Air pollution episodes in the Pacific Northwest

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Introduction

Ground level ozone (O₃) adversely impacts public health,^{1,2} and can damage ecosystems.^{3,4} Ambient O₃ is formed in the atmosphere by a complex system of reactions between gaseous oxides of nitrogen (NO_x), volatile organic compounds (VOC), carbon monoxide (CO) and sunlight. Historically, controls on NO_x and VOC emissions from mobile, electric generation, chemical solvents and other industries have succeeded in reducing ambient O₃ pollution.⁵

Recently, the Environmental Protection Agency (EPA) promulgated a revised O₃ National Ambient Air Quality Standard (NAAQS), requiring the annual 4th highest daily maximum of 8-hr average O₃, averaged over three years, to be less than 70 ppb. In the case where a monitor does not attain the NAAQS, the local and state agencies and the EPA are required to define a non-attainment area encompassing sources of emissions that likely influence the high pollution at the monitor to a significant degree. To estimate the impact of emissions from various sectors and regions on pollution, Eulerian grid-based chemical transport models (CTMs) such the Community Multi-scale Air Quality (CMAQ)⁶ model and the Comprehensive Air quality Model with extensions (CAMx)⁷ are frequently employed. The Pacific Northwest, an area characterized by complex terrain and meteorology, is one such region where CTMs have been used to understand the complexities of photochemical smog formation and response to control.⁸⁻¹² Like many regions of the U.S., O₃ pollution in the Pacific Northwest has decreased substantially over the past decade and as of 2016, the Seattle-Tacoma metropolitan area is in attainment of the 70 ppb O₃ NAAQS. However, the region has a history of high ozone episodes ¹³ and between 2012 and 2015, different monitors the Seattle-Tacoma area saw a total of 13 instances where O₃ concentrations exceeded 70 ppb.

The nonlinear relationship between O_3 pollution and its precursor emissions leads to difficulties in developing pollution reduction strategies and controls. Developments in CTMs, such as the decoupled direct method in three dimensions (DDM-3D), have benefited policymakers by directly and efficiently quantifying the impacts of emission sources on air pollutants, even from small sources.^{14–16} DDM, which is implemented in CMAQ, calculates the sensitivity of air pollutants to small changes in precursor emissions and is accurate for up to 30% perturbations from the base case emissions.^{15,17} In a previous work, Tsimpidi et al.¹² used DDM to quantify the sensitivity of O_3 and particulate matter (aerodynamic diameter < 2.5 µm; PM_{2.5}) in the Puget Sound area to precursor emissions of NO_x and VOCs from onroad mobile, elevated point, nonroad, area and biogenic sources during a high O_3 episode in 2006. Tsimpidi et al. found that, due to the chemical composition of the atmosphere and amount of NO_x and VOC emissions during that time, VOC or VOC plus NO_x controls would lead to O_3 reductions in the Seattle-Tacoma metropolitan regions while NO_x controls alone could increase O_3 in the metropolitan area.

In the present work, we investigate two recent O_3 NAAQS exceedance episodes in the Puget Sound region using CMAQ with DDM to quantify impacts of precursor emissions. To develop an effective and efficient control strategy, policymakers need to know not only which emission sectors to control but where geographically to implement controls. Rather than focus our analysis solely on the sensitivities of O_3 to emissions from each source sector, we also quantify the impacts of emissions from different

counties in the region on O_3 pollution, and include trajectory analysis to target periods to capture specific source regions. This type of analysis coincides with the need to implement effective pollution control measures that may vary spatially and the legal requirement that non-attainment areas be defined.

Modelling Approach

Ozone concentration and sensitivity to precursor emissions were simulated using a suite of models to process meteorology, allocate emissions and simulate chemistry and transport of chemicals in the atmosphere for two multiday episodes.

