



Targeting Houston's ozone: How sector-specific emissions drive spatiotemporal sensitivity

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Abstract. The Higher-Order Decoupled Direct Method (HDDM) is applied to a 2019 regulatory photochemical transport
10 modeling episode to evaluate tropospheric ozone (O₃) responses to source-specific nitrogen oxide (NO_x) and volatile organic
compound (VOC) emissions in Houston, Texas. The Houston airshed contains a unique mix of industrial and urban emissions
that challenges air quality models in predicting O₃, adding uncertainty in their use of determining effective regulatory policy.
The regulatory air quality model evaluated in this study predicts that high O₃ plumes are VOC-limited and NO_x-inhibited in
the morning, before transitioning to a NO_x-limited regime midday and throughout the afternoon. Mean O₃ HDDM sensitivities
15 in high O₃ plumes were highest for several source groups, including non-electric generating unit (EGU) VOC (2.65 ppb), non-
EGU NO_x (2.41 ppb), marine NO_x (2.25 ppb), on-road NO_x (1.48 ppb), and area source VOC (1.38 ppb). In predictions of
the maximum daily 8-hour average (MDA8) O₃ concentrations, there were strong interactions between industrial and urban
emissions in O₃ plumes formed to the southwest of Houston. The importance of nonlinear chemistry varies by source, with the
model predicting a strong contribution from second-order and cross-sensitivities for non-EGU and marine sources. The
20 substantial influence of both NO_x and VOC sources on O₃ sensitivity highlights the need for improved emissions inventories,
and more detailed sensitivity analysis.

1. Introduction

Tropospheric ozone (O₃) is formed from the photochemical reaction of volatile organic compounds (VOCs) and nitrogen oxide
(NO_x) emissions, and the Houston-Galveston-Brazoria (HGB) region features a diverse mixture of anthropogenic sources that
25 emit these species (Seinfeld, 2016; EPA, 2020). These sources include the usual NO_x and VOC emissions associated with
large urban areas; however, HGB also features significant industrial sources (Brannen, 2025). The combination of urban and
industrial sources results in a complex atmospheric composition that has significant implications on O₃ formation and its
response to emission controls.

Policymakers have developed emission control strategies that recognize the importance of both NO_x and VOC emissions, and
30 the resulting mitigation policies in HGB have addressed both urban NO_x and industrial VOC sources ("Controlling Ozone



Pollution,” 2026). These policies were based on observational and modeling data that demonstrated that O₃ exceedances in HGB were influenced by NO_x emissions from mobile sources and VOC and NO_x emissions from industrial activity (Allen, 2017; U.S. Department of Commerce, 2025; University Corporation for Atmospheric Research, 2025; Parrish et al., 2009). Targeting industrial sources, the Texas Commission on Environmental Quality (TCEQ) developed policies focused on episodic emissions of highly reactive VOCs, defined as 1,3-butadiene, propene, ethene, and all butene isomers. These policies targeted flares, fugitive leaks, storage tank cleaning, plastics production, and other petrochemical processes through strict controls and a cap-and-trade program (Allen, 2017; Kleinman et al., 2002; Kleinman et al., 2003; Daum et al., 2003; Berkowitz et al., 2004; Ryerson et al., 2003; Couzo et al. 2012; Couzo et al., 2013; Vizuite et al., 2011; Kim et al., 2011; Texas Commission on Environmental Quality, 2002). From 2002–2012, these programs successfully reduced concentrations of 1,3-butadiene and ethene at the Milby Park and Lynchburg Ferry monitors by as much as 1.5 and 3.5 ppb (Myers et al., 2015). TCEQ has also implemented NO_x controls, and observed VOC and NO_x concentrations at monitors across HGB decreased between 2000 and 2019 at rates of 0.4–1.34 and 0.04–1.04 ppb/yr (Chism et al., 2025; Soleimanian et al., 2022). These policies ultimately led to attainment of the older 1-hour average O₃ National Ambient Air Quality Standard (NAAQS) (“Houston-Galveston-Brazoria: Ozone History,” 2002). This previous success in attainment demonstrates the importance of management policies that address both urban and industrial emission sources and suggests the efficacy of any future policy depends on understanding the spatial and temporal changes of O₃ sensitivity to a diverse emission inventory.

Previous studies have quantified the sensitivity of HGB O₃ to precursor NO_x and VOC emissions. Due to the non-linear response of O₃ concentrations to emissions changes, modeling studies of the region have relied on sophisticated sensitivity techniques such as the Decoupled Direct Method (DDM) and Higher-Order Decoupled Direct Method (HDDM) (Cohan et al., 2005; Koo et al., 2008; Xiao et al., 2010). A DDM analysis of Houston during an O₃ episode in 2006 found that O₃ was predominantly VOC-sensitive in the morning, then shifted to NO_x-sensitive conditions in the afternoon. Across the domain, the first-order sensitivities were positive meaning that an increase in emissions led to an increase in O₃. Parts of eastern HGB, however, showed NO_x-inhibited conditions with afternoon first-order NO_x sensitivities reaching as low as -50 ppb O₃/ton NO_x/day. First-order VOC sensitivities reached 31 ppb O₃/ton VOC/day. Using a June 2005 modeling episode, Koo et al. (2008) found similar spatial variability where episode-average O₃ sensitivity to mobile NO_x emissions ranged from -4.76–4.16 ppb, and sensitivity to total VOC emissions was as high as 3.21 ppb. Using an observation-constrained box model for a September 2013 episode, Mazzuca et al. (2013) found that O₃ was VOC-sensitive for the entire day at monitoring sites in eastern Houston and the downtown region, but NO_x emissions produced more O₃ further from the urban core. Conditions changed from being VOC-sensitive in the morning to NO_x-sensitive in the afternoon at locations in Galveston and suburban Houston, similar to Xiao et al.’s (2010) findings (Mazzuca et al., 2013). These studies illustrate the complex chemistry in the HGB airshed featuring spatially and temporally heterogeneous O₃ responses to changes in NO_x and VOC precursors. Understanding how O₃ responds to reductions in different emissions sources is critical to developing effective O₃ reduction strategies. This is especially important for HGB given that the region is currently in nonattainment of the 2008 (0.075 ppm)



and 2015 (0.070 ppm) NAAQS for 8-hour average O₃ (“Houston-Galveston-Brazoria: Current Attainment Status”, 2026;
65 “Controlling Ozone Pollution,” 2026).

The TCEQ has developed a regulatory modeling platform (base year 2019) using the Comprehensive Air Quality Model with
Extensions (CAMx) for its State Implementation Plan (SIP) (Chism et al., 2024). The emission inventory used to support this
modeling episode has been evaluated recently and those analyses highlight issues that may impact O₃ sensitivity, namely
possible gaps in NO_x and VOC emissions. In a 2024 study, aircraft remote sensing data were used to evaluate sector-specific
70 NO_x emissions used in the 2019 HGB SIP modeling episode (Goldberg et al., 2024). The authors reported that CAMx
predictions of column nitrogen dioxide (NO₂) were biased up to −31%, with underestimates attributed to on-road mobile
sources, railyards, and other industrial sources. A second study assessed the 2019 modeling episode’s ability to predict VOCs
by comparing model predictions with public and private surface observations (Vizuite et al., 2026). The analysis found
substantial negative bias in model predictions (normalized mean bias ranging from −33.2% for benzene to −71.6% for ethane)
75 that were most pronounced during nighttime hours (22:00–06:00 local time). The authors found that doubling the
anthropogenic VOC emissions improved agreement for reactive species (benzene, ethene), but left alkane biases largely
unresolved. These two studies indicate gaps in the 2019 VOC and NO_x emission inventory that could impact O₃ sensitivity,
and the model’s response to emission controls. For example, previous DDM modeling studies in HGB have found that biases
in the emissions inventory as small as 10% can impact whether the model predicts that NO_x or VOC controls would be more
80 effective at reducing O₃ concentrations (Xiao et al., 2010).

