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Examining TROPOMI formaldehyde to nitrogen dioxide ratios in the Lake Michigan region: implications for ozone exceedances

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Table S1. Dates of 2019, 2020, and 2021 ozone (O_3) exceedance days in the Chicago-Naperville-Elgin, Illinois-Indiana-Wisconsin, core-based statistical area (hereafter the Chicago metropolitan area, or "CMA" for short). An O_3 exceedance day is defined as having at least one ground monitor in the U.S. EPA Air Quality System (AQS) measuring a maximum daily 8-hour average (MDA8) O_3 value greater than 70 parts per billion (ppb). The "# stations" column indicates how many monitors in the CMA measured an exceedance.

2019		
Dates	**# stations**	**Day of week**
5-Jun	4	Wed
26-Jun	1	Wed
28-Jun	1	Fri
29-Jun	6	Sat
1-Jul	1	Mon
3-Jul	3	Wed
5-Jul	1	Fri
8-Jul	1	Mon
9-Jul	12	Tue
13-Jul	1	Sat
25-Jul	2	Thu
2-Aug	2	Fri
3-Aug	3	Sat
Total: 13 days		
10 weekdays, 3 weekends		

2020		
Dates	**# stations**	**Day of week**
4-Jun	5	Thu
5-Jun	10	Fri
8-Jun	3	Mon
16-Jun	2	Tue
17-Jun	15	Wed
18-Jun	20	Thu
19-Jun	16	Fri
27-Jun	2	Sat
1-Jul	4	Wed
2-Jul	1	Thu
3-Jul	14	Fri
6-Jul	14	Mon
7-Jul	6	Tue
8-Jul	3	Wed
9-Jul	4	Thu
17-Jul	2	Fri
25-Jul	5	Sat
7-Aug	1	Fri
15-Aug	4	Sat
21-Aug	3	Fri
Total: 20 days		
17 weekdays, 3 weekends		

2021		
Dates	**# stations**	**Day of week**
22-May	1	Sat
3-Jun	14	Thu
4-Jun	5	Fri
11-Jun	5	Fri
17-Jun	5	Thu
18-Jun	8	Fri
20-Jul	5	Tue
22-Jul	6	Thu
23-Jul	4	Fri
26-Jul	2	Mon
27-Jul	1	Tue
28-Jul	5	Wed
4-Aug	3	Wed
7-Aug	2	Sat
23-Aug	1	Mon
25-Aug	6	Wed
26-Aug	4	Thu
27-Aug	4	Fri
13-Sep	1	Mon
1-Oct	3	Fri
Total: 20 days		
18 weekdays, 2 weekends		

Table S2. Distribution of the number of CMA O_3 exceedance days by year and day of week. The last two columns report the percentage of exceedances that occurred on weekdays and weekends for each row's time period.

CMA ozone exceedance day of week distribution										
Year(s)	**Monday**	**Tuesday**	**Wednesday**	**Thursday**	**Friday**	**Saturday**	**Sunday**	**All days**	**Weekdays**	**Weekends**
2019	2	1	3	1	3	3	0	13	77 %	23 %
2020	2	2	3	4	6	3	0	20	85 %	15 %
2021	3	2	3	4	6	2	0	20	90 %	10 %
All years	7	5	9	9	15	8	0	53	85 %	15 %

Table S3. Kolmogorov-Smirnov (K-S) test results for comparison of the TROPOMI ozone season and CMA exceedance day composites. For each variable, 1000 K-S tests were performed using a random subsampling approach at the 98 % confidence level. In the "median p-value" column, values <0.001 are represented as 0, and bolded values indicate overall statistically significant results (median p-value <0.020). The "wind divergence – tails" variable refers to only subsampling values greater or less than one standard deviation from the mean wind divergence value. *Sig. diff. = significant difference.

2-subsample K-S test results: ozone season vs. CMA exceedance days				
Variable	**Percentage of tests with a *sig. diff.**	**Median p-value**	**Full sample size**	**Subsample size**
HCHO bias corrected	100 %	**0.000**	1146	286
NO_2	100 %	**0.000**	1146	286
FNR bias corrected	100 %	**0.000**	1146	286
Wind divergence	1.8 %	0.117	880	220
Wind divergence – tails	97.1 %	**0.001**	241	60
2-m temperature	100 %	**0.000**	1242	310

Table S4. Kolmogorov-Smirnov (K-S) test results for comparison of the weekday and weekend composites. For each variable, 1000 K-S tests were performed using a random subsampling approach at the 98 % confidence level. In the "median p-value" column, values <0.001 are represented as 0, and bolded values indicate overall statistically significant results (median p-value <0.020). The "wind divergence – tails" variable refers to only subsampling values greater or less than one standard deviation from the mean wind divergence value. *Sig. diff. = significant difference.

2-subsample K-S test results: weekdays vs. weekends				
Variable	**Percentage of tests with a *sig. diff.**	**Median p-value**	**Full sample size**	**Subsample size**
HCHO bias corrected	100 %	**0.000**	1146	286
NO_2	71.9 %	**0.013**	1146	286
FNR bias corrected	100 %	**0.000**	1146	286
Wind divergence	0 %	0.607	880	220
Wind divergence – tails	0 %	0.821	241	60
2-m temperature	65.5 %	0.023	1242	310

Table S5. Comparison of U.S. EPA Air Quality System (AQS) 2019–2021 mean surface NO_2 measurements at 13:00 local time during the ozone season (OS) and during CMA ozone exceedance days (Ex). Both AQS surface measurements and TROPOMI column observations (**Fig. 3c** in the main text) indicate an average percent increase in NO_2 levels of approximately 20 % on exceedance days relative to all days across the ozone season. *Site identifiers take the form of "X (a_b_c)" where X is the letter indicating the location of the AQS surface monitor in **Fig. S1** below, and a = state code, b = county code, and c = site number in the AQS system. These sites were chosen for analysis because they had data during the entire 2019–2021 study period. AQS data used in this analysis were downloaded from https://www.epa.gov/outdoor-air-quality-data.

