 100 ppb h^{-1}.[1] These large increases were associated with reactive plumes of HRVOC emissions measured by aircraft in several studies during the Texas Air Quality Study field campaign in 2000.[2–4] The TCEQ's proposed HRVOC emissions controls limited both routine emissions and short-term, or 'upset,' releases at facilities with the potential to emit more than ten tons of HRVOCs per year. Exempting all but the largest industrial facilities assumed that smaller HRVOC sources do not have a large effect on rapid O_3 production. The Environmental

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Protection Agency approved the TCEQ's SIP, and the emissions controls became Texas state law in 2005.

The 2004 SIP highlighted the significance of rapid O_3 increases to violations of the 1-h federal standard, but these increases also contribute greatly to violations of the 8-h O_3 standard. Many of Houston's highest 8-h O_3 peaks are characterised by sudden increases in concentrations of at least 40 ppb in 1 h, or 60 ppb in 2 h.[5] Measurements from 2000 to 2011 show that these increases, called non-typical O_3 changes (NTOCs), increase the likelihood of a monitor violating the 1997 0.08-ppm 8-h O_3 standard.[6] Nearly 60 % of days with NTOC measurements violated the 8-h O_3 standard, but just 1 % of typical O_3 days exceeded the federal limit.

The cause(s) of every NTOC is an open question, but evidence linking them to HRVOC emissions has accumulated since the TCEQ's 2004 SIP.[7–9] Speciated hydrocarbon measurements found ethene and propene among the most likely[10] VOCs to contribute significantly to rapid O_3 production. A recent study found that some chemical flares operate at combustion and destruction efficiencies lower than required by regulation, and that these flares are significant sources of alkenes.[11] Furthermore, it is known that large-scale, short-term HRVOC emissions from industrial sources occur often and with notable temporal variability in Houston.[12–17] It is these emissions, in addition to routine HRVOC emissions, that the TCEQ primarily targeted in 2004. Unfortunately, emission upsets are not predictable, and the emissions event database maintained by the TCEQ (http://www11.tceq.texas.gov/oce/eer/index.cfm, accessed 23 October 2012) contains reports from facilities that are often just best estimates of the VOC releases. At any single facility, HRVOC upsets are rare, and it has been difficult to link specific NTOCs to reported emissions upsets. Although HRVOC emissions and NTOCs have received increased attention, there has not been a comprehensive effort to look at all NTOCs over a long time frame. The studies mentioned above have generally had short windows of data collection corresponding with field campaigns. The limited spatial and temporal scales of most field campaigns reduce the chance of measuring a NTOC and tracing it back to a particular emission event.

The number of ground monitors in Houston has increased since the early 2000s when the NTOC phenomenon was first observed. For example, there were 246 NTOCs measured in 2003, and the largest 1-h increase was 156 ppb. By 2011, the number of NTOCs dropped to 39 with a maximum 1-h O_3 increase of 72 ppb. Despite this increase in spatial coverage, the frequency and magnitude of NTOCs have declined markedly. The most dramatic declines occurred just after the TCEQ implemented targeted HRVOC controls for short-term and routine emissions. NO_x and mobile source reductions also took effect during this period, however, so it is difficult to disentangle the benefits directly attributable to the HRVOC controls. Notwithstanding the improvements, NTOCs still occur in Houston at monitors that have yet to achieve the 2008 0.075-ppm 8-h O_3 standard. One possible explanation is that the smaller industrial facilities that were exempted from the 2004 HRVOC limits do, in fact, contribute to the NTOC problem. Other potential causes could be meteorological. Air mass recirculation, a stalled sea breeze and entrainment from a rapidly rising planetary boundary layer are all possible explanations for NTOCs. A closer examination of the problem and the factors that lead to NTOC formation is required.

This work considers local meteorological conditions and ambient pollutant concentrations in an attempt to determine the necessary preconditions for the large hourly O_3 increases found in the observational record. The data used in this study date back to 2000, which provides a wide time frame during a dynamic period in which aggressive emission control strategies were implemented. This provides built-in observational sensitivity experiments to help

understand how varying meteorological conditions and industrial emissions affect NTOCs. Using over ten years of measurement data, we have identified candidate days with unusually large hourly O_3 increases. We combine wind field measurements with pollutant observations from a dense network of ground station monitors to determine the necessary conditions and likely geographic origins of the NTOCs. Our analysis examines the assumption made in the TCEQ's 2004 SIP – that HRVOC emissions are responsible for many NTOCs and O_3 violations. Ultimately, a description of the conditions that can lead to NTOCs may help environmental regulators develop effective control strategies that efficiently bring ambient O_3 levels in Houston below the federal standard.

Experimental

Twenty-five ground station monitors were used in this study, and they are listed in Table 1 with their official names, four-letter abbreviation, TCEQ identification number, Aerometric Information Retrieval System (AIRS) number and measured parameters. These are the same monitors that were used in the TCEQ's 2010 SIP. Monitor locations are shown in Fig. 1. Each of these monitors measures a variety of chemical (e.g. O_3, SO_2) and meteorological parameters (e.g. wind speed, wind direction) with a time resolution of 1 h. The red star marks the Sam Houston Tollway Bridge, which is approximately the centre of the ship channel region. These data are maintained by the TCEQ and are available publicly (http://www.tceq.texas.gov/airquality/monops/hourly_data.html, accessed 13 January 2013). The data record spans 2000–2011, although not all monitors have data that begins in 2000.

Hourly HCHO concentrations for three monitors are available for select days from 2003 to 2011. HCHO values were reported from 0600 to 0800 and 1300 to 1500 hours. These data were obtained from the EPA's Air Quality System (http://www.epa.gov/ttn/airs/airsaqs/, accessed 1 April 2012), which is a repository for ambient air quality data.

A NTOC is defined as an increase in O_3 concentrations of at least 40 ppb in 1 h, or 60 ppb in 2 h. This definition is consistent with our earlier work on NTOCs.[5,6]

Results

This study analysed local wind conditions and concentrations of O_3, HCHO and SO_2. The following subsections – meteorology, HCHO and SO_2 – show our analysis of each parameter and how it relates to O_3 and NTOCs.