The 2019 HGB SIP modeling episode presents a unique opportunity to evaluate whether there continues to be spatial and
temporal differences in O₃ responses to the wide range of emission sources present in HGB. Previous regulatory HDDM
analyses in Houston have aggregated O₃ sensitivities by sector and geography, thus limiting the ability to translate modeled
findings into source-specific and region-specific regulatory decisions (Koo et al., 2008; Xiao et al., 2010). Using HDDM in
85 CAMx, and the most recent emissions inventory for the 2019 HGB SIP modeling platform, this study quantifies how the
efficacy of source-specific NO_x and VOC controls vary across space and time and offers insight into future regulatory
decisions.

2. Data and methods

2.1 Model and domain

90 Air quality modeling was completed, following U.S. Environmental Protection Agency (EPA) guidance for O₃ SIPs, using
CAMx version 7.20 with revision 5 of the Carbon Bond VI chemical mechanism and meteorological inputs generated by the
Weather Research and Forecasting model version 4.1.5; CAMx was selected due to its established application by TCEQ for
air quality planning in the HGB nonattainment area (Chism et al., 2025; Wayland and Timin, 2018; Yarwood et al., 2024;
UCAR 2019). The modeling configuration used in this analysis follows what was used in TCEQ’s 2025 SIP for the 2015 O₃
95 NAAQS, apart from enabling the HDDM option (Chism et al., 2025).



We focused our analysis on 12 regulatory O₃ monitoring locations in HGB that have not, as of 2019, attained the 2015 O₃ NAAQS and are shown in Fig. 1. Consistent with TCEQ's 2025 SIP and EPA guidance, the 10 highest modeled maximum daily 8-hour average (MDA8) O₃ concentrations at each monitor were chosen (Chism et al., 2025; Wayland and Timin, 2018). This resulted in 34 simulation days since some simulation days were a top 10 day at multiple monitors (Supplementary Tables 1 and 2). Ozone concentrations and sensitivities were resolved at an hourly time scale, with midnight sensitivities set to zero for individual simulation days (e.g., April 6), and subsequent days initialized using restart files from preceding simulations (e.g., April 25–26).

Subset of 4-km Grid Used for HDDM Analysis

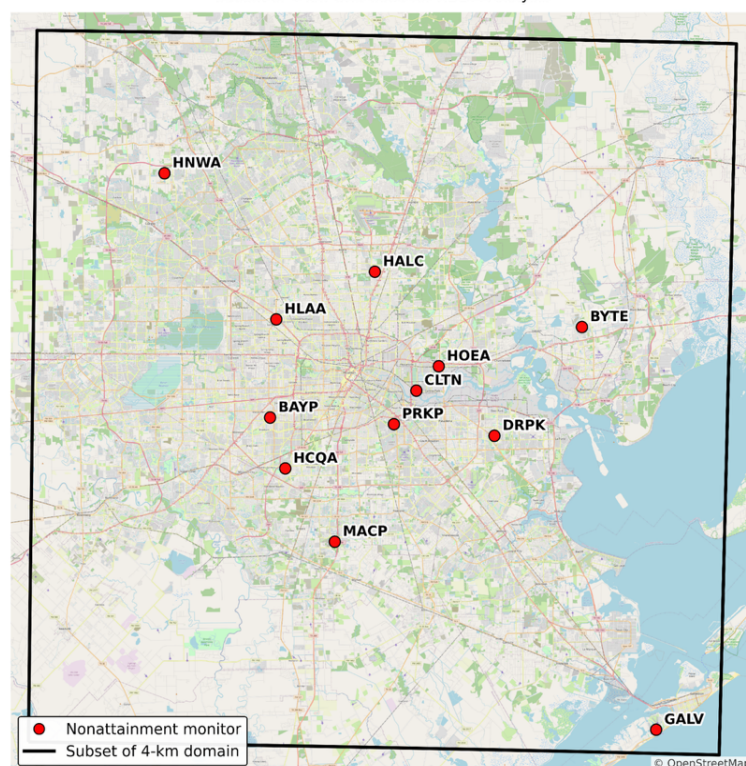


Figure 1. A 48x40 subset of grid cells was extracted from the 4-km grid and used for data analysis. The nonattainment monitors depicted are in violation of the 2015 O₃ NAAQS as of 2019, the base year used by TCEQ in their SIP.

A nested modeling domain was applied to capture regional-to-urban scale processes, with horizontal grid resolutions of 36 km, 12 km, and 4 km. Analysis was conducted on a 48 × 40 subset of the 4 km domain encompassing the HGB nonattainment area (Fig. 1). Emissions inputs were based on a 2019 inventory developed in accordance with EPA requirements, incorporating the National Emissions Inventory and state and federal emissions models used in TCEQ's 2025 SIP (Chism et al., 2025). In addition to the base case inventory, a sensitivity simulation and HDDM analysis were conducted in which VOC emissions from area and non-electric generating unit (EGU) point sources were augmented by a factor of two (2xVOC scenario) motivated by a recent study indicating that anthropogenic VOC emissions in the HGB region may be underestimated for



industrial sources (Vizuet et al., 2026). The 2xVOC scenario was therefore used as a bounding sensitivity case to evaluate the implications of potential VOC underestimation on O₃ sensitivity estimates, and source-sector contributions.

115 2.2 Higher-order decoupled direct method (HDDM)

DDM enables efficient computation of first-order sensitivities of modeled pollutant concentrations to emission inputs by solving sensitivity equations simultaneously with the governing concentration equations, thereby avoiding multiple brute-force simulations (Yarwood et al., 2024; Dunker et al., 2002; Dunker, 1984). HDDM extends this framework by incorporating second-order and cross-sensitivity terms, allowing the representation of nonlinear chemical responses (Dunker et al., 2002; 120 Dunker, 1984; Hakami et al., 2003; Hakami et al., 2004; Yang et al., 1997). Sensitivity coefficients are obtained by differentiating the model governing equations with respect to specified input parameters.

The first-order sensitivity of O₃ to precursor emissions is defined as

$$S_{O_3,j}^{(1)} = \frac{\delta C_{O_3}}{\delta E_j}, \quad (1)$$

and the second-order sensitivity is defined as

$$125 \quad S_{O_3,j}^{(2)} = \frac{\delta^2 C_{O_3}}{\delta E_j^2}, \quad (2)$$

where C_{O_3} is the O₃ concentration, and E_j represents emissions of precursor j (NO_x or VOC). The cross-sensitivity between NO_x and VOC emissions is defined as

$$S_{O_3,NO_x,VOC} = \frac{\delta^2 C_{O_3}}{\delta E_{NO_x} \delta E_{VOC}}. \quad (3)$$

HDDM has been implemented in CAMx and widely applied to quantify both first- and higher-order sensitivities of O₃ to precursor emissions in the HGB region (Koo et al., 2008; Xiao et al., 2010; Yarwood et al., 2024). In this study, O₃ sensitivities to NO_x and VOC emissions were calculated for multiple emissions source groups. Because O₃ formation exhibits nonlinear dependence on NO_x and VOCs, higher-order sensitivity terms are required to accurately characterize responses to larger emissions changes (Seinfeld, 2016; Cohan et al., 2005; Hakami et al., 2003). Second-order sensitivities quantify curvature in the concentration–emissions relationship, capturing diminishing or enhancing returns in O₃ response to emissions controls, 135 while cross-sensitivities describe interactions between NO_x and VOC perturbations (Dunker et al., 2002; Dunker, 1984; Hakami et al., 2003; Hakami et al., 2004; Yang et al., 1997). Together, these terms can be combined in a Taylor series expansion to approximate O₃ responses to simultaneous changes in multiple precursors:

$$C_{O_3} \approx C_{O_3,0} + \epsilon_{NO_x} S_{O_3,NO_x}^{(1)} + \frac{1}{2} \epsilon_{NO_x}^2 S_{O_3,NO_x}^{(2)} + \epsilon_{VOC} S_{O_3,VOC}^{(1)} + \frac{1}{2} \epsilon_{VOC}^2 S_{O_3,VOC}^{(2)} + \epsilon_{NO_x} \epsilon_{VOC} S_{O_3,NO_x,VOC}, \quad (4)$$

where C_{O_3} is the predicted O₃ concentration after perturbation and $C_{O_3,0}$ is the baseline O₃ concentration before perturbation.

140 The parameters ϵ_{NO_x} and ϵ_{VOC} represent the fractional changes in NO_x and VOC emissions. $S^{(1)}$ and $S^{(2)}$ are first- and



second-order O_3 sensitivities, and $S_{O_3,NOx,VOC}$ is the NOx-VOC cross-sensitivity. Sensitivities are semi-normalized and reported in ppb.