AQS surface NO_2: ozone season vs. CMA exceedance days

Site*	Ozone season mean (OS) [ppb]	Exceedance days mean (Ex) [ppb]	Ex – OS [ppb]	Ex % change from OS
A (17_31_119)	13.01	17.69	+4.68	+36 %
B (17_31_219)	8.94	10.21	+1.27	+14 %
C (17_31_3103)	10.77	13.16	+2.39	+22 %
D (17_31_4002)	6.65	7.20	+0.55	+8 %
E (17_31_76)	5.65	5.98	+0.33	+6 %
F (18_141_15)	2.17	1.45	-0.72	-33 %
G (18_89_22)	2.71	2.76	+0.05	+2 %
H (55_79_56)	7.69	9.04	+1.35	+18 %
All sites	**7.27**	**8.62**	**+1.35**	**+19 %**
TROPOMI composite – full domain	**1.75 molec. cm^{-2}**	**2.11 molec. cm^{-2}**	**+0.36 molec. cm^{-2}**	**+21 %**

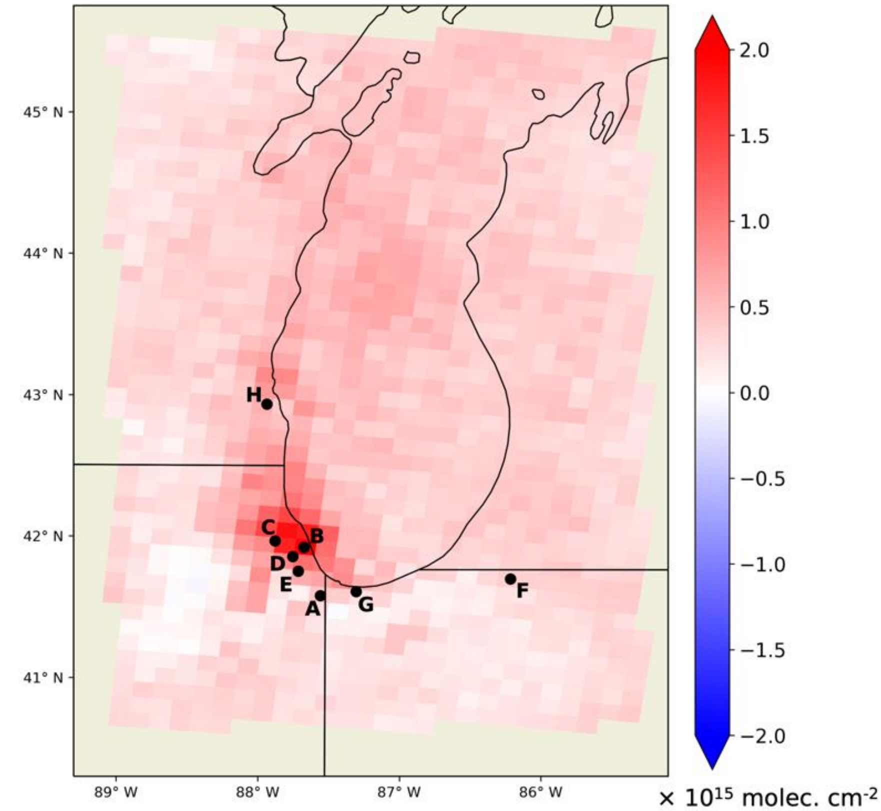

Figure S1. Difference between the OS and Ex TROPOMI NO_2 composites (Ex – OS) with the locations of the AQS surface monitors from **Table S5** denoted by black circles.

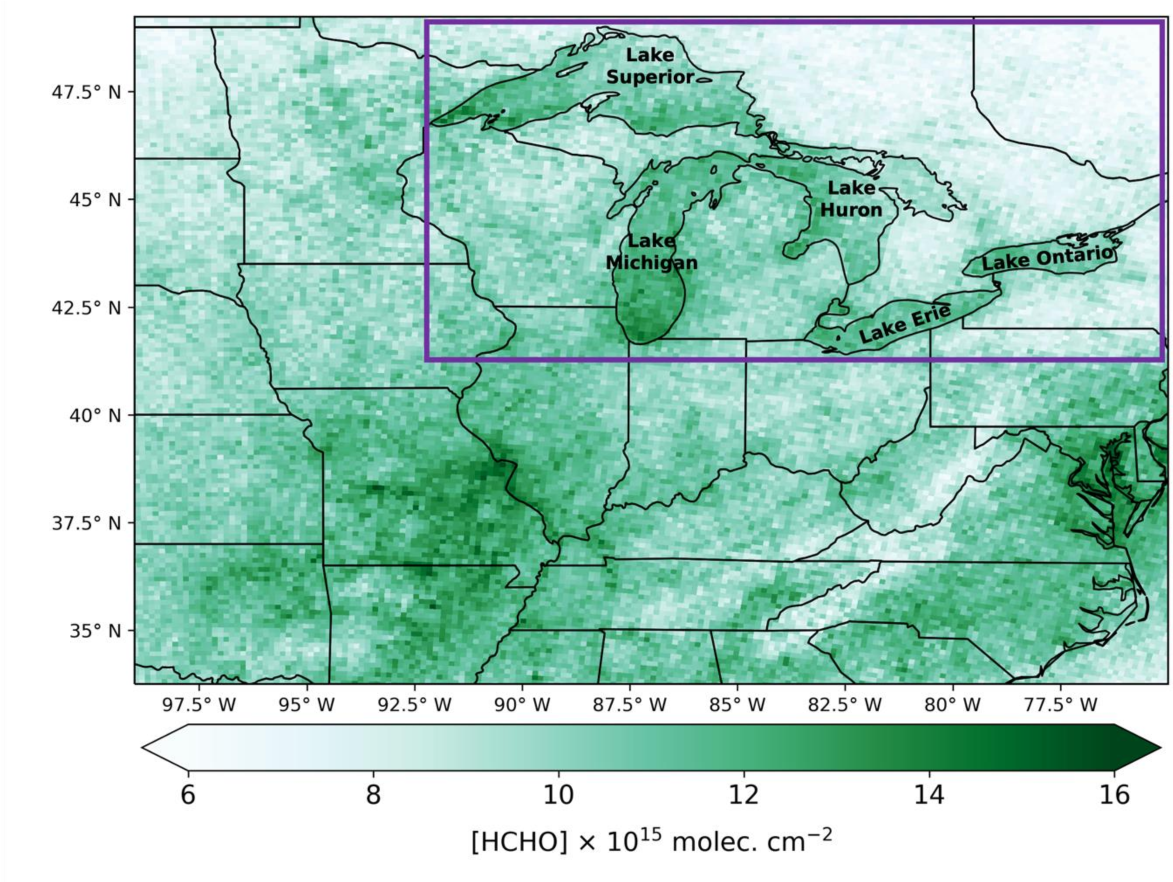

Figure S2. TROPOMI-derived composite of 2019–2021 mean tropospheric HCHO vertical column densities (VCDs) in the Lake Michigan region during CMA ozone exceedance days. As seen in the purple box, higher HCHO VCDs are seen over the surfaces of the Great Lakes compared to the surrounding land areas.