Meteorological analysis

Couzo et al.[6] found that most NTOCs are measured at monitors near the ship channel. In Fig. 2, we expand on that finding. These plots show the wind speed and direction that were measured during NTOCs between 2000 and 2011. Each black marker shows a unique event, so the figure also shows the number of NTOCs that were observed at each monitor. These six monitors (CLIN, HALC, HCQA, MACP, TXCT and WALV) were chosen because they represent a full range of geographic diversity in Houston. CLIN is on the western end of the ship channel and near downtown, WALV is north-east of the ship channel and far from downtown, HALC is north-west of the ship channel and north of downtown, HCQA and MACP are southwest of the ship channel and south of downtown and TXCT is south of the ship channel and far from downtown. Although there is some scatter in each plot, they generally show strong preference for a narrow range of wind directions. The black markers are clustered in the direction of the ship channel, which indicates NTOCs almost always occur when winds are blowing from Houston's industrial centre to the monitor. The red arrow points toward the red star in Fig. 1 and, thus, shows the direction of the ship channel relative to each monitor. The grey markers in Fig. 2 show the wind speed and direction that

were measured at the time of peak 1-h O_3 levels on all days. Only data from April to October is shown here. These data do not cluster in the direction of the ship channel meaning that peak O_3 comes from a diversity of directions. In some cases (e.g. HALC and HCQA), peak O_3 levels often occur when the monitor is upwind of the ship channel.

The histograms in Fig. 2 show the distribution of peak 1-h O_3 levels on typical days (grey) and NTOC days (black) for all available data during the O_3 season (April–October) from 2000 to 2011. The distributions show that peak 1-h O_3 levels on NTOC days are shifted towards higher concentrations.

Meteorology is also a critical component of O_3 formation in Houston. The meteorological conditions necessary for high O_3 levels are well known. They have been described in detail and are characterised at surface monitors by low wind speeds and a rotational wind field.[14,18,19] Despite the unquestionable importance of meteorology on O_3 formation, an analysis of winds and 8-h O_3 violations in Houston determined that O_3-conducive meteorological conditions are necessary but insufficient to[20] produce high O_3 levels and NTOCs.

NTOCs tend to happen under stagnant or near-stagnant conditions. This is also true for typical high O_3 levels. Distributions of 3-h average wind speed are shown in Fig. 3 for NTOC days (left), days that violated the 1997 0.08-ppm 8-h O_3 standard (middle) and days that did not violate the standard (right). To obtain this average, we used the wind speed from the hour during which peak O_3 levels was observed and measurements from the previous 2 h. A 3-h average was used because it has the effect of smoothing out the hour-to-hour variability and longer averages are a poor indicator of local effects. It is clear that NTOCs occur on days with low wind speeds, lower even than typical high O_3 level days. The 25th, 50th and 75th percentile 3-h average wind speeds preceding NTOCs are 3.4, 4.6 and 6.3 km h^{-1}. For typical days that violate the 1997 O_3 standard, those values are 5.9, 8.3 and 12.7 km h^{-1}. Days that did not reach the 0.08-ppm standard generally had wind speeds that were slightly lower than violation days. The 25th, 50th and 75th percentile values for non-violation days were 5.4, 7.1 and 10.8 km h^{-1}.

Fig. 4 shows, on a fractional basis, the time of day when all NTOCs and peak 1-h O_3 levles are measured for all monitors. NTOCs generally occur in the late morning and into the early afternoon. NTOCs peak at 0900 and 1000 hours with 78 % occurring before 1300 hours. Peak 1-h O_3 levels occur later in the day; 1400 hours is the most frequent time for peak 1-h O_3 levels. More than half (56 %) of all peak 1-h O_3 levels occur at 1200 hours or later.

Formaldehyde analysis

HCHO is a known marker for photochemical oxidation reactions that lead to O_3 formation; it is also, itself, a precursor to O_3. Oxidation of HRVOCs produces substantial yields of HCHO. For example, each ethene molecule that is attacked by the hydroxyl radical ($OH^{\bullet}$) produces 1.44 molecules of HCHO.[21] Two monitors had 1-h HCHO measurements on NTOC days –CLIN and DRPK. For each monitor, HCHO measurements were separated into two groups according to whether they occurred before or after the measured NTOC. HCHO concentrations were greater following a NTOC. The Mann–Whitney non-parametric statistical test was used to determine whether the differences between HCHO values before and after a NTOC are statistically significant. For both monitors, these differences were statistically significant (CLIN: U =2, $P \ll 0.01$; DRPK: U =36, $P \ll 0.01$). This is not a surprising finding because most NTOCs occur in the late morning. It is expected that HCHO concentrations will rise throughout the photochemical day because it is a product of VOC oxidation. Elevated HCHO concentrations in the morning, though, could be indicative of primary emissions.

Next, we compared distributions of hourly HCHO values on typical and NTOC days at each monitor again using the Mann–Whitney non-parametric test. The test results are shown in Fig. 5. Distributions of 1-h HCHO measurements for NTOC days are shown in black and the distributions for typical O_3 level days are shown in grey. For each monitor, HCHO measurements did not differ significantly in the morning. Results of the Mann–Whitney test show statistical significance in the afternoon, however. At CLIN (Fig. 5a), HCHO concentrations on NTOC days are significantly greater at 1300 (U =3, P =0.032) and 1400 hours (U =39, P =0.012). At DRPK (Fig. 5b), HCHO concentrations on NTOC days are significantly greater at 1400 (U=80.5, P =0.003) and 1500 hours (U =54, P =0.014).