In this work, HDDM was applied to compute first-order, second-order, and cross sensitivities of hourly O_3 concentrations to NOx and VOC emissions from eight source groups at the 4 km spatial resolution. Source group definitions were selected to capture sensitivities from key anthropogenic emissions sectors in the HGB region (Chism et al., 2025; “Houston-Galveston-Brazoria: Ozone History,” 2024). Section 2.3 lists the source groups considered in this HDDM analysis.

First- and second-order self-sensitivities were combined using a Taylor series expansion to calculate a metric defined as the HDDM Sensitivity (defined below for the sensitivity of O_3 to NOx from an arbitrary source group). This value approximates O_3 responses to proportional changes in either NOx or VOC emissions from a source group assuming that the emissions of the other species from that group remain constant.

$$HDDM \text{ Sensitivity} = S_{O_3,NOx}^{(1)} - \frac{1}{2} S_{O_3,NOx}^{(2)} \quad (5)$$

2.3 Emissions sectors

Ozone sensitivities were calculated for eight emissions source groups (Table 1) representing key anthropogenic sectors in the HGB region: EGUs, non-EGU point sources, marine vessels, area (nonpoint) sources, on-road mobile sources, non-road mobile sources, off-road equipment, and oil and gas operations. Source group definitions were generally consistent with those used in SIP modeling (Chism et al., 2025; “Houston-Galveston-Brazoria: Ozone History,” 2024). First-order, second-order, and cross-sensitivity coefficients for hourly O_3 concentrations with respect to NOx and VOC emissions were calculated for each source group using HDDM. A subset of storage tanks and flares were separated from the non-EGU point source inventory for separate analysis not reported here. Thus, our sensitivities for the non-EGU point source group were obtained by combining (summing) the separate sensitivities to those storage tanks and flares with non-EGU point sources.

Table 1. Summary statistics for HDDM sensitivities (ppb) to NOx and VOC source groups. Sensitivities were extracted from high O_3 plumes between 10:00 AM local time and the hour after model-predicted maximum O_3 concentrations on the 31 high O_3 days. A description of plume identification is provided in Sect. 2. HDDM sensitivities to a given emitted precursor (e.g. NOx) are defined as the maximum O_3 change achieved with a 100% reduction in that precursor with a 0% reduction in the other precursor (e.g. VOC).

Source Group	Mean	Median	Maximum	Minimum	Standard Deviation
Non-EGU VOC	2.65	1.87	11.04	0.00	2.37
Non-EGU NOx	2.41	2.41	9.67	-13.50	2.80
Marine NOx	2.25	2.30	15.66	-11.66	2.89



Source Group	Mean	Median	Maximum	Minimum	Standard Deviation
On-Road NOx	1.48	1.32	6.09	-3.29	1.52
Area VOC	1.38	1.28	5.14	0.00	0.95
Non-Road NOx	0.76	0.69	3.21	-1.73	0.90
Area NOx	0.58	0.60	2.11	-1.13	0.67
EGU NOx	0.57	0.39	4.22	-1.99	0.92
Off-Road NOx	0.50	0.40	5.69	-1.83	0.71
Non-Road VOC	0.48	0.42	1.69	0.00	0.34
On-Road VOC	0.29	0.26	1.14	0.00	0.21
Marine VOC	0.15	0.12	0.75	0.00	0.13
Oil and Gas VOC	0.10	0.06	0.73	0.00	0.12
Off-Road VOC	0.05	0.04	0.36	0.00	0.04
Oil and Gas NOx	0.03	0.01	0.43	-0.08	0.05
EGU VOC	0.01	0.01	0.04	0.00	0.01

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2.4 Plume-tracking methodology

For each day selected for the HDDM analysis (Supplemental Table 2), the temporal domain was restricted to hours between 10:00 AM local time and the hour after the peak modeled 1 hr O₃ concentration occurred to isolate the period of highest O₃ production. The earliest modeled O₃ peak occurred at 12:00 PM on 14 June, and the latest occurred at 5:00 PM on 1 June,



170 3 June, 13 June, 25 July, 14 August, and 15 August. On half of the modeled days, daily maximum hourly O_3 concentrations occurred at 4:00 PM or 5:00 PM. For each hour, HDDM sensitivities were extracted from the grid cell with the maximum modeled O_3 concentration, following the high O_3 plume to create a “pseudo-Lagrangian” analysis that captured the source groups and precursor emissions most influential on plumes representing the most severe O_3 pollution. Modeled O_3 plumes occur in downtown Houston and to its north, west, and southwest, which is consistent with meteorological patterns and emissions from the urban core (Supplemental Figure 1) (Couzo et al., 2013; Darby, 2005; Vizuite et al., 2022).

175 When the maximum hourly O_3 concentration in the HDDM analysis domain occurred outside of the Houston-influenced plume, an alternate grid cell was selected to maintain the plume-specific dataset. On 14 June, 14 August, and 1 September, the model predicted abnormal plumes in the Gulf of Mexico or northeast of the HGB region (Supplemental Figure 2). Our method does not include the sensitivities within these plumes because they were not formed from precursors emitted within the analysis domain. The grid was constrained to exclude these plumes, and sensitivities within Houston-influenced plumes were analyzed.

180 On 13 April, 26 April, and 24 July, no plume was observed downwind of Houston, even after the grid was constrained (Supplemental Figure 3). These three days were excluded from the overall analysis, thus yielding a total of 31 analysis days. The dates of 13 April and 24 July were included in the monitor-specific analysis; however, 13 April was a top 10 day at GALV and 24 July was a top 10 day at HNWA (see Fig. 1 for monitoring site abbreviations). As a result, it is likely that our reported sensitivities for these two monitors are conservative because each includes a day with high O_3 that originated outside of the

185 HGB region (i.e., not “controllable” O_3).

2.5 Monitor-specific sensitivity methodology

We also analyzed O_3 response at individual nonattainment monitors, limiting our analysis to the top 10 modeled MDA8 O_3 days for each monitor. While there is some overlap in days between monitors, each one has a unique set of top 10 days that were analyzed. Our focus was on the top 10 MDA8 O_3 days for each monitor for two reasons. First, consistent with the plume-tracking methodology (Sect. 2.4), our interest is in how precursor emissions impact high O_3 . Second, the top 10 MDA8 O_3 days are “policy relevant” following EPA modeling guidance. Sensitivities were extracted from the model grid cell that contains a given monitor’s latitude and longitude, and the temporal domain was restricted to hours between 10:00 AM local time and the hour after the peak modeled 1-hr O_3 concentration occurred, as in the plume-tracking methodology.

195 3. Results and discussion

3.1 Spatiotemporal variability in high O_3 plumes

Ozone sensitivity to NO_x and VOC emissions exhibited substantial spatiotemporal variability and substantial variability across source groups. The results in this section are aggregated across all 31 analysis days in high O_3 plumes (see Sect. 2.4), thus describing how maximum O_3 concentrations respond to precursor emissions. Table 1 provides summary statistics for all NO_x and VOC source groups. Ozone is sensitive to both NO_x and VOC emissions with the mean sensitivity to non-EGU VOC

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being the greatest (2.65 ppb), followed by non-EGU NO_x (2.41 ppb), marine NO_x (2.25 ppb), on-road NO_x (1.48 ppb), and area VOC (1.38 ppb). The prominence of these five source categories suggests that both industrial emissions (non-EGU and marine sources) and routine emissions from traffic and urban activity (on-road and area sources) play an important role in Houston O₃ formation. Several NO_x source groups exhibited strong negative minimum sensitivities, indicating that NO_x titration is an important process in HGB. No VOC source groups had negative sensitivities, which is consistent with O₃ formation chemistry. Figure 2 shows the distribution of O₃ sensitivities to the 10 most influential source groups. Non-EGU NO_x, which has the second largest mean sensitivity value, has the widest distribution of sensitivities. In general, as the mean sensitivities among the source groups decrease, so do the ranges of sensitivities (i.e., width of distribution). Considering these 10 source groups, total mean sensitivity to NO_x emissions is 8.6 ppb and total mean sensitivity to VOC emissions is 4.5 ppb.