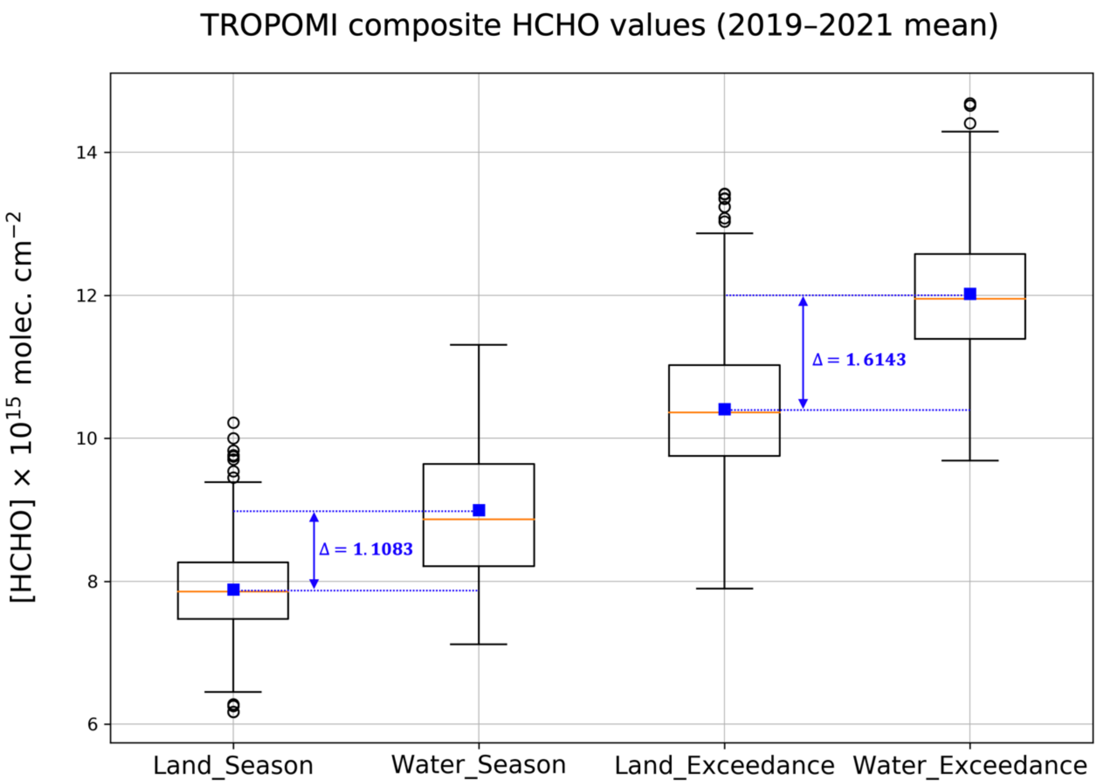

Figure S3. Boxplot distributions of TROPOMI HCHO vertical column densities (VCDs) for the O_3 season and CMA exceedance day composites separated by over land and over water values. The median of each distribution is represented by an orange horizontal line, the mean is denoted by a blue square, and outliers are represented by circles outline in black. The difference in means between the over land and over water values (Δ) is the "absolute over water bias" value in **Table S6** below.

Table S6. HCHO absolute and relative over water bias values for the O_3 season and CMA exceedance day composites. The absolute over water bias value is calculated by subtracting the mean HCHO over land value from the mean HCHO over water value. The relative over water bias value is calculated as $(\frac{HCHO_{water\_mean} - HCHO_{land\_mean}}{HCHO_{land\_mean}}) \times 100\ \%$.

Composite category	Absolute over water bias	Relative over water bias
Ozone season	1.1083×10^{15} molec. cm^{-2}	+14.05 %
CMA exceedance days	1.6143×10^{15} molec. cm^{-2}	+15.51 %

