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# Estimating ozone and secondary PM<sub>2.5</sub> impacts from hypothetical single source emissions in the central and eastern United States

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Estimating ozone and secondary PM<sub>2.5</sub> impacts from hypothetical single source emissions in the central and eastern United StatesKirk R. Baker <sup>a,\*</sup>, Robert A. Kotchenruther <sup>b</sup>, Rynda C. Hudman <sup>c</sup><sup>a</sup> U.S. Environmental Protection Agency, Research Triangle Park, NC, USA<sup>b</sup> U.S. Environmental Protection Agency, Seattle, WA, USA<sup>c</sup> U.S. Environmental Protection Agency, San Francisco, CA, USA

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## ABSTRACT

Secondary pollutant impacts from emissions of single sources may need to be assessed to satisfy a variety of regulatory requirements including the Clean Air Act New Source Review and Prevention of Significant Deterioration programs and the National Environmental Policy Act. In this work, single source impacts on O<sub>3</sub> and secondary PM<sub>2.5</sub> are estimated with annual 2011 photochemical grid model simulations where new hypothetical sources are added to the central and eastern United States with varying precursor emission rates and emission release heights. Impacts from these hypothetical sources are tracked with photochemical grid model source apportionment. Single source impacts on downwind 8-hr maximum O<sub>3</sub> tend to increase as emissions of NO<sub>x</sub> or VOC increase. Downwind impacts on PM<sub>2.5</sub> sulfate and nitrate also tend to increase as emissions of SO<sub>2</sub> and NO<sub>x</sub> increase. For all secondary pollutants, impacts from these hypothetical sources tend to decrease as distance from the source increases. However, peak impacts on O<sub>3</sub> and secondary PM<sub>2.5</sub> are not at the facility fence-line but typically within 50–100 km depending on the emissions rate, precursor pollutant, and emissions release point. Downwind impacts are not uniform directionally from these sources due to varying downwind availability of chemical reactants and prevailing meteorology. Peak impacts for O<sub>3</sub> (~15 ppb) and PM<sub>2.5</sub> sulfate (~8 µg/m<sup>3</sup>) were within 50 km of these hypothetical sources and peak impacts for PM<sub>2.5</sub> nitrate (~1 µg/m<sup>3</sup>) were within 125 km. The daily maximum 8-hr O<sub>3</sub> and maximum daily average PM<sub>2.5</sub> sulfate and nitrate ion impacts for the new hypothetical sources modeled here are generally consistent with those reported in literature. Additional assessments of single source impacts on secondary pollutants are still needed to provide a more comprehensive assessment of different source types and source environments.

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## 1. Introduction

Human exposure to fine particulate matter (PM<sub>2.5</sub>, particles with aerodynamic diameter <2.5 µm) has been linked to a range of adverse health effects including cardiovascular and pulmonary disease (Künzli et al., 2005), lung cancer, and premature mortality (Pope III and Dockery, 2006). Exposure to ozone (O<sub>3</sub>) has been linked to premature mortality (Bell et al., 2004) as well as aggravation of chronic health conditions such as bronchitis, emphysema and asthma (Devlin et al., 1997). Industrial facilities are well known

sources of primary PM<sub>2.5</sub> emissions and can also emit gaseous SO<sub>2</sub>, NO<sub>x</sub>, and VOC that can be precursors to secondarily formed O<sub>3</sub> and PM<sub>2.5</sub>. The New Source Review (NSR) permitting program was established as part of the 1977 Clean Air Act Amendments. Non-attainment NSR permits are required for new major stationary sources or existing major stationary sources making a major modification in areas designated as nonattainment of the National Ambient Air Quality Standards (NAAQS). For areas attaining the NAAQS, sources may be required to obtain Prevention of Significant Deterioration (PSD) permits. Permits under PSD sometimes require a demonstration showing whether the new emission source will allow downwind areas to remain within the specific air quality guidelines.