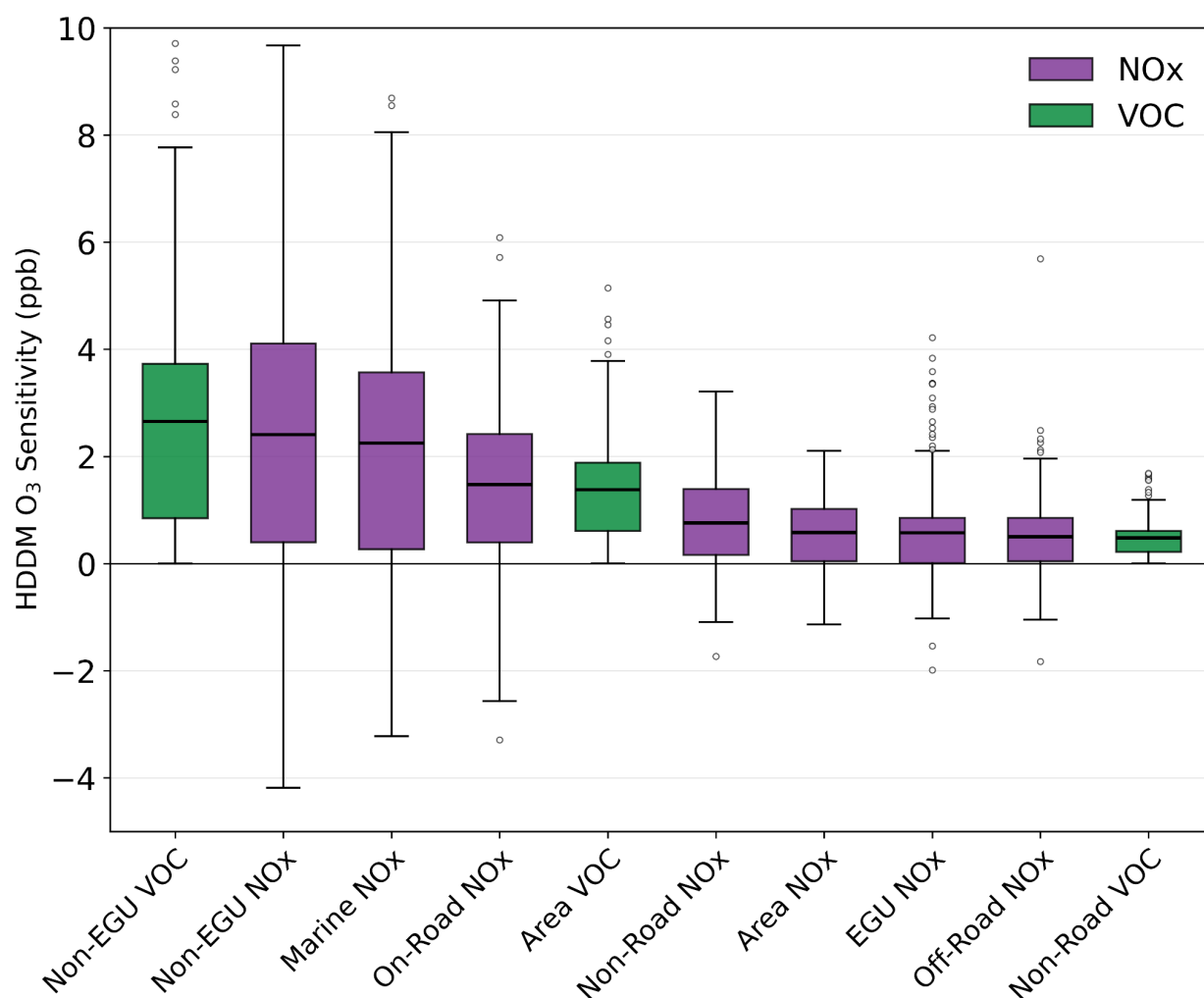


Figure 2. Distribution of HDDM sensitivities to the top 10 source groups. NO_x source groups are shaded purple, and VOC source groups are shaded green. Boxes represent the interquartile range (25th-75th percentiles), whiskers extend to 1.5 times the interquartile range, individual points represent values outside the whiskers, and black horizontal lines indicate the arithmetic mean.



215 Sensitivities were extracted from high O₃ plumes between 10:00 AM local time and the hour after model-predicted maximum O₃ concentrations on 31 high O₃ days. A description of plume identification is provided in Sect. 2. HDDM sensitivities to a given emitted precursor (e.g., NO_x) are defined as the maximum O₃ change achieved with a 100% reduction in that precursor with a 0% reduction in the other precursor (e.g., VOC).

Table 2 describes how often each source group dominates O₃ sensitivity to precursor emissions. Considering sensitivity to only NO_x emissions sources, O₃ responses were most sensitive to the non-EGU source group on 16 days, the on-road source group on 8 days, and the marine source group on 7 days. For VOC emissions, maximum sensitivities were most sensitive to the non-EGU source group on 24 days, and the area source group on 7 days. When looking at combinations of dominant NO_x and VOC source groups, non-EGU emissions again appeared the most often. Out of all 31 analysis days, 16 days were most sensitive to the NO_x and VOC non-EGU source groups. There were five days with maximum sensitivities to marine NO_x and non-EGU VOCs and another five days dominated by on-road NO_x and area VOCs. The on-road NO_x and non-EGU VOC source groups combined to dominate O₃ sensitivities on three days. Two days were dominated by marine NO_x and area VOCs.

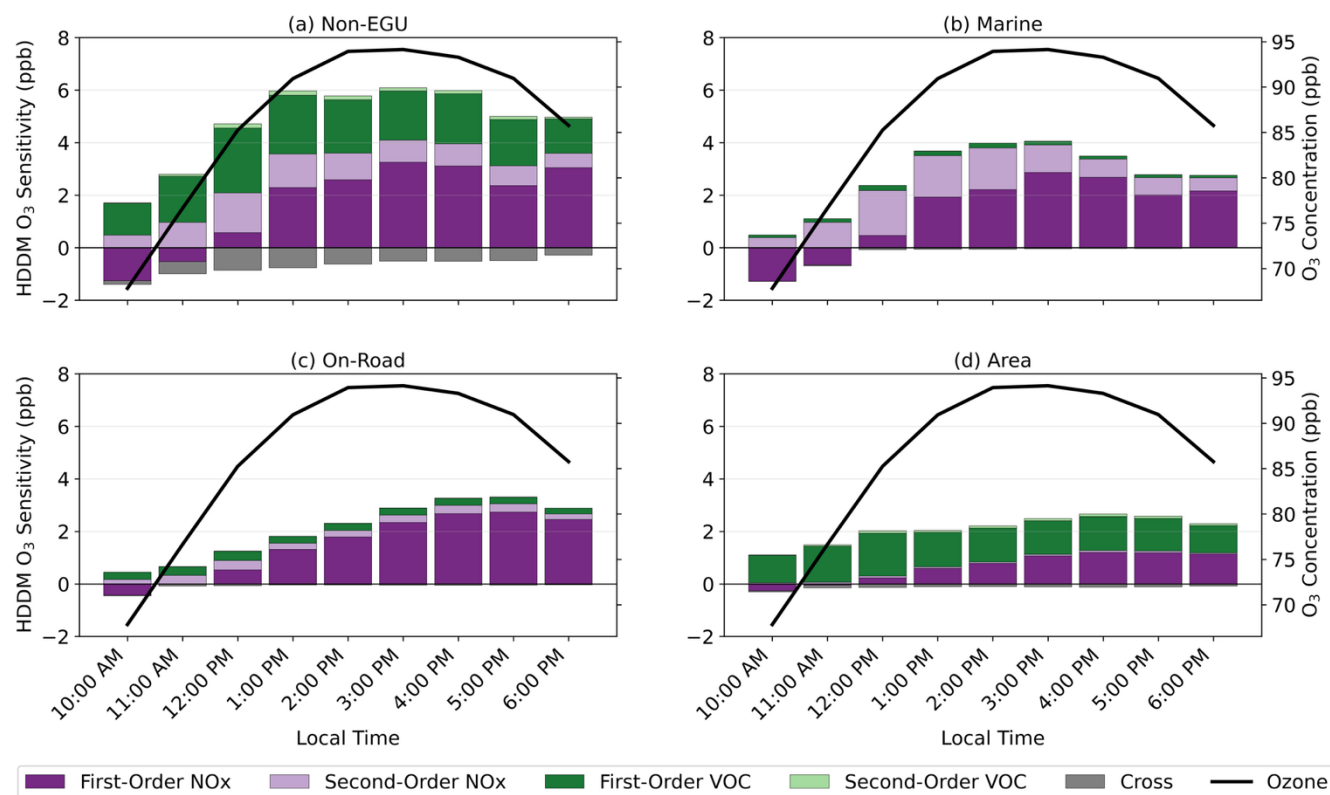
Table 2. Dominant source groups within high O₃ plumes across 31 high O₃ days. The table provides the frequency with which O₃ was most sensitive to a particular source group. For example, NO_x sensitivities to non-EGU sources were highest on 16 days, and VOC sensitivities to non-EGU sources were highest on 24 days. On 16 days, sensitivities were highest to both non-EGU NO_x and non-EGU VOC sources.