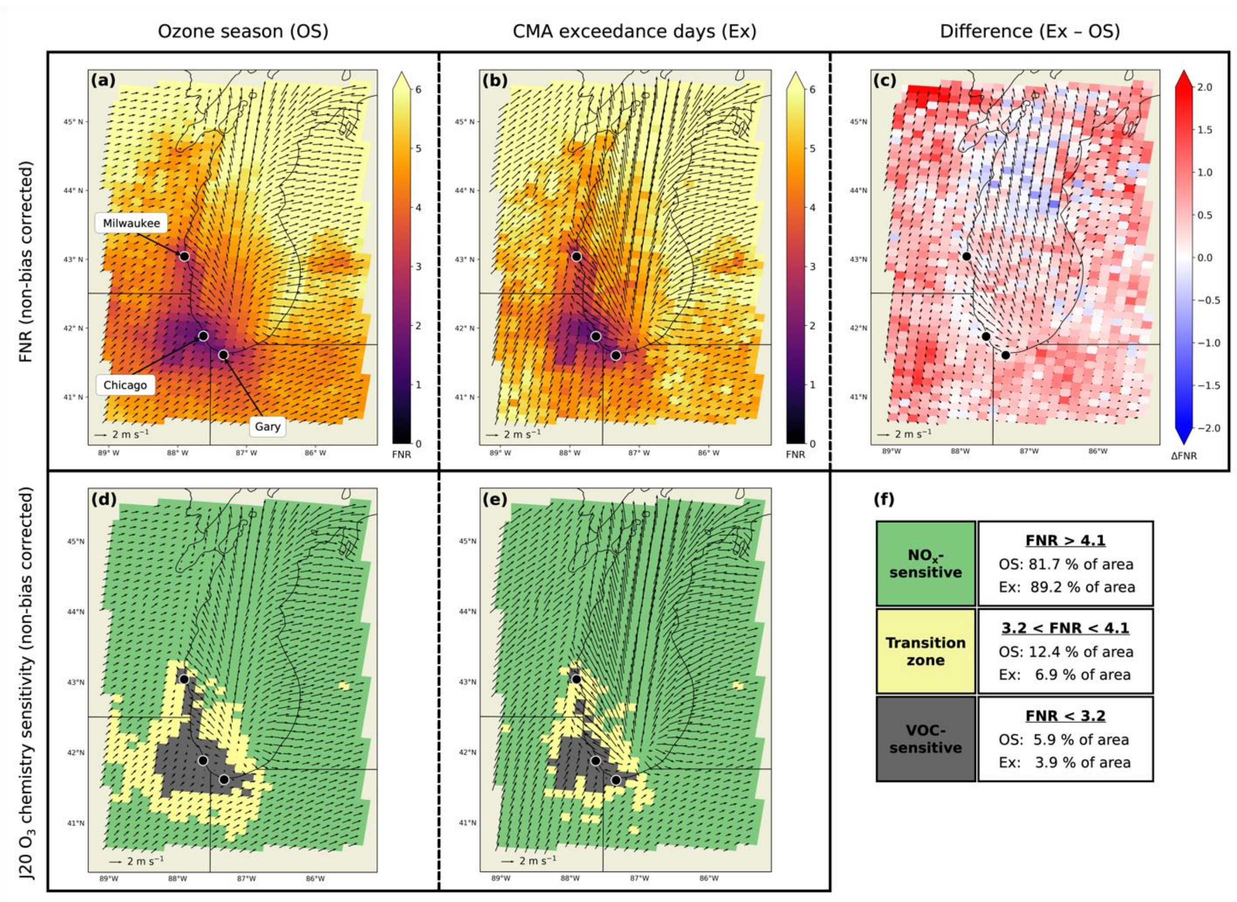

Figure S4. TROPOMI-derived 2019–2021 FNR values calculated using non-bias corrected HCHO values in the Lake Michigan region during: (a) the ozone season (OS), (b) CMA exceedance days (Ex), and (c) the difference between them (Ex – OS). Jin et al. (2020; "J20")* threshold interpretation of 2019–2021 ozone chemistry sensitivity using non-bias corrected FNR values during: (d) the ozone season, (e) CMA exceedance days, and (f) the percent of the domain area classified as each J20 sensitivity regime. Mean 10-meter winds are represented by arrows.

*Jin, X., Fiore, A. M., Boersma, K. F., De Smedt, I., and Valin, L.: Inferring changes in summertime surface ozone–NO_x–VOC chemistry over U.S. urban areas from two decades of satellite and ground-based observations, Environ. Sci. Tech., 54(11), 6518–6529, https://doi.org/10.1021/acs.est.9b07785, 2020.

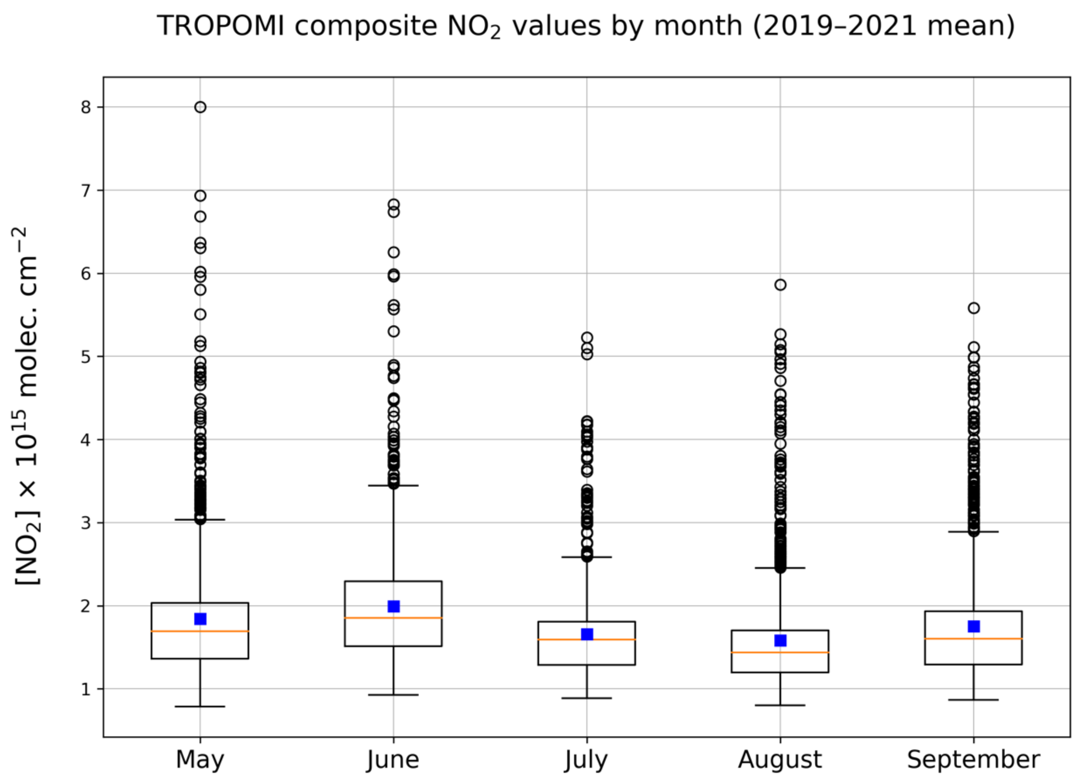

Figure S5. Boxplot distributions of 2019–2021 mean TROPOMI NO_2 composite values for each month of the ozone season. Means of the distributions are denoted by a blue square, medians are denoted by an orange horizontal line, and outliers are denoted by circles outlined in black. The outlier values mostly represent grid boxes in the Chicago metropolitan area where NO_2 VCDs are much higher than the rest of the study domain. NO_2 VCDs do not appear to exhibit a strong intra-seasonal cycle during the ozone season in the Lake Michigan region.