Episodes

Two recent high ozone episodes (28 July to 4 August, 2015 and 8 July to 14 July, 2014) were chosen based on the following criteria: Ozone concentrations exceeded the 8-hr NAAQS at one or more monitors, most notably the Enumclaw monitor, located outside of the Seattle-Tacoma metropolitan area and is often subject to the highest monitored ozone levels in the region; there were no significant wildfire events that would significantly impact ozone in the Puget Sound region; and that the meteorological model used (Weather Research and Forecasting, WRF)¹⁸ was able to accurately characterize the meteorology at Enumclaw and other monitors in the domain. We also used HYSPLIT¹⁹ to calculate 24-hour back trajectories from the Enumclaw monitor and forward trajectories originating in northwestern Washington (Figure 1 and Figure 2) to specifically address the question of the potential impact of sources located in that region (e.g., refineries) on high levels of ozone at Enumclaw. These air masses will also capture be impacted by Canadian emissions. During the 2014 episode, on the day when peak ozone was monitored at Enumclaw, HYSPLIT back trajectories show air masses reaching the Enumclaw monitor were generally transported from the West and South West, from the direction of Olympia and Tacoma, WA. During that time, air parcels originating in northwestern Washington were transported north, away from Seattle and Enumclaw monitors. Similar trajectories were seen the next day, July 11th, when observed O_3 was still relatively high (not shown). On the peak ozone day during the 2015 episode, air parcels originating from near the oil refineries were transported south, toward Seattle and the Enumclaw monitor. Back-trajectories for the following day, July 31st, 2015, show air parcels originating from west of Enumclaw. Two other episodes were considered (2 July to 10 July, 2012 and 8 August to 19 August, 2012) but were ultimately not chosen because they were not recent and because smoke from regional wildfires was observed at several area monitors, thereby complicating the ozone analysis.



Figure 1 HYSPLIT 24 hour back-trajectories with parcels ending at the Enumclaw monitor (47.14 N° 121.94° W) using NARR meteorology. Back-trajectories are calculated for parcels arriving at the Enumclaw monitor at 06:00 (light blue), 12:00 (green), 18:00 (dark blue) and 24:00 (red) on the peak O3 days, 7/12/2014 (left) and 7/30/2015 (right).



Figure 2 HYSPLIT 24 hour forward trajectories with parcels beginning near an oil refinery (48.80 N° 122.53° W) using NARR meteorology. Forward trajectories are calculated for parcels arriving leaving the refinery at 06:00 (light blue), 12:00 (green), 18:00 (dark blue) and 24:00 (red) on the peak O3 days, 7/12/2014 (left) and 7/30/2015 (right).

Air Quality

CMAQ (version 5.0.2)²⁰ model was used to simulate air pollutant chemistry and transport. Gas phase chemistry is modeled using the CB05 mechanism.²¹ CMAQ is run on a 4km grid resolution domain spanning 300 km by 504 km. The modeling domain was derived from the 4km nested WRF modeling domain discussed in the next section. The domain has 13 vertical layers reaching up to ~16 km above the surface, with 6 layers below 1 km. We expanded the 4km domain from Tsimpidi et al., extending the boundary north to include Vancouver, BC and south to include Portland, OR and east so that the domain boundary lays to the east of the Cascade Mountains (Figure 3).

Boundary conditions for the 4km domain are interpolated from concentration fields simulated by the Model for Ozone and Related Chemical Tracers (MOZART-4)²² (<u>http://www.acom.ucar.edu/wrf-chem/mozart.shtml</u>). A more traditional approach, and the approach used in Tsimpidi et al., is to nest a high resolution domain in larger, coarse resolution domains, and use the CMAQ default static boundary

conditions that are typical of a "clean" background to drive the largest coarse resolution domain. In the present study, however, we decrease the computational cost by removing the additional coarse domain simulations. To ensure that major emission sources are not excluded in the one domain approach, the grid is designed such that all major cities near to Seattle are included in the domain. Also, since the grid resolution of the MOZART concentration fields is coarse (1.9 X 2.5 degrees) compared to our domain we extended the eastern boundary to ensure that the boundary concentrations were interpolated from MOZART grids that represented concentrations east of the Cascade Mountains which block return flow. In other words, for the eastern boundary, we do not interpolate from MOZART grid cells west of the Cascades. The default CMAQ v5.0.2 profile was used to prepare initial conditions. The decoupled direct method in three dimensions (DDM-3D) was used to calculate the sensitivity of O₃ concentrations to the boundary and initial conditions. The sensitivity of daytime O₃ to the boundary condition at the Enumclaw monitor is less than 0.1 ppb per % perturbation in boundary condition species concentration. After two days of spin-up, the sensitivity of O₃ to the initial condition is close to zero.