Sources Groups with Highest Sensitivity		No. of Days
NO _x	VOC	
Non-EGU	Non-EGU	16
Marine	Non-EGU	5
On-Road	Area	5
On-Road	Non-EGU	3
Marine	Area	2

230 The timing and magnitude of O₃ sensitivities to the top emissions source groups is provided in Fig. 3. In each panel, the stacked bars show first- and second-order sensitivity to NO_x and VOC emissions as well as the HDDM cross-sensitivity term. Hourly O₃ concentrations are given by the black line. All values (sensitivities and O₃ concentrations) are averaged across the 31 analysis days. For each source group, NO_x sensitivities are negative in the late morning and increase throughout the afternoon. This indicates a shift from NO_x inhibition to a NO_x-limited environment. Maximum NO_x sensitivities of 4.1 ppb occur at 3:00 PM for non-EGU source groups, 3.9 ppb at 3:00 PM for marine source groups, 3.1 ppb at 5:00 PM for on-road source groups, and 1.3 ppb at 4:00 PM for area source groups. VOC sensitivities show less hourly variability and peak earlier in the day. Maximum VOC sensitivities of 2.6 ppb occur at 12:00 PM for non-EGU and 1.7 ppb at 12:00 PM for area source groups. Cross terms are always negative, which means that the combined sensitivity to NO_x and VOC emissions is less than the sum of the individual responses to NO_x-only or VOC-only source groups. Only the non-EGU source group, however, has appreciable cross terms. Non-EGU cross terms range from -0.9 to -0.1 ppb; the cross terms for other source groups are between



245 approximation to those VOC source groups is likely sufficient.



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Figure 3. Mean 1-hr O₃ concentrations (black line) and sensitivities (stacked bars) to four source groups. HDDM sensitivities are separated into first- and second-order NO_x, first- and second-order VOC, and NO_x-VOC cross terms. NO_x sensitivities are shaded purple, and VOC sensitivities are shaded green; cross terms are shaded gray. Sensitivities were extracted from high O₃ plumes between 10:00 AM and 6:00 PM local time on 31 high O₃ days. A description of plume identification is provided in the Sect. 2. HDDM sensitivities to a given source group are defined as the maximum O₃ change achieved with a 100% reduction in both NO_x and VOCs.

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Figure 4 shows MDA8 O₃ concentrations averaged across days that are dominated by the NO_x-VOC source group combinations listed in Table 2. While the magnitude of modeled MDA8 O₃ concentrations is relatively consistent regardless of which NO_x-VOC source group combinations dominate, different combinations lead to high O₃ in different locations. Days dominated by non-EGU NO_x and non-EGU VOC sources have maximum O₃ in the urban core of Houston, with peak concentrations reaching 74.2 ppb just east of downtown (Fig. 4a). When marine NO_x and non-EGU VOC source groups dominate, MDA8 O₃ shifts to the north of downtown and reaches 69.0 ppb, suggesting the influence of southerly winds that lead to interactions between coastal and industrial sources (Fig. 4b). When on-road NO_x and area VOC sources dominate, maximum MDA8 O₃ reaches 69.2 ppb east of the urban core (Fig. 4c). When on-road NO_x and non-EGU VOC emissions



yield the largest O₃ sensitivity, maximum MDA8 O₃ reaches 72.5 ppb to the northwest of Houston's urban core (Fig. 4d). This pattern of MDA8 O₃ formation has been explained elsewhere as resulting from an injection of industrial VOCs into an urban plume laden with sufficient amounts of NO_x (Kleiman et al., 2002; Kleinman et al., 2003; Ryerson et al., 2003; Couzo et al., 2012; Vizuite et al., 2011; Henderson et al., 2010). Lastly, days dominated by marine NO_x and area VOC emissions produce maximum MDA8 O₃ of 79.8 ppb over Galveston Bay and offshore in the Gulf of Mexico, areas likely to be affected by marine NO_x sources (Fig. 4e).

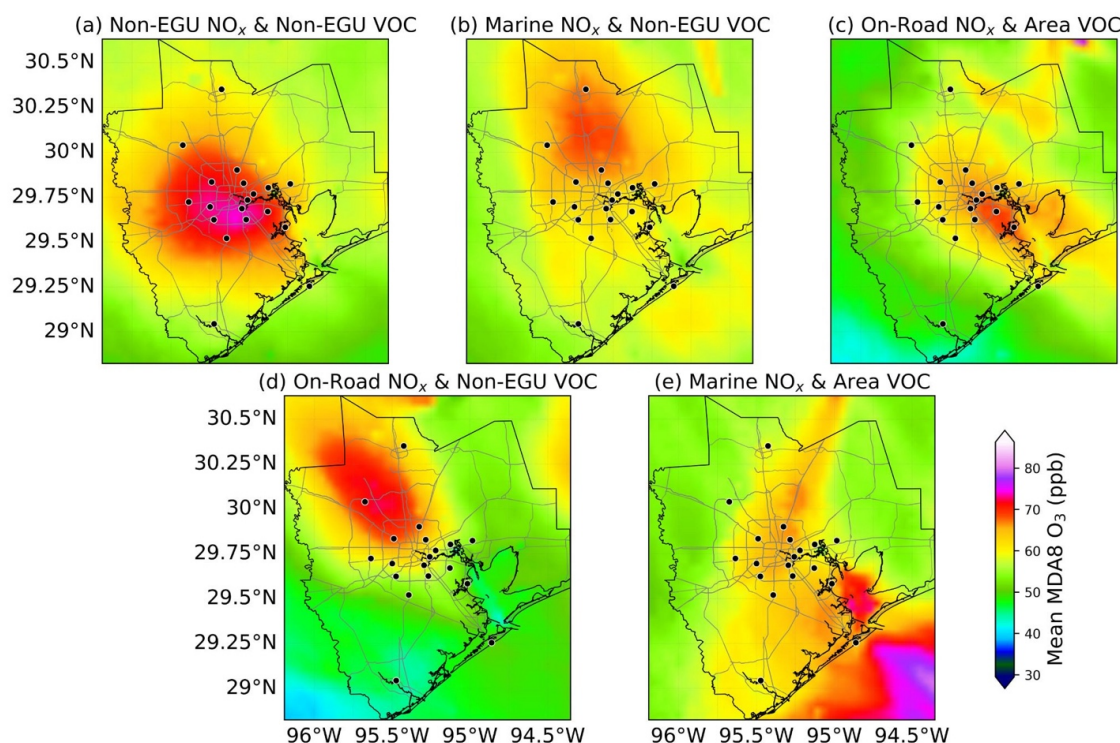


Figure 4. Mean modeled maximum daily 8-hour average (MDA8) O₃ concentrations across days dominated by the following NO_x-VOC source group combinations: (a) non-EGU NO_x & non-EGU VOC (16 days), (b) marine NO_x & non-EGU VOC (5 days), (c) on-road NO_x & area VOC (5 days), (d) on-road NO_x & non-EGU VOC (3 days), and (e) marine NO_x & area VOC (2 days). Black dots show the O₃ nonattainment monitors, and the black border outlines the HGB nonattainment area.