We also looked at O_3 and HCHO levels on specific NTOC days. Fig. 6a shows measured time series data at the CLIN monitor on 23 October 2003. The black line shows 1-h O_3 concentrations, and the black dots show 1-h HCHO values. The shaded regions extend up to the 90th (dark grey) and 95th percentile (light grey) of HCHO concentrations for all typical O_3 level days. In Fig. 6a, there is a 156-ppb increase in O_3 at 1100 hours. Before this NTOC, the morning HCHO measurements were less than the 90th (0600 hours) and 95th percentile (0700 hours) of HCHO concentrations. After the NTOC, though, 1-h HCHO values are well outside these distributions reaching 27 ppb at 1300 hours These results are consistent with Fig. 5a.

Fig. 6b shows measured time series data at the DRPK monitor on 28 June 2006. This NTOC (40-ppb increase) occurred at 0700 hours, then 1 h later, the HCHO concentration was 24 ppb, which is well above the 95th percentile for all DRPK HCHO measurements at that hour. HCHO values for all other times, however, are within shaded regions. Taken together, Figs 5 and 6 indicate that HCHO concentrations rise substantially for a short period following a NTOC, and that this rise is significantly greater than the routine diurnal HCHO cycle.

Sulfur dioxide analysis

Many SO_2 measurements exhibit behaviour that looks similar to NTOCs. That is, concentrations of SO_2 increase dramatically from one hour to the next. These non-typical SO_2 increases often occur just before or at the exact moment a NTOC is measured. Fig. 7 shows such an instance at the HROC monitor on 9 July 2005. The figure shows an O_3 (black line) increase of 52 ppb at 1100 hours. During the same hour, SO_2 (red line) values increase from 8.7 to 35.9 ppb. The shaded regions extend up to the 90th (dark grey) and 95th percentile (light grey) of SO_2 concentrations on all typical O_3 level days. At the time of the sudden increase in pollutant concentrations, the SO_2 value is well above the 95th percentile for all HROC SO_2 measurements at that hour. Also in Fig. 7, we show the wind measurements that were taken at HROC on 9 July 2005. The wind barbs along the top of the figure show wind speed and direction for each hour. Half barbs indicate 5 km h^{-1} and full barbs indicate 10 km h^{-1} winds; the barbs are additive. Circles indicate stagnant conditions. Leading up to the NTOC, the winds were blowing from the SE direction and with low speeds. Just before the O_3 and SO_2 increase, the winds shift and blow due west. Interestingly, the industrial ship channel is east of the HROC monitor. Thus, the NTOC and sudden increase in SO_2 occurred when the monitor was down-wind of Houston’s industrial region.

Fig. 7 is not an isolated occurrence; SO_2 concentrations above the 95th percentile preceded 209 NTOCs out of a total of 367 NTOCs at the six monitors that measure both O_3 and SO_2. Fig. 8 shows this analysis for these six monitors. The height of the black bars shows the number of NTOCs that were measured at each monitor. The height of the grey bars shows the number of those NTOCs that had an SO_2 concentration above the 95th percentile up to 5 h before the NTOC. With the exception of CLIN, a majority of NTOCs were preceded by

large SO_2 values. At HROC, for example, 55 out of 72 NTOCs were preceded by a significant increase in SO_2 concentrations.

Discussion

This study benefitted from a long, continuous measurement record from a large number of monitoring stations across Houston. During this period, 2000–2011, there have been significant changes to emissions in the region, and much progress has been made in lowering O_3 concentrations. Fig. 9 shows design values (grey markers) for each monitor from 2002–2011. (A monitor's design value is the 3-year average of the annual fourth highest daily maximum 8-h average O_3 level as defined by Title 40, Section 50.15, Appendix P of the Code of Federal Regulations, 73 FR 16511, 27 March 2008) Beginning in 2007, design values began to decline, and, by 2009, all monitors were below the 0.08-ppm 8-h O_3 federal standard (dashed line). Emissions reductions described in the TCEQ's 2004 SIP, especially the HRVOC restrictions, likely played a substantial part in the lower O_3 design values.

In Vizuete et al.,[5] we described a method for determining the influence of NTOCs on the attainment process by removing or 'filtering' NTOC days from the design value calculation. The black markers in Fig. 9 show the filtered design values for each monitor. Looking ahead to the 2008 0.075-ppm standard (solid line), removing NTOC days brings ten additional monitors into attainment. The individual monitors are not labelled in Fig. 9, but the monitors with design values below 0.075 ppm in 2011 only after filtering are CLIN, CNR2, HCHV, HLAA, HTCA, HWAA, LYNF, SBFP, SHWH and TXCT. Thus, the NTOC phenomenon is still a policy-relevant phenomenon despite their reduced frequency and magnitude.

With that in mind, this study has characterised some major differences between typical O_3 level days and NTOC days. We have described meteorological preconditions and geographic origins, and found evidence for heightened photochemical O_3 production on NTOC days.

Most NTOCs occur when monitors are directly downwind of the industrial ship channel. Fig. 2 shows that air masses originating in the ship channel produce NTOCs that are measured at the monitors. The NTOCs are usually measured in the late morning before the meteorological recirculation that is commonly seen on high O_3 level days. In fact, peak O_3 levels generally occur later in the day and are often measured when the winds are not blowing from the ship channel to the monitor. This indicates that some of the processes that lead to NTOC formation do not fit perfectly within the accepted paradigm of typical high O_3 level formation. That paradigm holds that high O_3 levels typically occur in the afternoon following the recirculation of photochemically aged air masses. NTOC formation in the late morning is potentially due to the accumulation of O_3 precursors overnight, although 1-h automated gas chromatograph data (not shown) did not reveal meaningful differences of HRVOC concentrations on NTOC days compared to typical O_3 level days. Another plausible explanation for late morning NTOC formation is entrainment from the free troposphere as the planetary boundary layer rises. This finding merits further study and will be a focus of a future 3D modelling simulation.

We have suggested the importance of industrial HRVOC emissions previously,[5,6] and the results presented here provide evidence for that position. Short-term releases of HRVOCs are known to occur in the ship channel,[12–17] and modelling has [22,23] shown that these releases can lead to rapid O_3 increases. Given the low wind speeds observed on NTOC days, there is sufficient time for these HRVOC releases to produce the observed O_3 increases.