Figure 3 4km CMAQ modeling domain with urban areas highlighted in blue. O_3 monitors relevant to this study are highlighted and named in red

DDM-3D²³ is used to calculate the first-order sensitivity, S_{ij} , of the concentration of a species to perturbations in an input parameter such as emission rate or initial and boundary condition:

$$S_{ij} = P_j \frac{\partial C_i}{\partial P_i}$$

where C_i is the concentration of species *i* and P_j is the unperturbed input parameter (e.g., emission rate from source *j*). DDM-3D calculates the sensitivity coefficients of all modeled species to a user defined list of input parameters. First-order sensitivities are generally accepted as being accurate for up to 30% change in input parameter. Second-order sensitivities have also been implemented in CMAQ and are accurate for up to 50% perturbation from the base case. The focus of this study is to quantify the firstorder impact of emission sources from various geographic areas, as defined by county boundaries in this study, in the Pacific Northwest on O₃. Rather than calculating the sensitivity of O₃ to every sector in every county, which would be computationally expensive, we grouped some counties with commonalities together (e.g., a large portion of the urban areas surrounding Seattle are located in King, Pierce and Snohomish counties).

	Refinery		Point Source		Other Anth	ropogenic	Biogenic	All Sources, excluding biogenic	All Sources, excluding biogenic
Geographic Area	NOx	VOC	NOx	VOC	NOx	VOC	VOC	NOx	voc
King, Pierce, Snohomish			ENOXpKPS	EVOCpKPS	ENOX_KPS	EVOC_KPS			
Kitsap								ENOX_KIT	EVOC_KIT
Island, Skagit, Whatcom	ENOX_REF	EVOC_REF			ENOX_ISW	EVOC_ISW			
Thurston								ENOX_THU	EVOC_THU
Full Domain							EVOC_BIO		

Table 1 Input parameter list for which sensitivities of O3 are calculated and the names used throughout the paper

Meteorology

We used the Weather Research and Forecasting (WRF version 3.6)¹⁸ model to generate meteorological fields using three nested domains having grid resolutions of 36km, 12km and 4km with the 4km domain centered over the Puget Sound region. The modeling domain uses a Lambert Conformal Projection centered at 40°N, 97°W. The 36, 12, and 4km domains extend over 165 x 129, 49 x 61, and 82 x 133 grid cells, respectively with 38 vertical layers spanning to 10,000 Pa. Initial and boundary conditions were produced from 32km grid resolution North American Regional Reanalysis (NARR) fields provided at 3-hr increments.²⁴ Four-dimensional data assimilation grid nudging was used for the 36 and 12km domains while no nudging was employed for the 4km domain.

The WRF simulation physics were modeled using the following: the Lin et al. ²⁵ scheme was used for microphysics; the RRTMG schemes ²⁶ were used for shortwave and longwave radiation; the revised MM5 Monin-Obukhov ²⁷ scheme is used for surface layer physics; the Unified Noah land-surface model ²⁸ was used; the Yonsei University (YSU) ²⁹ scheme was used for planetary boundary layer; and the effects of shallow and deep cumulus clouds were modeled using the Kain-Fritsch ³⁰ scheme.

The model performance was evaluated against hourly meteorological observations from the United States and Canada (Table 2). The 4km domain model performance was well within the typical range for

air quality model applications.³¹ The model performance at the Indian Hill weather station was evaluated independently to examine the meteorological fields specifically at a higher elevation characteristic of regional airflow. The model performed well at the Indian Hill site although the surface temperature bias for the 2015 was slightly outside the typical range reported by Emery et al (within 0.5 K).³¹ The hourly WRF outputs were processed for CMAQ using the Meteorology-Chemistry Interface Processor (MCIP version 3.6).³²

Table 2 WRF model	performance	evaluation	metrics for	or the	observations	in the	entire	4km	domain	and a	at the	e Indian	Hill
weather station													

		Wind Speed		Wind Direction		Air Temperature		Surface Humidity		
		Bias	RMSE	Bias Gross Error		Bias	RMSE	Bias	Gross Error	
Monitors	Episode	(m sec⁻¹)	(m sec⁻¹)	(degree)	(degree)	(K)	(K)	(g kg⁻¹)	(g kg⁻¹)	
All Sites	2015	-0.23	1.7	5.98	48.9	-0.24	3.0	0.83	1.4	
	2014	-0.12	1.9	4.03	49.8	0.04	3.0	0.37	1.3	
Indian Hill	2015	-0.57	1.0	-26.18	37.8	-0.99	1.4			
	2014	-0.22	1.1	-24.75	60.9	0.29	2.1			