Spatial patterns of O₃ sensitivities are given in Fig. 5, which shows mean sensitivities to the five source groups with the largest influence on O₃ formation. NO_x sensitivities are generally larger in magnitude and spatial extent compared to VOC sensitivities. Sensitivity to on-road NO_x is greatest in the northwestern quadrant of HGB, reaching 2.9 ppb, while the eastern region is influenced strongly by marine NO_x, reaching -12.7 ppb, especially in shipping lanes where large negative sensitivities are apparent. Non-EGU NO_x, non-EGU VOC, and area VOC source groups have the largest sensitivities near the urban core, with maximum mean sensitivities of 1.5 and 2.2 ppb for the two non-EGU source groups, while area VOC sensitivities are smaller, reaching a maximum of 0.7 ppb. Sometimes sensitivities overlap spatially with MDA8 O₃ as in the case of on-road NO_x (Fig. 4d and 5d), but this is not always the case. For example, sensitivities to non-EGU VOC and NO_x sources (Fig. 5a



and 5b) do not overlap with MDA8 O₃ on days where those two source groups dominate (Fig. 4a). This discrepancy underscores the importance of day-specific meteorology in O₃ formation. Another factor complicating a direct comparison between Fig. 4 and 5 is the fact that Fig. 5 averages source group sensitivities across all 31 analysis days while Fig. 4 averages MDA8 O₃ on specific days that are dominated by NO_x–VOC source group combinations.

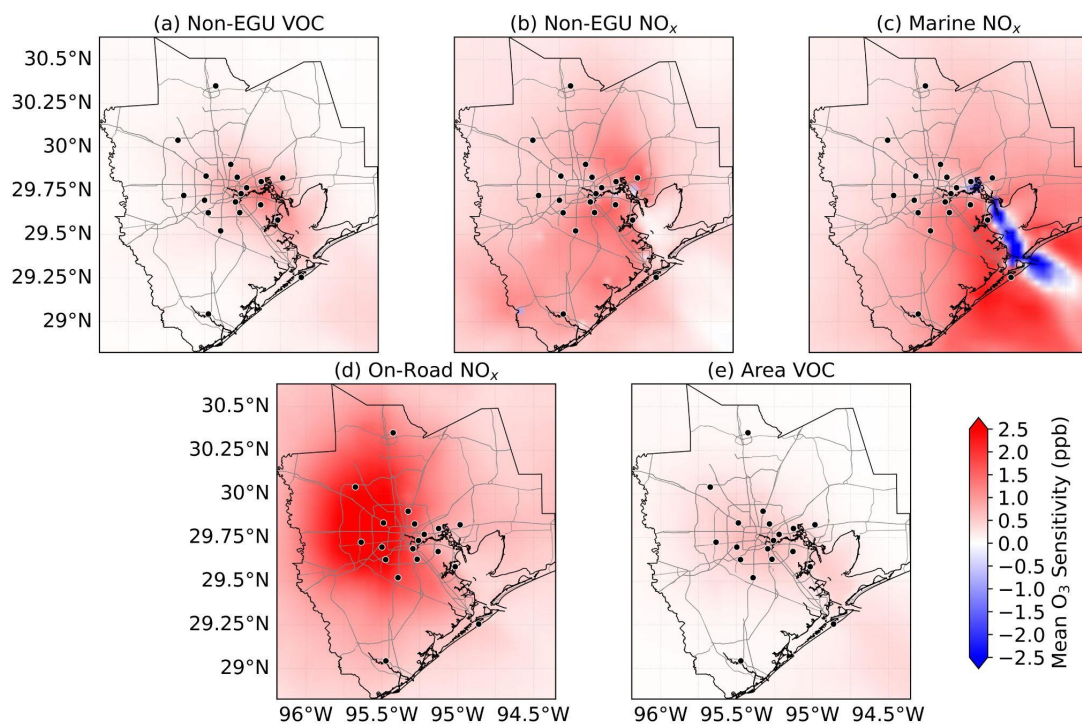


Figure 5. Mean 1-hr O₃ sensitivity to (a) non-EGU NO_x, (b) marine NO_x, (c) non-EGU VOC, (d) on-road NO_x, and (e) area VOC during periods of high O₃ formation between 10:00 AM local time and the hour after each daily maximum O₃ concentration occurs. Black dots show the O₃ nonattainment monitors, and the black border outlines the HGB nonattainment area.

3.2 Policy relevant sensitivity at non-attainment monitors

The overlapping sensitivities shown in Fig. 5 highlight the policy relevant importance of both NO_x and VOC emissions from multiple source groups. Many O₃ monitors are influenced by several source groups, and the relative impact of several source groups is shown in Fig. 6 for each monitor. Mean sensitivities for each monitor were calculated according to Sect. 2.5. The figure rows represent the ten most influential source groups across all 31 analysis days organized in descending order of importance (as in Table 1 and Fig. 2). The columns represent each monitor arranged from west to east. NO_x and VOC source groups are shaded purple and green, and the intensity of shading indicates the relative importance of each source group. For example, the deep purple shading for on-road NO_x at the six western-most monitors indicates that these are the greatest NO_x sensitivities to any source group occurring at any monitor. Similarly, the largest VOC sensitivities occur at the eastern monitors as a result of non-EGU sources. Thus, Fig. 6 illuminates which monitors are sensitive to which source groups, and which source groups influence which monitors. Some of the spatial patterns visible in Fig. 5 are also apparent in Fig. 6. For example,



on-road NO_x sensitivities are largest at monitors in the western part of HGB, and non-EGU and area VOC sensitivities are largest near the east.

Source Group	Non-EGU VOC	0.6 (+60%)	0.9 (+61%)	1.1 (+53%)	0.9 (+57%)	0.9 (+63%)	0.7 (+73%)	1.9 (+63%)	2.2 (+62%)	1.7 (+78%)	2.6 (+66%)	1.4 (+101%)	0.5 (+72%)
	Non-EGU NO _x	0.9 (+30%)	1.1 (+40%)	0.8 (+64%)	1.4 (+33%)	2.2 (+21%)	1.9 (+21%)	1.6 (+66%)	1.5 (+72%)	1.9 (+41%)	1.9 (+59%)	2.4 (+20%)	0.7 (+27%)
	Marine NO _x	0.6 (-9%)	0.7 (+4%)	0.7 (+7%)	0.9 (+2%)	1.4 (-13%)	1.5 (-23%)	1.1 (+22%)	1.0 (+32%)	1.3 (-11%)	1.3 (+7%)	1.6 (-46%)	2.2 (-71%)
	On-Road NO _x	2.9 (+7%)	3.8 (+16%)	3.1 (+14%)	3.7 (+15%)	3.0 (+9%)	2.8 (+7%)	1.8 (+26%)	1.4 (+23%)	1.2 (+8%)	1.2 (+20%)	0.9 (-8%)	1.0 (-4%)
	Area VOC	0.6 (+56%)	1.2 (+62%)	0.9 (+53%)	1.1 (+56%)	0.8 (+52%)	0.6 (+59%)	1.4 (+61%)	1.1 (+57%)	0.6 (+57%)	1.1 (+61%)	0.5 (+71%)	0.4 (+64%)
	Non-Road NO _x	1.4 (+11%)	1.3 (+19%)	1.2 (+18%)	1.5 (+19%)	1.4 (+12%)	1.2 (+9%)	0.7 (+37%)	0.5 (+38%)	0.6 (+14%)	0.6 (+33%)	0.4 (-2%)	0.4 (-10%)
	Area NO _x	1.1 (+8%)	1.2 (+17%)	1.1 (+16%)	1.4 (+18%)	1.3 (+12%)	1.1 (+8%)	0.7 (+35%)	0.5 (+35%)	0.5 (+14%)	0.5 (+32%)	0.4 (-7%)	0.4 (-3%)
	EGU NO _x	0.2 (+30%)	0.3 (+37%)	0.1 (+79%)	0.4 (+31%)	0.5 (+21%)	0.6 (+19%)	0.3 (+57%)	0.3 (+63%)	0.5 (+26%)	0.4 (+64%)	0.7 (+6%)	0.2 (+50%)
	Off-Road NO _x	0.5 (+11%)	0.8 (+11%)	0.8 (+18%)	1.0 (+16%)	1.0 (+12%)	1.2 (+11%)	0.9 (+28%)	0.7 (+29%)	0.6 (+15%)	0.4 (+26%)	0.3 (-7%)	0.2 (+0%)
	Non-Road VOC	0.2 (-23%)	0.3 (-26%)	0.3 (-26%)	0.3 (-25%)	0.2 (-24%)	0.2 (-24%)	0.4 (-22%)	0.3 (-23%)	0.2 (-22%)	0.4 (-21%)	0.1 (-22%)	0.1 (-35%)
		HNWA	BAYP	HLAA	HCQA	MACP	HALC	PRKP	CLTN	HOEA	DRPK	BYTE	GALV
		Nonattainment Monitor											