Even routine emissions could accumulate in sufficient quantity as they are oxidised and slowly advected to the monitors.

Fig. 5 shows statistically significant increases of HCHO concentration in the hours immediately following NTOCs. This suggests that the increases in O_3 levels on some NTOC days are due at least in part to heightened chemical production above usual levels. Although there is some debate about the exact ratio of primary to secondary HCHO production in Houston,[24–28] the nature of the HCHO has little bearing on the conclusion that the NTOCs are the result of chemical production. If the HCHO is primary, this is direct evidence for an emission event as HCHO could be emitted, for example, from an overactive and inefficient industrial process flare. If the HCHO is secondary, this is indirect evidence for the importance of HRVOC emissions because both elevated secondary HCHO and O_3 levels have been found in industrial plumes.

We also found interesting SO_2 behaviour on most NTOC days, as exhibited in Fig. 7. High SO_2 concentrations have been used as a marker for certain types of industrial activity,[29] especially combustion processes and fluidised catalytic cracking units. In fact, a previous study found that a large industrial source in Texas City co-emitted large amounts of SO_2 and HCHO.[30] That many NTOCs are preceded by high concentrations of SO_2 and followed by high HCHO values points to industrial emissions as an important variable in NTOC formation.

This study provides further evidence that NTOC formation is different from typical high O_3 levels in Houston. In their 2004 SIP, the TCEQ proposed controlling routine and short-term HRVOC emissions from industrial facilities with the potential to release more than ten tons of HRVOCs per year. The frequency and magnitude of NTOCs has decreased dramatically since the emission controls took effect, but NTOCs still occur at some monitors. In fact, ten monitors have 2011 design values below the federal 0.075-ppb 8-h O_3 standard once NTOCs are filtered from the calculation. The industrial ship channel is consistently upwind of these O_3 events, so it is possible that smaller emission sources not affected by the HRVOC limits are contributing to the phenomenon, especially, given the large number of petrochemical facilities in the region. Another round of targeted emission controls may further reduce the frequency of NTOCs and continue the downward trend in Houston's O_3 design values.

Acknowledgments

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Environmental context

Ozone pollution in Houston, Texas, has been a public health concern for decades. Unusually large hourly changes in observed ozone concentrations have been correlated with a greater likelihood of violating the federal air quality standard. We investigate the geographic and chemical origins of these large hourly increases, which should help regulators better control ozone violations.

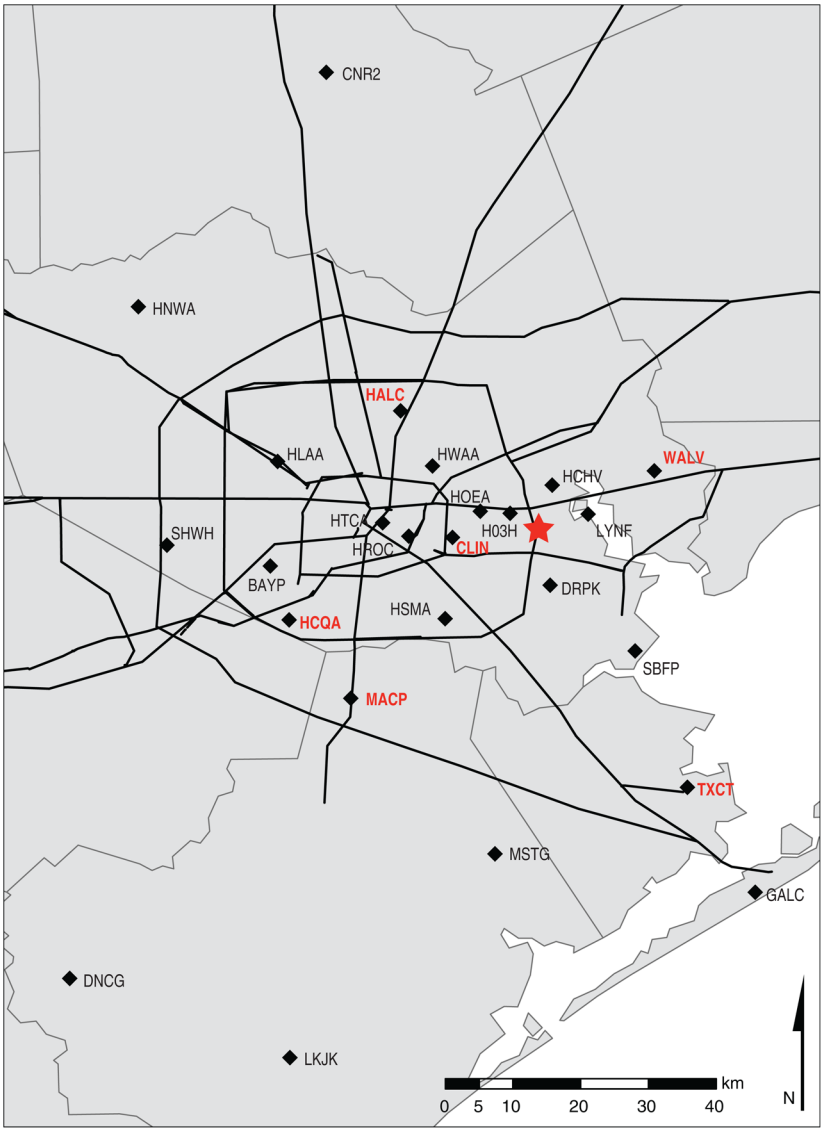

Fig. 1.

The locations and abbreviations of the 25 ground monitoring stations used in this study. The ship channel region is marked with a red star. The six monitors shown in Fig. 2 are labelled with red text.