Emissions

The Sparse Matrix Operator Kernel Emissions (SMOKE version 3.6)³³ was used to spatially and temporally allocate and to chemically speciate emissions for input to CMAQ. SMOKE converts emission inventories containing county-level emissions from the contiguous United States and Canada with varying temporal resolutions and produces hourly, gridded emissions. The resulting dataset consists of emissions of pollutants from mobile, area, point, fire, ocean, dust, biogenic and agricultural sources (Table 3). SMOKE simulations are based on the 2011 National Emissions Inventory (NEI version 6.2) modeling platform (https://www.epa.gov/air-emissions-modeling/2011-version-62-platform), the most recent NEI with a modeling platform at the time of this study, with updates to point and onroad mobile sources. Although the 2014 NEI emissions were available at the time, the modeling platform was not yet available. The 2011 version 6.2 modeling platform also provides the ancillary data used for temporal, spatial, and chemical allocation of emissions. The Surrogate Tool, a component of the Spatial Allocator (version 4.2), was used to convert shapefiles (e.g., population and road mile distribution) provided as part of the modeling platform to spatial surrogates that are used for spatially allocating county-level emissions to a grid. Biogenic emissions were developed using the Biogenic Emissions Inventory System (BEIS version 3.61) which estimates emissions from vegetation and soils based on version 4 of the Biogenic Emissions Land use Dataset (BELD4). The BELD4 includes 232 vegetation classes in the United States and only the 19 U.S. Geological Survey (USGS) categories in Canada. The modeling platform includes 2010 Canadian anthropogenic emissions provided by Environment Canada.

Since the episodes simulated in this study occur in 2014 and 2015 and the most recent NEI modeling platform represents emissions in 2011, updates were made to point source and onroad mobile emissions to make the dataset more representative of the time periods simulated. Washington 2013 and Oregon 2014 point source inventories were developed as part of the Air Indicator Report for Public Awareness and Community Tracking (AIRPACT-5, http://lar.wsu.edu/airpact/index.html) modeling and were used here. Onroad mobile emissions from Washington were updated using 2014 Motor Vehicle

Emissions Simulator (MOVES) ³⁴ inputs that have been developed for the 2014 NEI. Onroad emission development consists of producing emission rate lookup tables and activity data using MOVES2014 and converting the data using SMOKE-MOVES to formatted inputs for SMOKE. MOVES2014 was run in emission rate mode to produce emission rate lookup tables, containing emission rates differentiated by emission process, road type, vehicle type, speed, temperature, etc., for 4 representative counties in Washington. SMOKE uses activity data (e.g., vehicle population [VPOP] and vehicle miles traveled [VMT]) from every county in the modeling domain and calculates emissions using the representative county's emission rate lookup tables.

	2014 Episode		2015 Episode	
	NOx	VOC	NO _x	VOC
U.S. Area	98	619	88	556
U.S. Mobile	335	466	333	482
U.S. Nonroad	109	159	108	158
U.S. Point	83	35	83	35
U.S. Biogenic	24	3,256	25	3,294
Canada (non-Biogenic)	217	318	217	318

Table 3 Domain wide NO_X and VOC emission totals in tons day⁻¹

Results

Ozone Simulations and Evaluation

The highest simulated O_3 mixing ratios (up to 110 ppb) occur during the 2015 episode over Pierce County and into King County just south of Seattle (Figure 4). High simulated O_3 in the 2014 modeling also occurs over Pierce County but is highest in King County just east of Seattle (up to 100 ppb). To evaluate the model performance, the mean absolute gross error (MAGE), mean bias (MB), normalized mean error (NME), normalized mean bias (NMB) and root mean square error (RMSE) were calculated for all monitors in the domain and for the entirety of each simulation period (Table 4). MAGE and NME are indicators of overall discrepancy between the simulation and observations while the MB and NMB are indicators of systematic error and the RMSE incorporates the bias and the variance in the simulation and its bias.³⁵