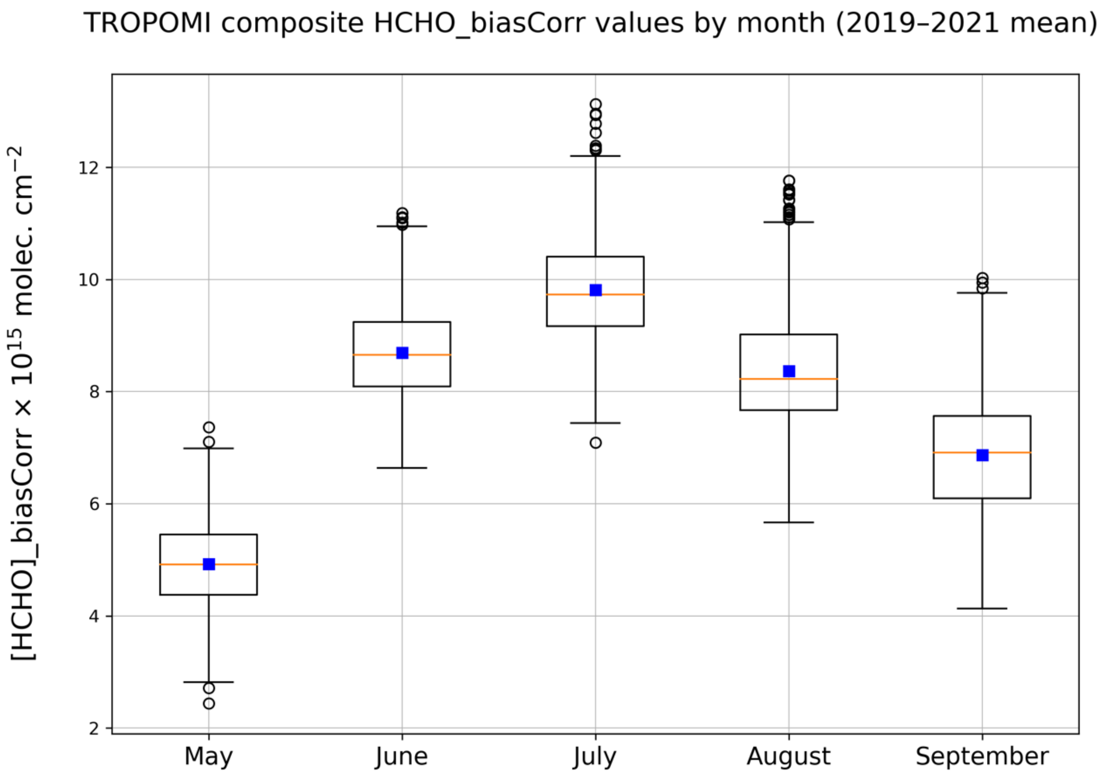

Figure S6. Boxplot distributions of 2019–2021 mean TROPOMI bias corrected HCHO composite values for each month of the ozone season. Means of the distributions are denoted by a blue square, medians are denoted by an orange horizontal line, and outliers are denoted by circles outlined in black. Both HCHO VCDs and 2-meter air temperatures (**Fig. S7** below) in the Lake Michigan region exhibit a strong intra-seasonal cycle during the ozone season.

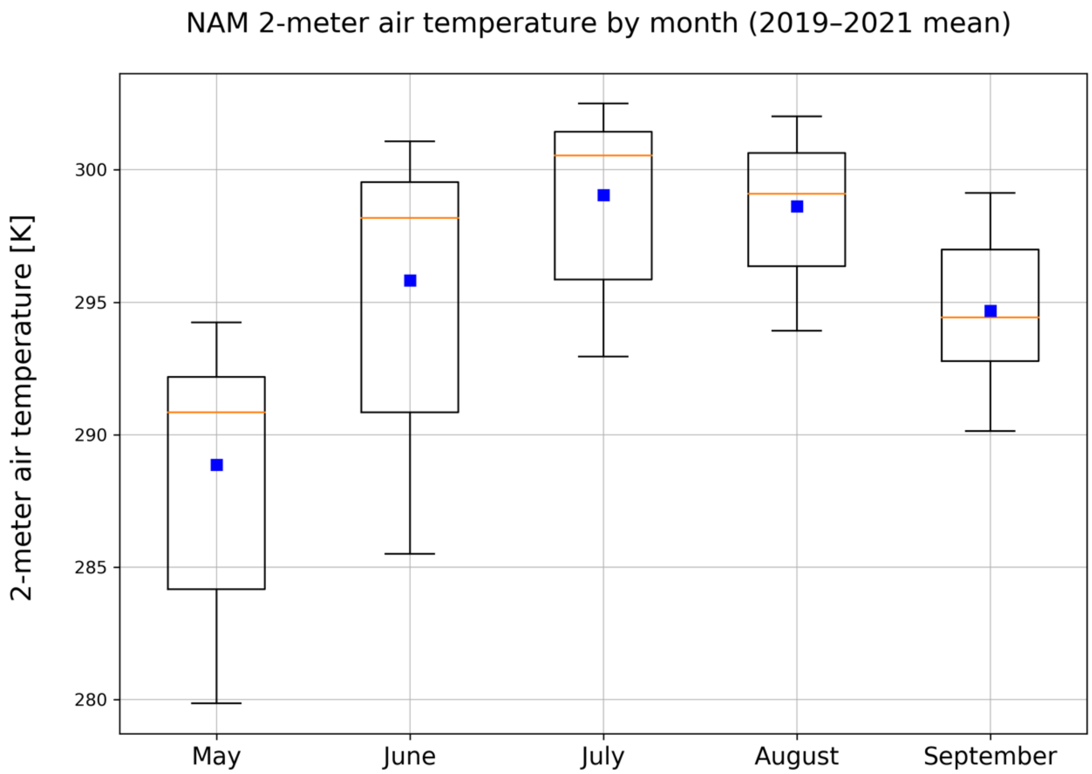

Figure S7. Boxplot distributions of 2019–2021 mean North American Mesoscale (NAM) analysis 2-meter air temperature composite values for each month of the ozone season. Means of the distributions are denoted by a blue square and medians are denoted by an orange horizontal line. Both 2-meter air temperatures and HCHO VCDs (**Fig. S6** above) in the Lake Michigan region exhibit a strong intra-seasonal cycle during the ozone season.