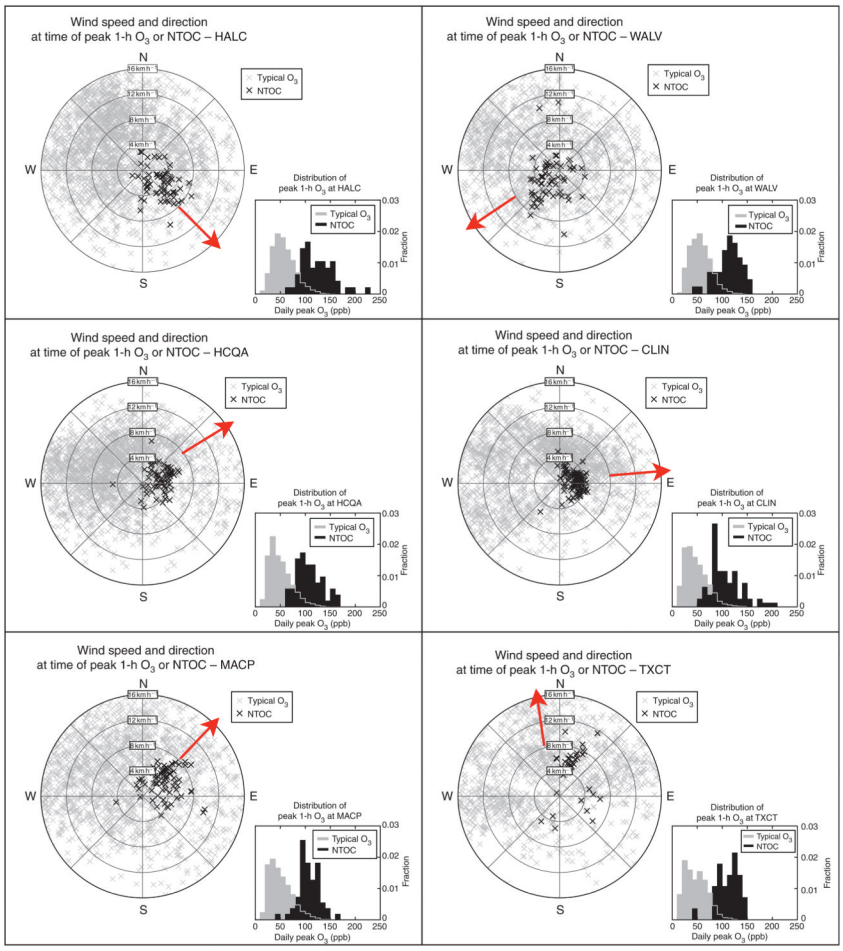

Fig. 2.

Wind speed, direction and peak 1-h O_3 levels on all typical and non-typical O_3 change (NTOC) days for six monitors (see Fig. 1 for location). The grey markers in the radar plot give the wind speed and direction at the time the peak 1-h O_3 level was measured on typical days. The black markers give the wind speed and direction at the time a NTOC was measured. The red arrow points toward the red star (ship channel marker) in Fig. 1. The histogram shows the distribution of peak 1-h O_3 levels on typical days (grey) and NTOC days (black). All available data during the O_3 season (April–October) from 2000 to 2011 is included in this figure.

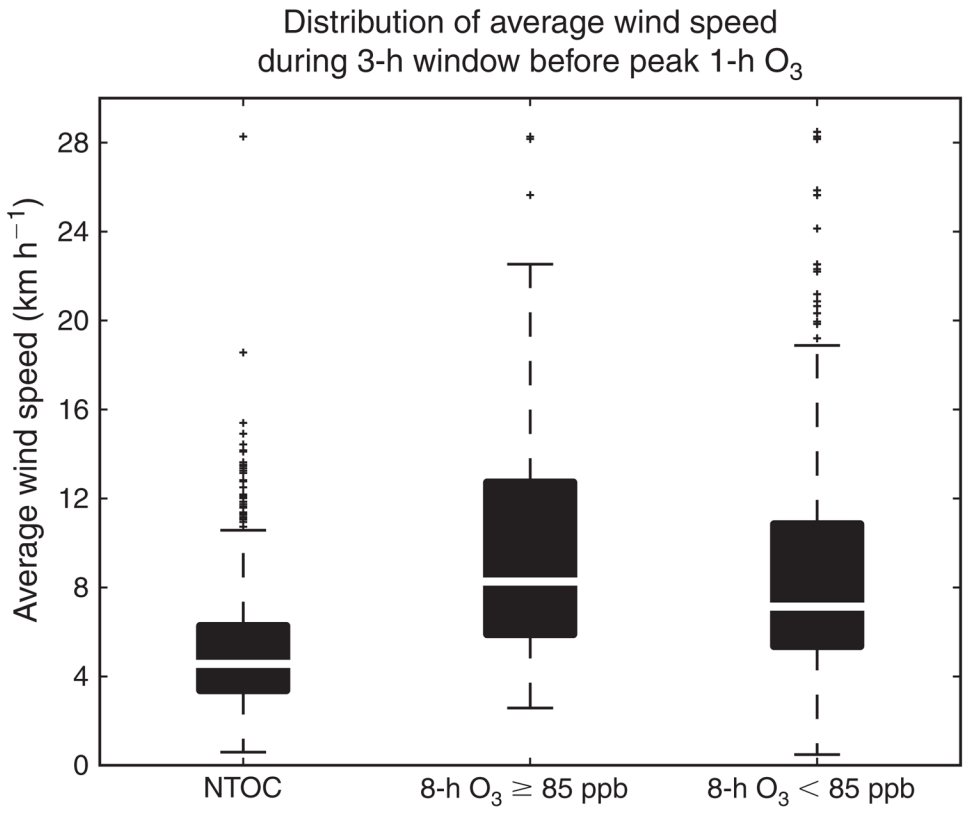

Fig. 3.

Box and whisker plots of 3-h average wind speed measurements on non-typical O_3 change (NTOC) days (left), days that violate the 85-ppb federal standard (middle) and days below the federal standard (right). Box tops, middles and bottoms give the 75th, 50th and 25th percentile values. Whiskers extend to the most extreme data point within 1.5 times the inner quartile range. The 3-h average wind speed was obtained by averaging the 1-h wind speed measurement during the hour of peak O_3 level with the wind speed measurements from the 2 h before the peak O_3 level. Available data from all monitors and years are included in this figure.