The U.S. Environmental Protection Agency recently entered into a legal agreement to formulate guidance to assess O<sub>3</sub> and secondarily formed PM<sub>2.5</sub> impacts from single sources for permit programs

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(U.S. Environmental Protection Agency, 2012). Air quality modeling methods to estimate the downwind impacts of primary pollutant emissions are well established through numerous dispersion modeling platforms that simulate plume dynamics and utilize meteorological data (<http://www.epa.gov/ttn/scram/dispersion/index.htm>). However, the downwind impacts on O<sub>3</sub> and secondarily formed PM<sub>2.5</sub> from emissions of precursors is more complex to estimate because of the non-linear chemistry involved and the interaction of the plume with ambient levels of oxidants, neutralizing agents, and meteorology.

Attempts to estimate point source secondary pollutant impacts by including chemical mechanisms into plume models (Gaussian and Lagrangian) have had limited success because they often lack integration of a realistic ambient chemical environment. Regional scale Eulerian based chemical transport models (CTMs) like the Community Multiscale Air Quality Model (CMAQ; <http://cmascenr.org/cmaq/>) and the Comprehensive Air Quality Model with Extensions (CAMx; <http://www.camx.com/>) are capable of providing a realistic chemical and physical environment. Single source impacts have been estimated using photochemical grid models through various methods including brute force emissions adjustments (Cohan et al., 2005; Bergin et al., 2008; Zhou et al., 2012; Baker and Kelly, 2014; Kelly et al., 2015), decoupled direct method (DDM) (Cohan et al., 2005, 2006; Bergin et al., 2008; Baker and Kelly, 2014; Kelly et al., 2015), and emissions tagging source apportionment (Baker and Foley, 2011; Baker and Kelly, 2014). While these studies support the appropriateness of using photochemical grid models for single source secondary impact assessments, they do not provide a robust range of impacts covering a diverse set of sources, source environments, and time scales.

A primary motivation for a new systematic assessment of hypothetical sources using photochemical grid model source apportionment is to contribute more information about downwind single source secondary impacts to the existing literature. Here, new photochemical grid model simulations are presented to provide information about single source secondary pollutant impacts for a variety of locations, source emission rates, and plume release points. Photochemical grid model simulations for the entire year of 2011 have been completed with 24 hypothetical sources added to the central and eastern United States with varying emission rates and plume release heights. These hypothetical sources were systematically located near existing industrial point sources and spread out to cover a large geographic area. This is intended to provide a robust set of single source impacts that cover a variety of different chemical (e.g. VOC-to-NO<sub>x</sub> ratio) and physical (e.g. meteorology and orography) regimes.

A review of published modeled single source secondary pollutant impacts is also presented to provide some context for the modeled impacts of the 24 hypothetical sources included in this analysis. Results from relevant photochemical model based single-source modeling studies published from 2005 through 2015 that report both the source emissions perturbation and corresponding change in downwind O<sub>3</sub> or PM<sub>2.5</sub> are summarized. Single source secondary impacts modeled as part of this study and those presented in existing literature provide some preliminary comparative information for future assessments done to support regulatory programs.

## 2. Methods

### 2.1. Air quality model simulations

Annual 2011 photochemical model simulations were performed for a domain covering the central and eastern United States with 12 km sized grid cells (Fig. 1). These simulations

include a baseline simulation and 4 additional simulations each with 24 additional hypothetical sources added to the existing baseline emissions. Each hypothetical source was individually tracked with source apportionment for downwind contribution to O<sub>3</sub> and PM<sub>2.5</sub>. All simulations were done using version 6.11 of the Comprehensive Air Quality Model with Extensions (CAMx) photochemical grid model ([www.camx.com](http://www.camx.com)) (Baker and Scheff, 2007; Vizuete et al., 2008). This CAMx application includes ISO-RROPIA inorganic chemistry (Nenes et al., 1998), gas phase reactions based on the Carbon Bond (CB6r2) mechanism, and aqueous phase reactions (ENVIRON, 2014). Chemical boundary inflow is extracted from a photochemical model simulation for 2011 with a larger geographic domain covering the continental United States, northern Mexico, and southern Canada with 12 km sized grid cells. A total of 25 layers resolve the vertical atmosphere to 50 mb with thinner layers nearer the surface (layer one height is approximately 20 m). More details about the meteorological model simulation used to supply inputs to the emissions and CAMx model are available elsewhere (U.S. Environmental Protection Agency, 2014b).