Model performance for the 2015 and 2014 episodes meet the published model performance criteria suggested by the EPA suggesting that the NMB and NME for 1-hr O3 for observations less than 60 ppb should be $\leq \pm 15\%$ and $\leq 35\%$, respectively.³⁶ In contrast to the EPA criteria, we use a cut-off of 40ppb rather than 60ppb because O₃ in the Puget Sound area is relatively low so the number of observations to perform the evaluation would decrease significantly otherwise. During the 2015 episode, the mean observed 1-hr O₃ for the monitoring stations in the domain was 26.6 ppb and the mean simulated O₃ at the locations of the monitors was 30.2 ppb. The NMB for all observations is 14% whereas the NMB for only the observations above 40 ppb is 2%. The difference indicates that, during the 2015 episode, the model has a small bias during periods with high O₃ mixing ratios but the model is biased high when O₃

mixing ratio is low. During the 2015 episode, the model over-predicts 1-hr and 8-hr max O_3 in the domain and especially at the Enumclaw monitor (Table 5). Time series of the 1-hr observed and simulated O_3 reveal the peak daytime over-prediction at Enumclaw as well as the Seattle Beacon Hill and Issaquah monitors (Figure 5). The model does, however, simulate peak episode O_3 occurring on the same days when peak O_3 is observed during the episode. Seattle peak observed O_3 rarely exceeds 40 ppb during the 2015 episode, in part due to a highly NO_X -rich atmosphere from local mobile source emissions depressing ozone levels. For the 2014 episode, peak 8-hr and 1-hr max O_3 is captured well with NMB of 3% for each. The model performs well for simulated max O_3 at Enumclaw monitor as well with 1-hr and 8-hr max NMBs of 9% and 8%, respectively.



Figure 4 Episode maximum 8-hr average O₃ concentration during the 2015 (left) and 2014 (right) episodes

	2015 I	Episode			2014 Episode			
	1-hr	1-hr (40ppb)	1-hr Max	8-hr Max	1-hr	1-hr (40ppb)	1-hr Max	8-hr Max
Mean observed								
(ppb)	26.4	51.0	48.5	42.0	25.9	51.6	49.3	41.8
Mean simulated								
(ppb)	30.2	51.8	55.3	47.6	25.1	44.4	50.7	43.5
Total no.	2650	667	110	110	2083	471	89	89
MAGE (ppb)	9.9	10.3	13.7	10.6	9.9	12.7	11.3	10.08
MB (ppb)	3.5	0.6	6.8	5.6	-0.8	-7.2	1.4	1.25
NME (%)	40%	26%	28%	25%	38%	25%	23%	24%
NMB (%)	14%	2%	14%	13%	-3%	-14%	3%	3%
RMSE (ppb)	13.5	14.8	18.2	13.7	13.3	16.1	15.2	13.59

Table 4 CMAQ O₃ mixing ratio performance for the modeling domain using observations for the AQS network

Table 5 CMAQ O3 mixing ratio performance at the Enumclaw monitor

	2015 Ep	oisode		2014 Episode				
		1-hr	1-hr	8-hr		1-hr	1-hr	8-hr
	1-hr	(40ppb)	Max	Max	1-hr	(40ppb)	Max	Max
Mean observed								
(ppb)	36.8	57.0	64.8	56.5	38.4	57.3	70.7	60.2
Mean simulated								
(ppb)	46.5	64.8	84.1	67.8	36.5	54.4	76.9	65.0
Total no.	162	56	6	6	141	61	6	6
MAGE (ppb)	13.3	12.8	21.2	12.7	10.8	11.9	14.7	9.60
MB (ppb)	9.6	7.7	19.2	11.2	-1.8	-2.9	6.2	4.78
NME (%)	36%	23%	33%	22%	28%	21%	21%	16%
NMB (%)	26%	14%	30%	20%	-5%	-5%	9%	8%
RMSE (ppb)	18.0	18.3	26.3	15.2	12.9	14.1	17.0	10.45



Figure 5 Simulated and observed O3 1-hr average mixing ratio for the 2015 episode. Gaps in the time series occur where no observation data is available



Figure 6 Simulated and observed O3 1-hr average mixing ratio for the 2014 episode. No O3 observations are available during the episode at the Cheecka Peak monitor

Sensitivity Analysis

In this study, first-order semi-normalized sensitivities describing the linear response of O_3 to small perturbations in NO_X and VOC emissions were used to quantify source impacts, and here, the sensitivity coefficients are expressed in ppb per % perturbation in emission. Positive coefficients represent a decrease in ozone mixing ratio in response to a 1% reduction of emission and negative coefficients represent an increase. Control strategies are typically focused on reducing the 8-hr daily maximum O_3

mixing ratio so sensitivity coefficients presented here represent the impact of emission perturbations on each episode's 8-hr maximum ozone for policy relevance. Time series of sensitivity coefficients of 1-hr O_3 mixing ratio are also presented to describe temporal variations in sensitivities.