Figure 6. Mean HDDM sensitivities to the top 10 source groups at each nonattainment monitor. NO_x source groups are shaded purple, and VOC source groups are shaded green. The intensity of shading indicates the relative importance of each source group – deeper colors have higher sensitivities. Monitors are arranged west to east. Mean sensitivities were extracted between 10:00 AM local time and the hour after model-predicted maximum O₃ concentrations on the top 10 high O₃ days at that monitor. See the Sect. 2 for details. HDDM sensitivities to a given emitted precursor (e.g., NO_x) are defined as the maximum O₃ change achieved with a 100% reduction in that precursor with a 0% reduction in the other precursor (e.g., VOC). The number in parentheses reveals the percent change of each sensitivity when anthropogenic VOC emissions are doubled (i.e., the 2xVOC scenario).

Most monitors are more strongly influenced by NO_x source groups. All monitors have at least two NO_x source groups with sensitivities greater than or equal to 1.0 ppb, and two monitors (MACP and HALC) have six NO_x source groups with sensitivities of at least 1.0 ppb. Conversely, only three monitors (PRKP, CLTN, and DRPK) have multiple VOC source groups with sensitivities of at least 1.0 ppb. In general, monitors farther to the west or east of HGB have large sensitivities (≥ 1.0 ppb) to fewer source groups; it is the more centrally located monitors that are strongly influenced by a greater number of source groups. For example, HCQA, MACP, and HALC each have six source groups with sensitivities greater than or equal to 1.0 ppb. The monitor-specific sensitivity analysis presented here is critical to developing effective O₃ control strategies. Marine NO_x may not influence monitors in the western part of HGB, but it is the most important source group at GALV (2.2 ppb) and the second most important at BYTE (1.6 ppb). On-road NO_x emissions, on the other hand, have a much smaller impact at those monitors but greatly influence O₃ formation at western monitors (up to 3.8 ppb). This analysis also stresses the importance of VOC emissions for certain monitors. At CLTN and DRPK, the most influential source group is non-EGU VOC (2.2 and 2.6 ppb) with half of the monitors having non-EGU VOC or area VOC in the top three most influential source groups.



320 Fig. 7 extends this monitor-specific inquiry by focusing on three monitors in different parts of HGB: BAYP in the west, HALC
in the north, and DRPK near the industrial Houston Ship Channel. As in Fig. 3, the stacked bars represent sensitivities and the
black line shows hourly O_3 . Each row shows a different source group at each monitor, which are organized by columns. Total
HDDM non-EGU sensitivity ($NO_x + VOC + \text{cross term}$) reaches a maximum of 5.4 ppb at 2:00 p.m. at DRPK but does not
peak until 5:00 p.m. at 2.6 ppb further to the west at BAYP. Furthermore, the VOC-only component of the total non-EGU
325 sensitivity at DRPK is nearly the same as the total HDDM sensitivity at BAYP and HALC during the morning and early
afternoon. On-road emissions show opposite behavior with BAYP more influenced (5.4 ppb at 2:00 p.m.) than DRPK (2.4 ppb
at 3:00 p.m.). Sensitivity to area emissions, on the other hand, does not show a west-to-east dependence in total HDDM
sensitivity, with maximum sensitivities of 2.5, 2.0, and 1.7 ppb at BAYP, HALC, and DRPK. The relative importance of area
 NO_x versus area VOC emissions, however, does change. Area source group sensitivities are dominated by NO_x emissions at
330 HALC and VOC emissions at DRPK, but BAYP shows more balance between the two though with a notable VOC-to- NO_x
shift throughout the day.

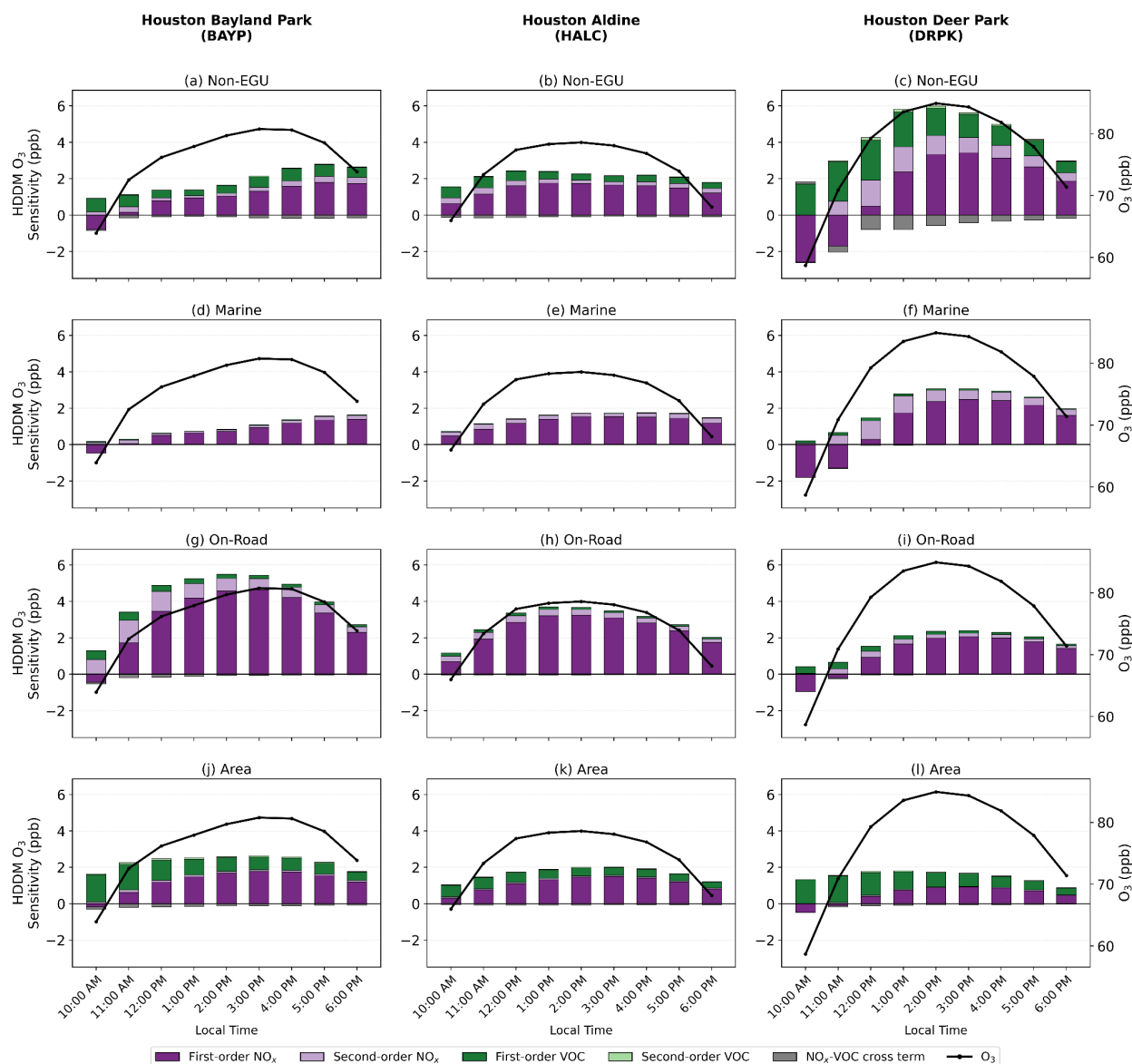


Figure 7. Mean 1-hr O_3 concentrations (black line) and sensitivities (stacked bars) to four source groups at three monitors. HDDM sensitivities are separated into first- and second-order NO_x , first- and second-order VOC, and NO_x -VOC cross terms. NO_x sensitivities are shaded purple, and VOC sensitivities are shaded green; cross terms are shaded gray. For each monitor, O_3 concentrations and sensitivities were extracted between 10:00 AM and 6:00 PM local time on the top 10 high O_3 days at that monitor. See Sect. 2 for details on how each monitor's grid cell was chosen. BAYP is located to the west of downtown Houston, HALC is north of downtown Houston, and DRPK is near the Houston Ship Channel.