Baseline emissions include anthropogenic sources based on version 2 of the 2011 National Emission Inventory (U.S. Environmental Protection Agency, 2014a) and biogenic sources estimated with the Biogenic Emission Inventory System version 3.6 (Carlton and Baker, 2011). Separate simulations were done where 24 hypothetical sources (see Fig. 1) were added to the baseline biogenic and anthropogenic emissions at varying emission rates of precursors and varying stack release characteristics (see Table S1) representing a “low” and “high” altitude plume release. Simulations where all 24 sources are emitting 500 and 1000 TPY of precursors (NO<sub>x</sub>, VOC, and SO<sub>2</sub>) were modeled with “low” plume release and additional simulations with sources emitting 1000 and 3000 TPY were modeled with “high” plume releases. These combinations result in a total of 4 different simulations that each included 24 hypothetical sources co-emitting NO<sub>x</sub>, VOC, and SO<sub>2</sub> in addition to the baseline emissions (e.g. mobile, point, area sources). VOC (Table S2) and NO<sub>x</sub> (90% NO and 10% NO<sub>2</sub>) speciation for each of these hypothetical sources are based on average speciation profiles for non-EGU point sources.

The hypothetical source locations are intended to maximize distance between these sources while also being placed near existing industrial point sources (see Fig. 1). Most of these locations are rural or in close proximity to urban areas (Table S3). The contribution from each of these hypothetical sources to model predicted O<sub>3</sub> and PM<sub>2.5</sub> sulfate and nitrate ions were tracked using reactive tracers in the photochemical model (Kwok et al., 2013, 2015; ENVIRON, 2014). Ozone contributions were estimated using Ozone Source Apportionment Technology and PM<sub>2.5</sub> contributions using Particulate Source Apportionment Technology as implemented in CAMx (ENVIRON, 2014). All precursors are co-emitted but their impacts on PM<sub>2.5</sub> and O<sub>3</sub> are tracked separately (e.g. NO<sub>x</sub> to O<sub>3</sub>, VOC to O<sub>3</sub>, etc.).

Photochemical models including CAMx have a Lagrangian based sub-grid plume treatment for representing plume chemistry and transport as an option for situations where grid volume dilution of emissions may not be desired (Karamchandani et al., 2011). Sub-grid plume treatment extensions in photochemical models typically solve for in-plume chemistry and use a set of physical and chemical criteria to determine when puff mass is merged back into the host model grid (Baker et al., 2014). Photochemical transport models have been shown to adequately capture single source impacts when applied using 4 km horizontal resolution when compared with downwind in-plume measurements (Zhou et al., 2012; Baker and Kelly, 2014). The horizontal grid resolution used here has been shown to provide similar single