Table S7. Approximations of how much the mean difference between the ozone season and CMA exceedance day composites for NO_2 (**Fig. 3c**), HCHO (**Fig. 5c**), and 2-meter air temperature (**Fig. 2f**) are due to monthly differences during the ozone season (intra-seasonal changes) versus environmental differences during ozone exceedance days (episodic events). The approximation methodology is explained in detail below the table.

	NO_2 [× 10^{15} molec. cm^{-2}]	HCHO [× 10^{15} molec. cm^{-2}]	Temperature [K]
(a) June–August mean	1.747 (Fig. S5)	8.96 (Fig. S6)	297.83 (Fig. S7)
(b) May–September mean	1.766 (Fig. S5)	7.73 (Fig. S6)	295.41 (Fig. S7)
(c) Difference [a – b]	-0.02	1.22	2.42
(d) Mean difference between OS and Ex composites [Ex – OS]	0.37 (Fig. 3c)	2.52 (Fig. 5c)	4.31 (Fig. 2f)
	NO_2	**HCHO**	**Temperature**
(e) Percent of (d) due to monthly differences during the ozone season (intra-seasonal changes) approximated as: $[(e) = \frac{c}{d} \times 100\,\%]$ if (e) < 0 %, report as 0 %; if (e) > 100 %, report as 100 %	0 %	48 %	56 %
(f) Percent of (d) due to exceedance day differences (episodic events) approximated as: $[(f) = 100\,\% - (e)]$	100 %	52 %	44 %

Methodology description: Because 94 % of CMA ozone exceedance days occur in June, July, and August (**Table S1**), it is possible that the differences we see between the ozone season and CMA exceedance day composites are due to intra-seasonal changes. More specifically, the inclusion of May and September data in the ozone season composite may be the cause behind the composite differences because the data used in the CMA exceedance day composites mostly comes from June–August TROPOMI observations. To approximate the effect of intra-seasonal changes, we created boxplot distributions by month for TROPOMI NO_2 and HCHO composite values and NAM temperature composite values. Then we compared the June–August mean values (when most exceedances occur) to the May–September mean values (entire ozone season). We estimate that the difference between the June–August mean and the May–September mean is the amount of change we expect to see in our difference composites (**Figs. 2f, 3c,** and **5c** in the main manuscript) due to intra-seasonal changes. Finally, we compared this difference to the mean difference we see in the main text difference composites (**Figs. 2f, 3c,** and **5c**). Dividing these two values gives us an estimate of how much (%) of the change shown in our main text figures are due to intra-seasonal differences, while the remaining amount of difference we prescribe as due to changes in environmental conditions on exceedance days (episodic events).

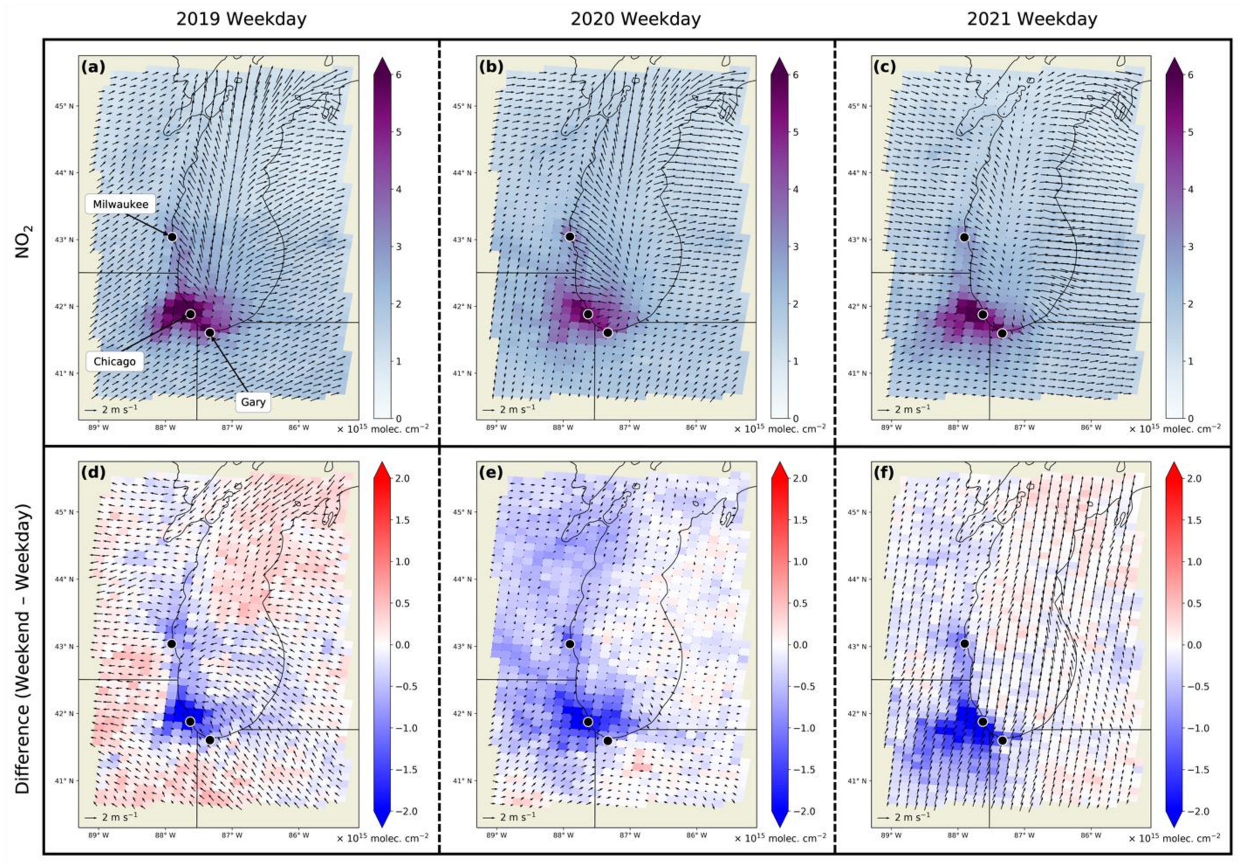

Figure S8. TROPOMI-derived composites of mean weekday tropospheric NO_2 VCDs in the Lake Michigan region during: (a) 2019, (b) 2020, and (c) 2021. The difference between weekday and weekend tropospheric NO_2 VCDs in the Lake Michigan region during: (d) 2019, (e) 2020, and (f) 2021. Mean 10-meter winds are represented by arrows.