The sensitivity of 8-hr maximum O_3 to each emission group tested (Table 1) are similar in magnitude and spatial variability between the 2014 and 2015 episodes (Figure 7 and Figure 8). During the 2015 episode, O_3 is most sensitive to anthropogenic NO_x emissions (excluding point source emissions) from King, Pierce and Snohomish counties (ENOX_KPS, up to 0.3 ppb per %) with the largest sensitivities located over King and Pierce counties just south of the Seattle urban center and with positive values stretching south toward Vancouver, WA. In the same region, during the 2014 episode, ENOX KPS is slightly smaller (up to 0.25 ppb per %) since 8-hr max O₃ mixing ratio during the 2014 episode is less than during the 2015 episode. Directly over the Seattle urban center, ENOX_KPS is negative with sensitivities up to -0.13 and -0.2 ppb per % during the 2015 and 2014 episodes, respectively. The negative sensitivity of O_3 to NO_x emission perturbations over the Seattle urban center is typical for urban areas which are characterized by a high NO_x to VOC ratio, referred to as NO_x-rich (or radicallimited). In these regions, NO_x emissions are consuming radicals which are needed to produce ambient O_3 , as well as the O_3 itself. As such, the reduction of NO_x emissions will increase ambient O_3 locally. The same NO_x-rich region is marked by a relatively large, positive sensitivity of O₃ to VOC emissions from the same emission group (EVOC_KPS) with sensitivity coefficients up to 0.18 and 0.23 ppb per % during the 2015 and 2014 episodes, respectively. O_3 sensitivities to point source NO_x and VOC emissions from King, Pierce and Snohomish counties (ENOXpKPS and ENOXpVOC, not shown) are relatively small compared to other anthropogenic NO_X emissions (which are dominated by mobile onroad and nonroad emissions), not exceeding 0.03 and 0.001 ppb per %, respectively, during peak 8-hr O_3 in either episode.

The sensitivity of O_3 to anthropogenic NO_x emissions (excluding refineries) from Island, Skagit and Whatcom counties (ENOX_ISW) is positive in parts of Skagit and Whatcom counties, reaching 0.12 ppb per %, and negative in Seattle metro area, up to -0.1 ppb per %. O_3 sensitivity to NO_x emissions from the refineries located in Island, Skagit and Whatcom counties (ENOX_REF, Figure 9) show a similar spatial pattern as ENOX_ISW with positive sensitivity outside of the Mt. Vernon and Bellingham metro areas and negative sensitivity near the metro areas although the magnitudes of the sensitivities are much smaller, not exceeding +0.03 and -0.05 ppb per %, respectively. During the 2015 episode, refinery NO_x has a very small positive impact on O_3 over the northern part of the Seattle urban center and further south along the southern coast of the Puget Sound. The positive sensitivity does not exceed 0.015 ppb per % perturbation.



Figure 7 O_3 sensitivity to parameters at each grid cell's 8-hr max O_3 during the 2015 episode



Figure 8 O₃ sensitivity to parameters at each grid cell's 8-hr max O₃ during the 2014 episode



Figure 9 O_3 sensitivity to refinery NO_x emissions during the 8-hr max ozone for the 2015 (left) and 2014 (right) episodes

At the Enumclaw monitor, where the highest O_3 mixing ratio was observed during both episodes, daytime peak O_3 is positively sensitive to anthropogenic NO_x emissions (excluding point sources) from King, Pierce and Snohomish counties with ENOX_KPS usually between 0.2 and 0.5 ppb per % (Figure 10 and Figure 11). On the high O_3 days in the 2015 episode (7/30/2015 – 8/1/2015), O_3 sensitivity to VOC emissions increases following the peak in ENOX_KPS. As NO_x emissions consume both ozone and radicals, less photochemistry takes places later in the day and the ambient air becomes more NO_x rich and thus more sensitive to VOC. At the same time, a slight increase in O_3 is seen in both modeled and observed O_3 mixing ratios at Enumclaw on 7/30/2015 and 8/1/2015 at night (Figure 5). O_3 sensitivities at Enumclaw to other emission groups analyzed in this study are small compared to those shown (Figure 10 and Figure 11).