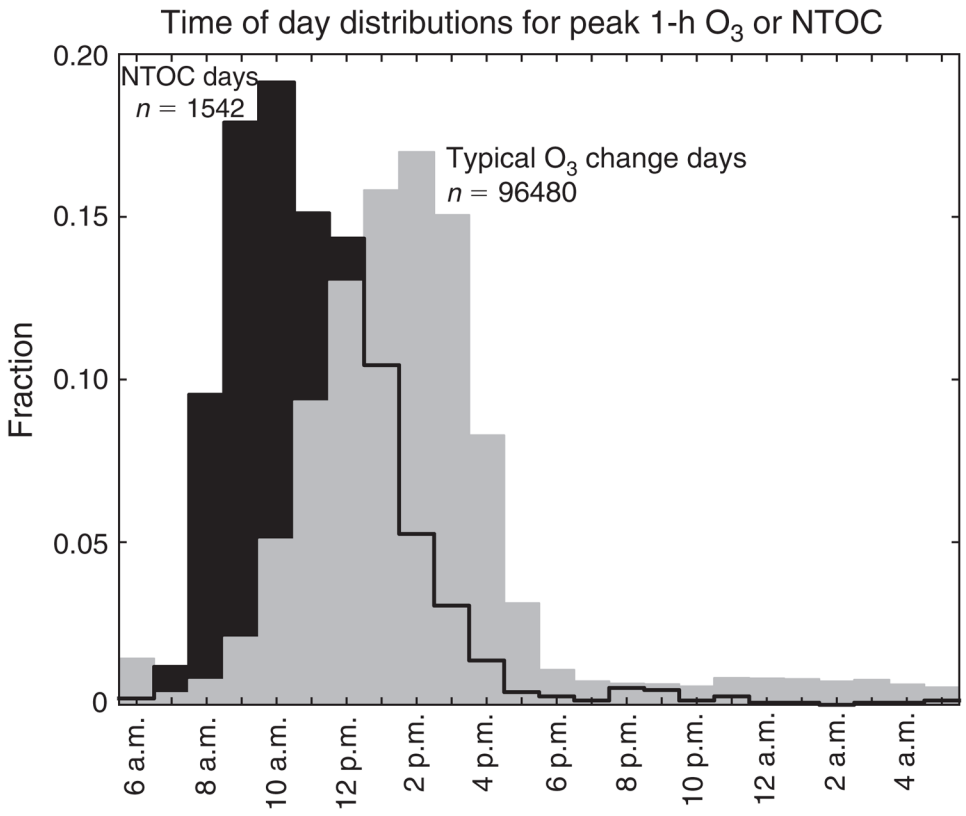

Fig. 4.

Distributions of the time of day during which non-typical O_3 changes (NTOCs) and peak 1-h O_3 levels occur. Available data from all 25 monitors and twelve years are included in this figure.

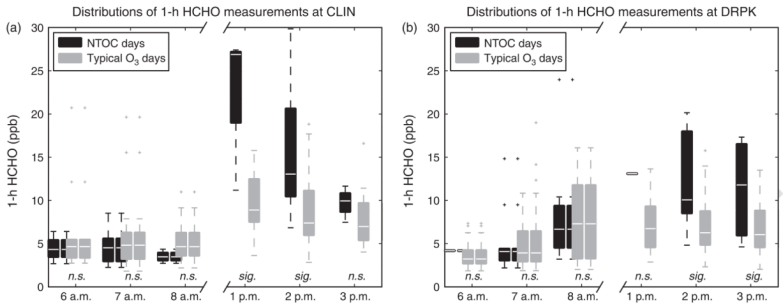

Fig. 5.

Box and whisker plots of 1-h HCHO measurements at CLIN (a) and DRPK (b) for non-typical O_3 change (NTOC) days (black) and typical O_3 level days (grey). Box tops, middles and bottoms give the 75th, 50th and 25th percentile values. Whiskers extend to the most extreme data point within 1.5 times the inner quartile range. The distributions are not significantly different (*n.s.*) in the morning before most NTOCs occur. Immediately following a NTOC, HCHO concentrations often increase substantially. Using the Mann–Whitney non-parametric test it was determined that differences between the typical and NTOC distributions are statistically significant (*sig.*) for CLIN at 1300 (U =3, P =0.032) and 1400 hours (U =39, P =0.012) and for DRPK at 1400 (U =80.5, P =0.003) and 1500 hours (U =54, P =0.014).

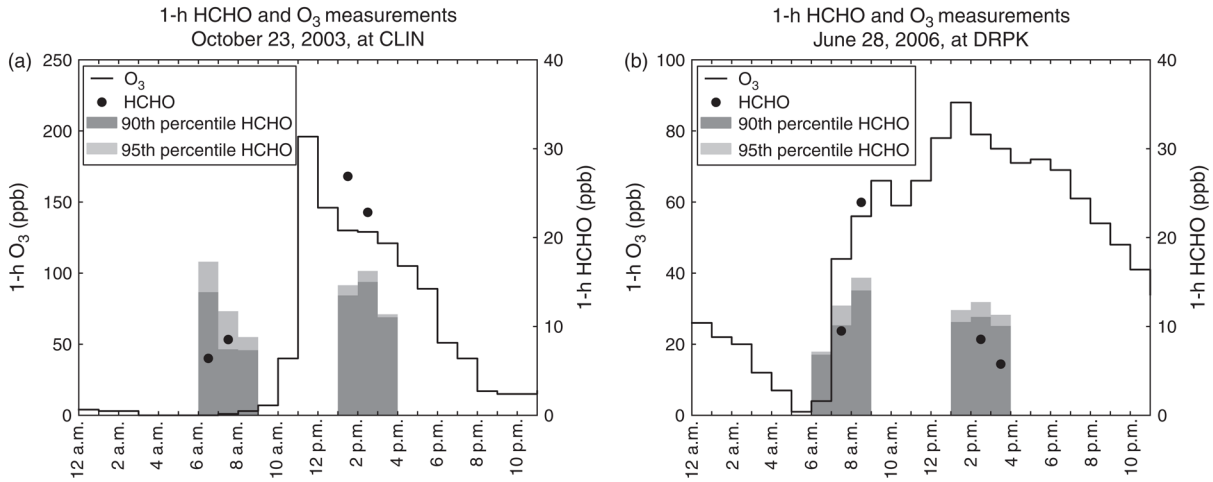

Fig. 6.