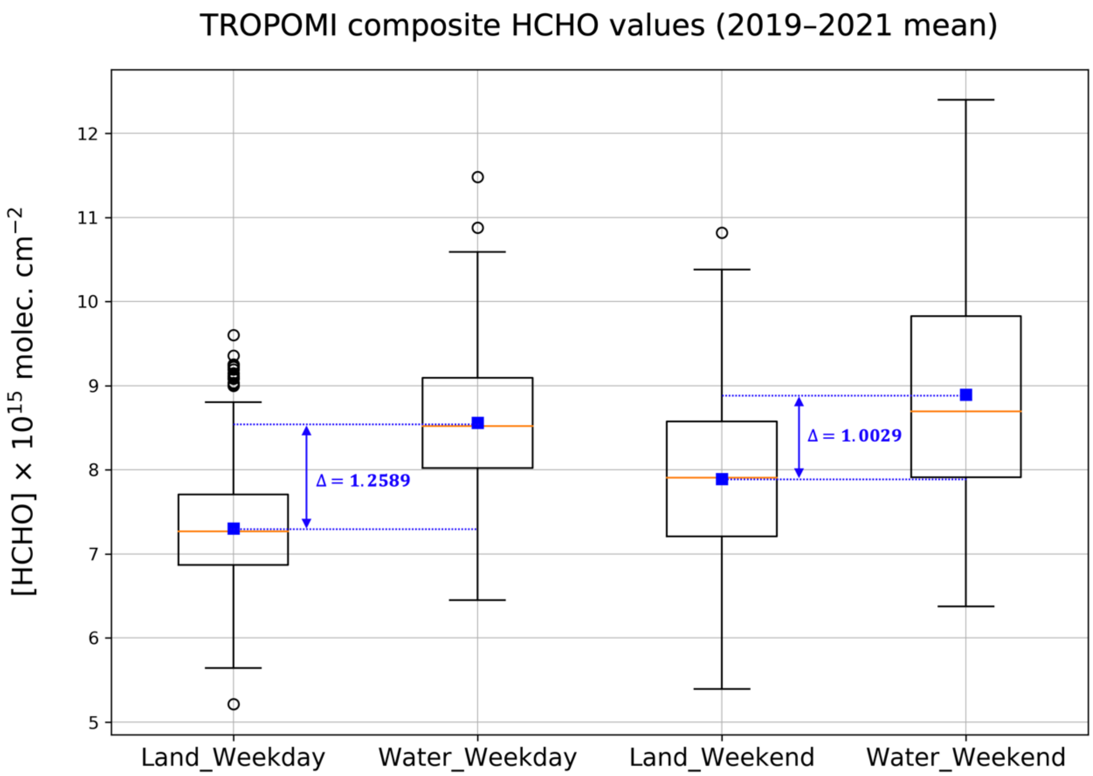

Figure S9. Boxplot distributions of TROPOMI HCHO VCDs for the weekday and weekend composites separated by over land and over water values. The median of each distribution is represented by an orange horizontal line, the mean is denoted by a blue square, and outliers are represented by circles outline in black. The difference in means between the over land and over water values (Δ) is the "absolute over water bias" value in **Table S8** below.

Table S8. HCHO absolute and relative over water bias values for the weekday and weekend composites. The absolute over water bias value is calculated by subtracting the mean HCHO over land value from the mean HCHO over water value. The relative over water bias value is calculated as $(\frac{HCHO_{water\_mean} - HCHO_{land\_mean}}{HCHO_{land\_mean}}) \times 100\ \%$.

Composite category	Absolute over water bias	Relative over water bias
Weekday	1.2589×10^{15} molec. cm^{-2}	+17.2 %
Weekend	1.0029×10^{15} molec. cm^{-2}	+12.7 %