In contrast to the Enumclaw monitor, O_3 sensitivity to NO_x emissions at the Seattle monitor is almost entirely negative with ENOX_KPS reaching -0.2 and -0.24 ppb per % during the 2015 and 2014 episodes, respectively. As discussed already, the Seattle urban center is NO_x -rich and we see a corresponding positive sensitivity to anthropogenic VOC emissions from King, Pierce and Snohomish counties, reaching 0.5 ppb per %.



Figure 10 Time series of hourly sensitivity of O₃ to sensitivity groups with the largest impacts at key monitors during the 2015 episode



Figure 11 Time series of hourly sensitivity of O_3 to sensitivity groups with the largest impacts at key monitors during the 2014 episode

Discussion

In this study, we simulated the sensitivity O₃ pollution to its sources using a regional modeling system, updated with the most up-to-date emissions inventory data, for two recent high O₃ episodes in the Pacific Northwest. During peak O_3 hours, ambient O_3 sensitivities at the monitors nearest to Seattle (at Enumclaw, Seattle and North Bend) are largest with respect to low level anthropogenic emissions coming from King, Pierce and Snohomish counties. This result is expected since the majority of the Seattle and Tacoma urban areas, as well as three major interstates highways, lay within these counties. NO_x emissions from these counties, in large part emitted by the onroad mobile sector, play an important role in O_3 pollution formation at the monitors surrounding Seattle, although the impacts can be opposite in effect depending on the location. Outside of Seattle, O_3 is positively sensitive to NO_X emissions (e.g. at Enumclaw and North Bend) and negative closer to the urban center. The reason for the difference is due to the regional variability in NO_x-rich vs. NO_x-limited regimes, the spatial extents of which appear to be changing over time. In Tsimpidi et al.,¹² the region where O_3 sensitivity to NO_X was negative (i.e. NOx-rich) extended from Seattle, South through Tacoma and into Thurston and Lewis Counties and East almost reaching the North Bend monitor. In the present study, however, the spatial extent of the NO_x-rich area is relatively small and limited near the Seattle urban center, likely resulting from a decrease in mobile NO_x emissions since 2005. In NO_x-rich regions, VOC controls will be most effective at reducing ambient O_3 . Recent research is showing that estimates of mobile NO_x emissions may be too high which may have a major impact on the spatial extent of Seattle's NO_x-rich region.³⁷⁻⁴²

Compared to emissions from King, Pierce and Snohomish counties, emissions from Thurston, Kitsap, Island, Skagit and Whatcom Counties have relatively small impacts on O_3 at monitors nearby Seattle, especially at Enumclaw monitor. Even with a 5% reduction in total anthropogenic NO_x from Kitsap County, the peak simulated 1-hr O_3 at the Enumclaw monitor would only be reduced by 0.05 ppb (Figure 12). The impact of the emissions from the remaining counties is even smaller. Simulated O_3 sensitivity at Enumclaw to anthropogenic emissions from Island, Skagit and Whatcom Counties is very small (less than 0.05 ppb per 5% emission perturbation) and the sensitivity to the refineries in Skagit and Whatcom Counties at the Enumclaw monitor is practically zero (Figure 12).

Of the emission groups tested here, biogenic VOC emissions are the 4th largest impactor of high O_3 at the Enumclaw monitor (Figure 12). The sensitivity of O_3 to biogenic VOC emissions increases in NO_x -rich regions such as the Seattle urban center and urban regions in Skagit and Whatcom counties. Simulated biogenic VOC sensitivity coefficients are much larger in Canada near Vancouver, BC and Victoria than anywhere else in the modeling domain. The large difference in sensitivities to biogenic emissions between the U.S. and Canada is an artifact of having a spatially non-continuous land use dataset (i.e. 232 BELD4 vegetation classes in the U.S. vs. 19 USGS classes in Canada). The influence of this discontinuity between U.S. and Canadian vegetation datasets on the photochemical modeling in this study and in similar studies should be investigated further.



Figure 12 Sensitivity of each episode 1-hr max O₃ mixing ratio (ppb per 5% perturbation) at three monitor locations

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