Ozone time series plot on 23 October 2003, at CLIN (a) and 28 June 2006, at DRPK (b). The black line shows 1-h O_3 concentrations, and the black dots show 1-h HCHO measurements for the stated date. The shaded boxes show the 90th (dark grey) and 95th percentile (light grey) of HCHO values on all typical O_3 level days for each hour when measurements were taken at both stations. (Note the different *y*-axis scales for 1-h O_3.)

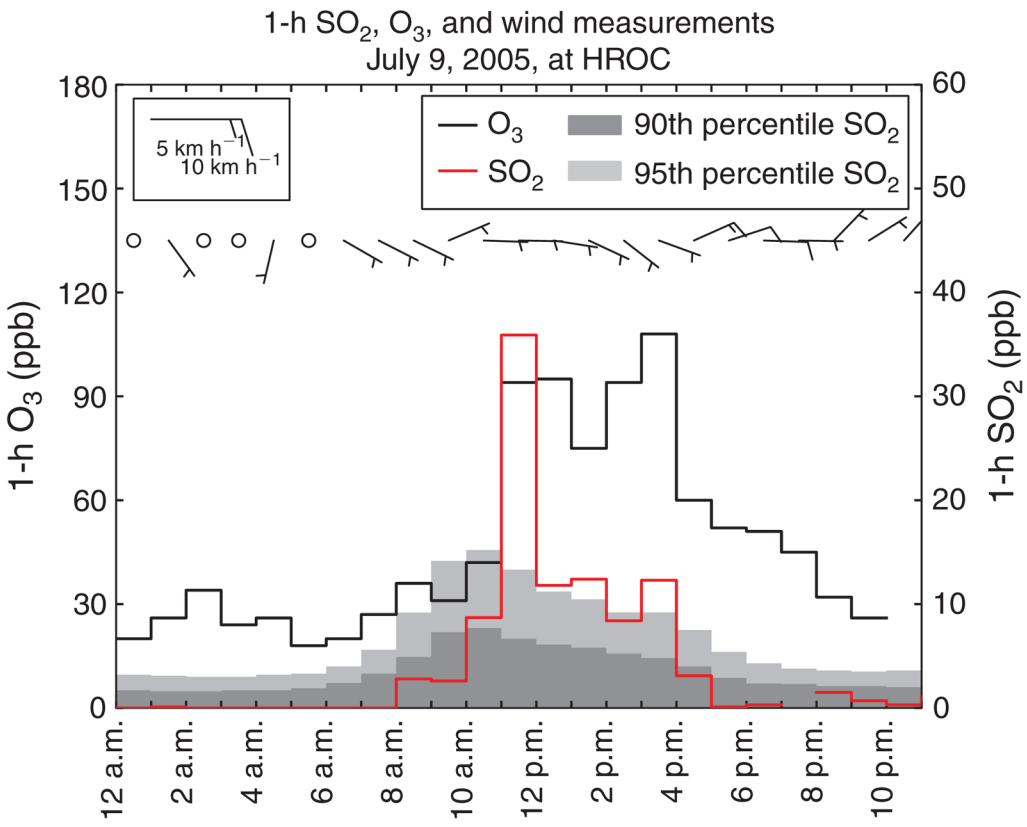

Fig. 7.

Ozone (black) and SO_2 (red) time series plot on 9 July 2005, at HROC. The wind barbs along the top of the figure show the hourly wind speed and direction for this date. The shaded boxes show the 90th (dark grey) and 95th percentile (light grey) SO_2 values on all days for each hour when measurements were taken.

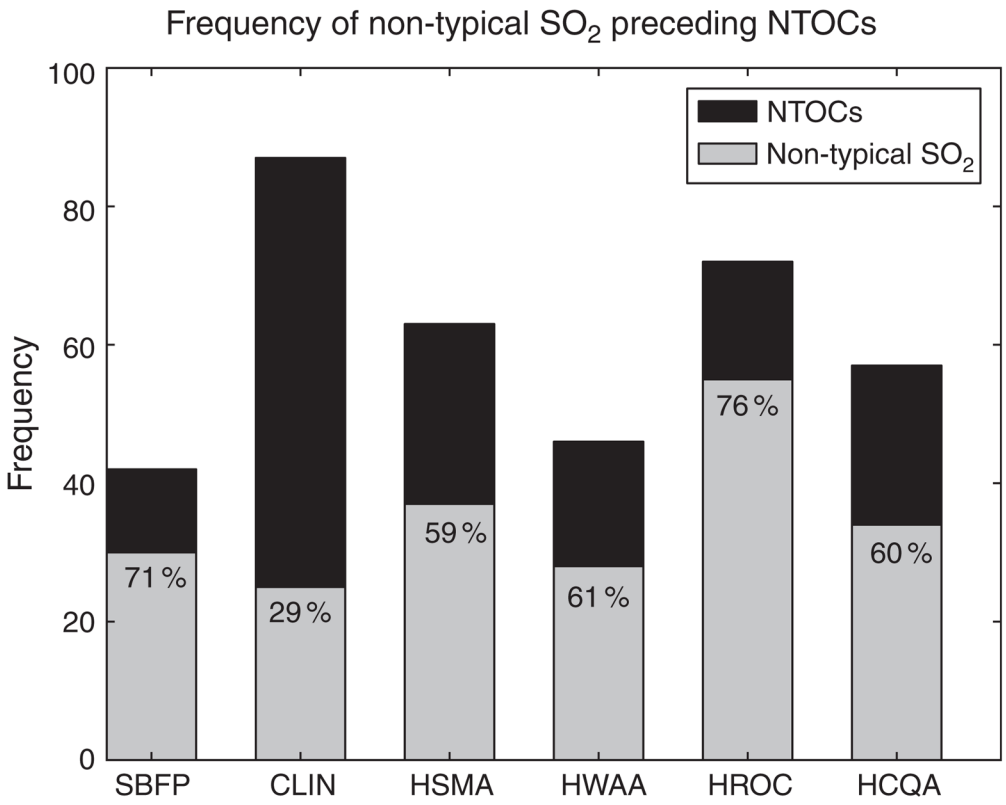

Fig. 8.