3.3 Enhanced 2xVOC sensitivity analysis

A recent evaluation of the emissions inventory in the 2019 modeling platform suggests that anthropogenic VOC emissions may be underestimated, particularly for industrial sources (Vizuet et al., 2026). To evaluate the implications of this uncertainty



for source-specific O₃ sensitivities, an additional HDDM simulation was conducted in which anthropogenic VOC emissions within HGB from the area and non-EGU source sectors were doubled. The 2xVOC simulation was used as a sensitivity analysis to assess how potential underestimation of anthropogenic VOC emissions affects HDDM-derived O₃ sensitivities.

Figure 8 compares mean HDDM sensitivities under the base and 2xVOC scenarios for the ten most influential source groups across all 31 analysis days according to the base case simulation. Increasing VOC emissions produced substantial changes in both VOC and NO_x sensitivities, although the magnitude and direction of the response differed among source categories. The largest change occurred for non-EGU VOC, which increased from approximately 2.7 ppb in the base case to about 5.5 ppb in the 2xVOC simulation. Non-EGU NO_x also increased substantially, from approximately 2.4–3.4 ppb. Area VOC increased from approximately 1.4–2.2 ppb, while on-road NO_x increased modestly from approximately 1.5–1.6 ppb. Smaller increases were observed for several other NO_x categories, including non-road, area, EGU, and off-road. In contrast, marine NO_x decreased from approximately 2.3–1.8 ppb, demonstrating that increased VOC emissions did not uniformly enhance O₃ sensitivity to NO_x across source sectors. Non-road VOC also decreased by about 27%.

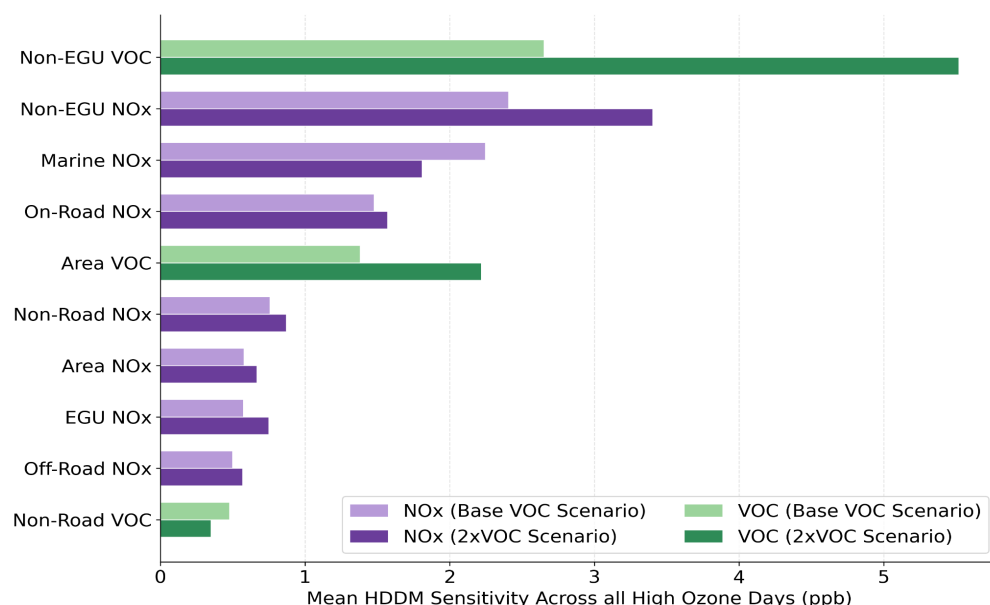


Figure 8. Mean HDDM sensitivities of the top 10 source groups using base case VOC emissions (light shading) and sensitivity case augmented VOC emissions (2xVOC, dark shading). NO_x source groups are shaded purple, and VOC source groups are shaded green. Sensitivities were extracted from high O₃ plumes between 10:00 AM local time and the hour after model-predicted maximum O₃ concentrations on 31 high O₃ days. A description of plume identification is provided in Sect. 2. HDDM sensitivities to a given emitted precursor (e.g., NO_x) are defined as the maximum O₃ change achieved with a 100% reduction in that precursor with a 0% reduction in the other precursor (e.g., VOC).

Monitor-specific responses to the 2xVOC perturbation were spatially heterogeneous (Fig. 6). Non-EGU VOC sensitivity increased at all monitors by 53–101%, while area VOC increased by 52–71%. Non-EGU NO_x sensitivity also increased consistently across the monitors (20–72%), with the largest increases at CLTN (+72%), PRKP (+66%), and HLAA (+64%). In contrast, marine NO_x exhibited a mixed response with increases at some monitors, but decreasing substantially at BYTE



365 (–46%) and GALV (–71%). This result is consistent with its overall decrease in Fig. 8. Other NO_x source groups generally showed smaller increases, whereas non-road VOC sensitivity decreased at all monitors (21–35%). These results indicate that the effects of increased VOC emissions on O₃ sensitivity are both source- and location-dependent, with the most consistent enhancements occurring for non-EGU and area VOC and non-EGU NO_x.

Overall, the 2xVOC simulation indicates that uncertainty in anthropogenic VOC emissions can substantially affect both the
370 magnitude and relative importance of source-specific O₃ sensitivities. The largest responses were observed for non-EGU VOC and non-EGU NO_x. The decrease in marine NO_x sensitivity and variable responses among other source categories, however, demonstrate that increased VOC availability does not uniformly enhance NO_x and VOC sensitivity. Instead, the response is source- and location-dependent, reflecting nonlinear interactions between NO_x and VOC emissions. Despite these changes, the five source categories with the largest mean sensitivities in the base case remained the five most influential categories in
375 the 2xVOC simulation, although their magnitudes and relative rankings changed.

4. Conclusion

This analysis demonstrates that the HGB regulatory model predicts O₃ formation that is governed by highly nonlinear and spatially heterogeneous responses to NO_x and VOC emissions. Across the 31 model-predicted high O₃ days, the most influential emission categories indicate that both industrial and mobile/area sources contribute significantly to O₃ formation.
380 These results, along with previous studies, provide further evidence that O₃ sensitivity in HGB is not uniform in space or time, and that emission source dominance varies by time and location (Xiao et al., 2010; Koo et al., 2008). Furthermore, the same emission source group can produce different O₃ responses under different meteorological conditions. Importantly, NO_x titration and strong second-order NO_x effects indicate that first-order sensitivity metrics alone are insufficient for fully characterizing O₃ response, particularly for NO_x control strategies. These findings are consistent with previous HDDM studies
385 highlighting the importance of second-order sensitivities (Xiao et al., 2010). These findings suggest O₃ mitigation strategies should be source- and location-specific to prioritize the most influential sectors. Further, gaps in the emission inventory altered both the magnitude and ranking of O₃ sensitivities, introducing uncertainty in identifying effective control strategies. Overall, the modeling suggests future work on addressing gaps in the emission inventories and further investigation of regionally differentiated implementation of control sources.

390 Data availability

CAMx input files are available at <https://www.tceq.texas.gov/airquality/airmod/data/tx2019>. CAMx concentration and HDDM sensitivity output files are available at <https://doi.org/10.5281/zenodo.23195563> for both the base model run and the 2xVOC scenario, along with emissions input files for the 2xVOC scenario. See the CAMx User's Guide for more information



about the model input and output files (https://www.camx.com/files/camxusersguide_v7.20.pdf). All files are saved in netCDF
395 format.

Author contributions

EC, CO, and WV conceptualized the study. AV and YG conducted the modeling, and all coauthors contributed to formal analysis and investigation. EC, CO, and YG created the visualizations. EC led the writing efforts, and all coauthors helped edit and review.

400 Competing interests

The authors declare that they have no conflict of interest.

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