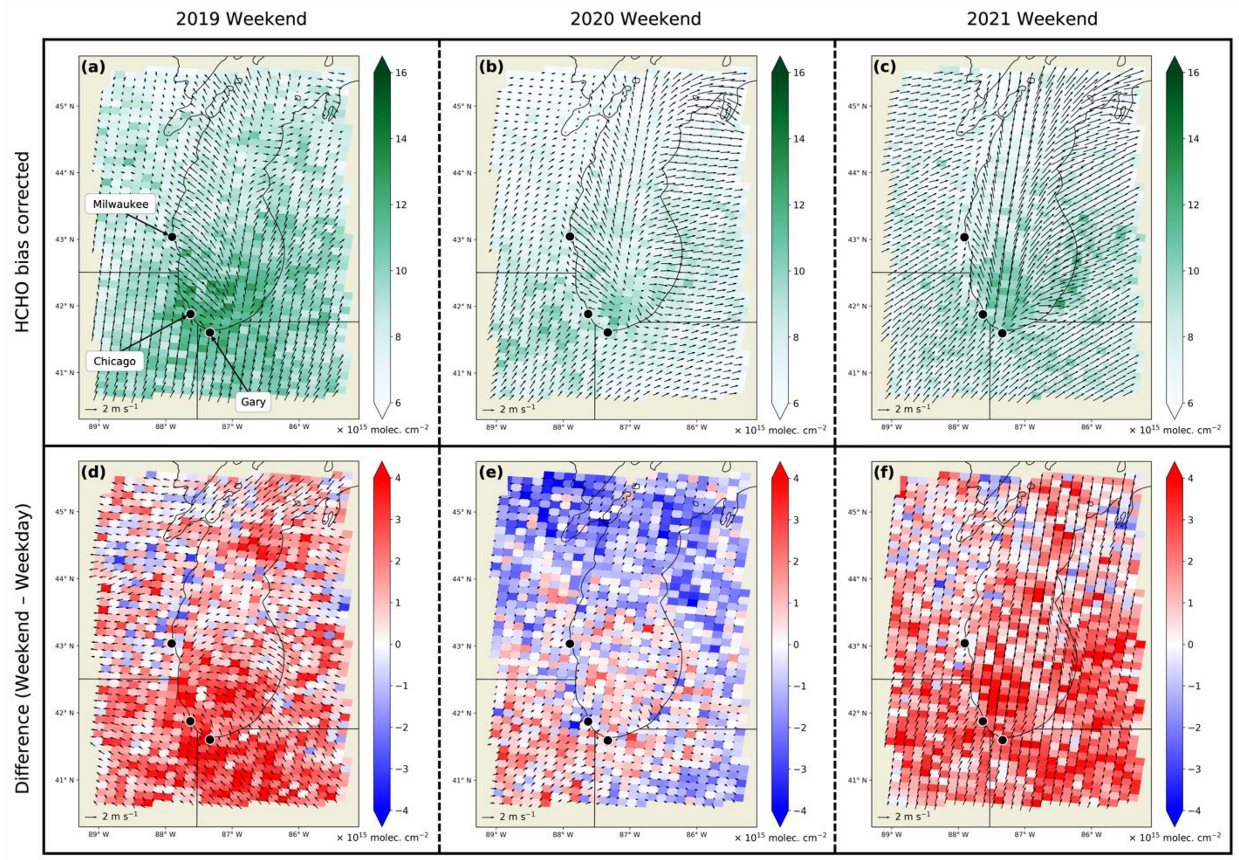

Figure S10. TROPOMI-derived composites of mean bias corrected weekend tropospheric HCHO VCDs in the Lake Michigan region during: (a) 2019, (b) 2020, and (c) 2021. The difference between bias corrected weekday and weekend tropospheric HCHO VCDs in the Lake Michigan region during: (d) 2019, (e) 2020, and (f) 2021. Mean 10-meter winds are represented by arrows.

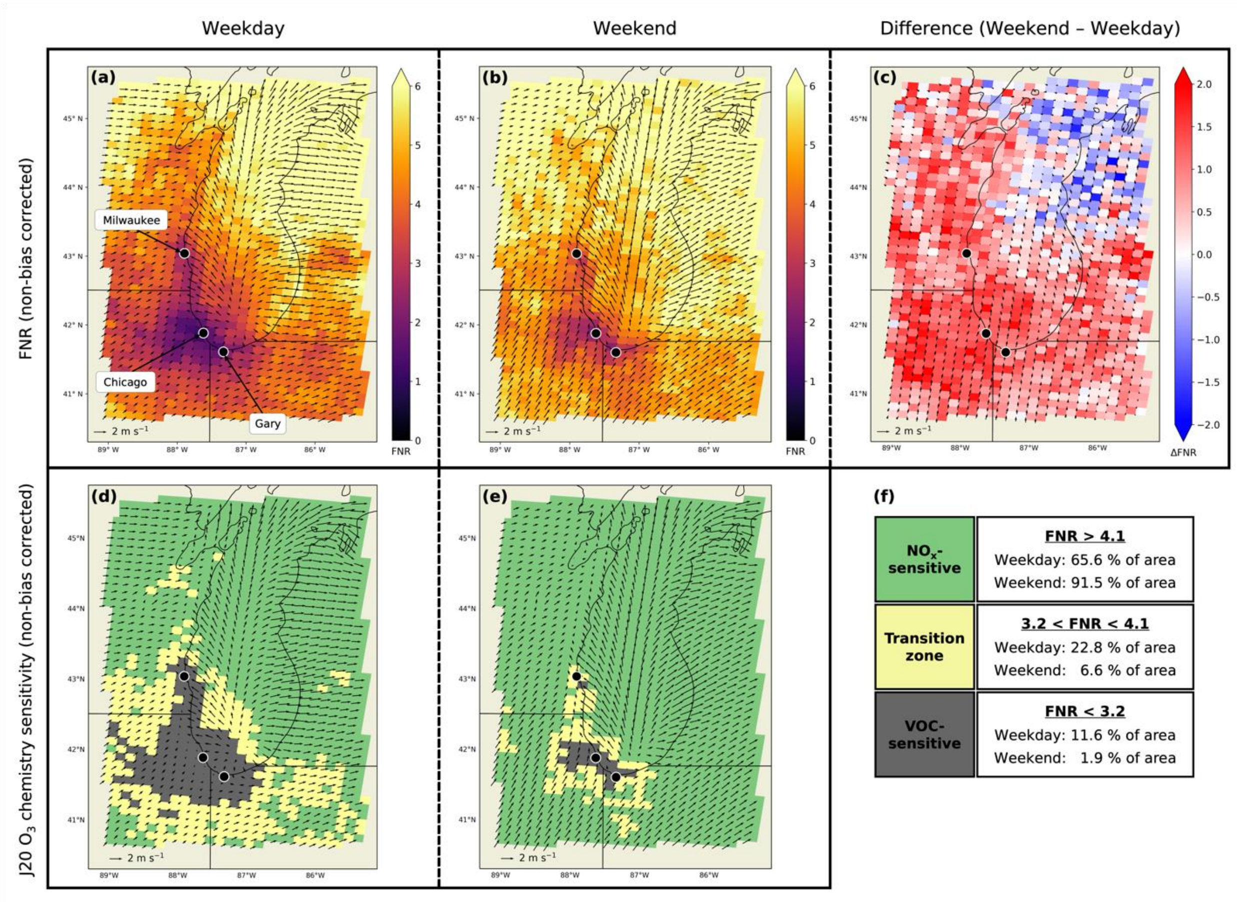

Figure S11. TROPOMI-derived 2019–2021 FNR values calculated using non-bias corrected HCHO values in the Lake Michigan region during: (a) weekdays, (b) weekends, and (c) the difference between them (weekend – weekday). J20 threshold interpretation of 2019–2021 ozone chemistry sensitivity using non-bias corrected FNR values during: (d) weekdays, (e) weekends, and (f) the percent of the domain area classified as each J20 sensitivity regime. Mean 10-meter winds are represented by arrows.