Frequency of non-typical SO_2 levels preceding non-typical O_3 changes (NTOCs) at six monitors. The black bars show the number of NTOCs measured at each monitor from 2000 to 2011; the grey bars show the number of NTOCs that had an SO_2 concentration above the 95th percentile up to 5 h before the NTOC.

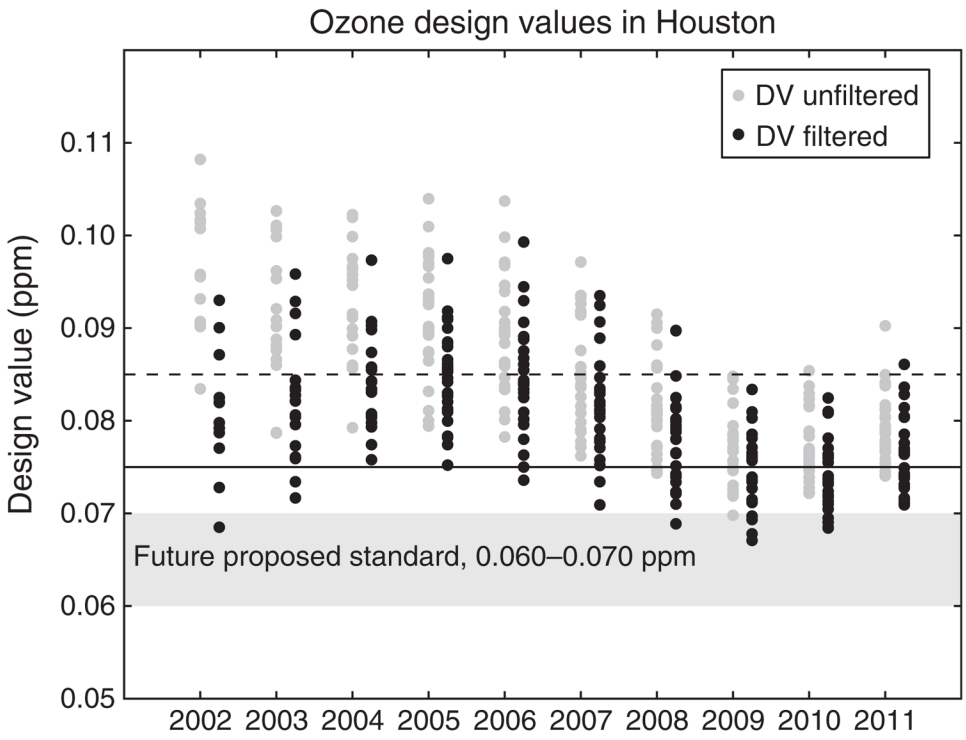

Fig. 9.

Ozone design values for the monitors used in this study from 2002 to 2011. Each grey marker shows the design value for a different monitor. The black markers show the design values for each monitor after all NTOCs have been removed ('filtered') from the calculation. The dotted black line marks the 1997 0.08-ppm 8-h O_3 standard; the solid black line marks the 2008 0.075-ppm 8-h O_3 standard; the grey shaded region marks the range of proposed future standards.

Table 1

Air quality monitors and measured parameters

Monitor name	Abbreviation	CAMS number	AIRS number	Measurements
Bayland Park	BAYP	53	48-201-0055	O_3, HCHO, ws/wd
Clinton	CLIN	403	48-201-1035	O_3, SO_2, ws/wd
Conroe Relocated	CNR2	78	48-339-0078	O_3, ws/wd
Danciger	DNCG	618	48-039-0618	O_3, ws/wd
Deer Park	DRPK	35	48-201-1039	O_3, HCHO, ws/wd
Galveston	GALC	34	48-167-0014	O_3, ws/wd
HRM-3 Haden Road	H03H	603	48-201-0803	O_3, ws/wd
Aldine	HALC	8	48-201-0024	O_3, ws/wd
Channelview	HCHV	15	48-201-0026	O_3, HCHO, ws/wd
Croquet	HCQA	409	48-201-0051	O_3, SO_2, ws/wd
Lang	HLAA	408	48-201-0047	O_3
Northwest Harris County	HNWA	26	48-201-0029	O_3, ws/wd
Houston East	HOEA	1	48-201-1034	O_3, ws/wd
Houston Regional Office	HROC	81	48-201-0070	O_3, SO_2, ws/wd
Monroe	HSMA	406	48-201-0062	O_3, SO_2
Texas Avenue	HTCA	411	48-201-0075	O_3
North Wayside	HWAA	405	48-201-0046	O_3, SO_2
Lake Jackson	LKJK	1016	48-039-1016	O_3, ws/wd
Lynchburg Ferry	LYNF	1015	48-201-1015	O_3, ws/wd
Manvel Croix Park	MACP	84	48-039-1004	O_3, ws/wd
Mustang Bayou	MSTG	619	48-039-0619	O_3, ws/wd
Seabrook Friendship Park	SBFP	45	48-201-1050	O_3, SO_2, ws/wd
Westhollow	SHWH	410	48-201-0066	O_3, ws/wd
Texas City	TXCT	620	48-167-0056	O_3, ws/wd
Wallisville	WALV	617	48-201-0617	O_3, ws/wd

AIRS, Aerometric Information Retrieval System; CAMS, Continuous Ambient Monitoring Station. Measurement abbreviations are O_3, ozone; HCHO, formaldehyde; SO_2, sulfur dioxide; ws/wd, wind speed and wind direction