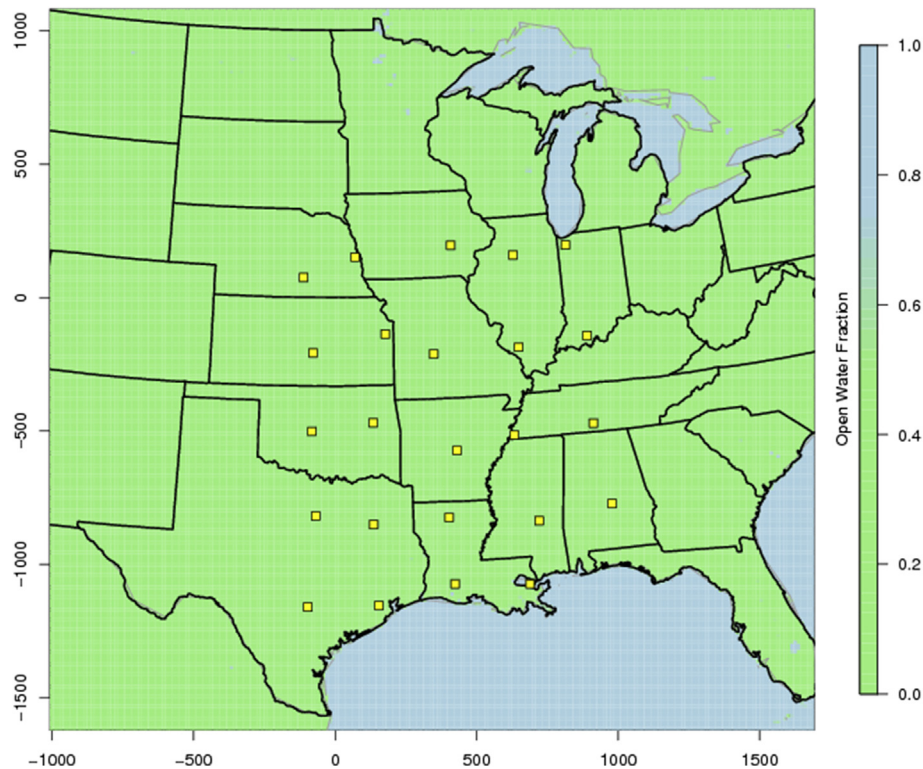


Fig. 1. Model domain and location of 24 hypothetical sources (shown as yellow squares).

source secondary impact response as perturbations done using finer (4 km) grid resolution (Cohan et al., 2006). Given that downwind secondary impact response is likely similar for these sources and this region the use of sub-grid plume treatment for the purposes of estimating project source impacts is not used for this analysis.

## 2.2. Review of existing single source impact assessments

A large body of work exists using photochemical transport models to estimate the aggregate effect of regional emissions on downwind ozone and  $PM_{2.5}$  air quality (Simon et al., 2012). However, few studies examine the effects of single sources. Since little relevant work has been published in peer review literature, we examined peer-reviewed literature as well as technical reports dating from 2005 through 2015 to maximize the number of studies available in this review. Relevant studies were identified using Web of Science (<http://www.webofknowledge.com/>), Google, Google Scholar, the EPA Support Center for Regulatory Atmospheric Modeling (<http://www.epa.gov/ttn/scram/reportsindex.htm>), and the Community Modeling and Analysis System annual conference meeting archive (<https://www.cmascenter.org/conference/archive.cfm>). Assessments providing 8-hr  $O_3$  impacts are shown in Table 1 and those showing  $PM_{2.5}$  impacts are presented in Table 2. Particular emphasis is placed on single source impact assessments (Kelly et al., 2015; U.S. Environmental Protection Agency, 2015) using a similar study design and post-processing approach employed here. These assessments include a summer and winter period where hypothetical sources are placed in both the central San Joaquin Valley and Los Angeles areas (Kelly et al., 2015) and a separate assessment of hypothetical sources placed in Detroit and Atlanta for an entire year (U.S. Environmental Protection Agency, 2015).

## 3. Results/discussion

Single source secondary pollutant impacts are assessed for hypothetical sources placed in the central and eastern United States using a photochemical grid model instrumented with source apportionment. Emission release height is varied and also emission rates of precursors for  $O_3$  and PM. These new simulations are intended to provide single source secondary impacts where source characteristics are well defined and post processing is consistent with the form of the NAAQS for  $O_3$  and PM.

### 3.1. $O_3$ impacts from single sources

The highest daily maximum 8-hr  $O_3$  single source impact in each grid cell over all modeled days in 2011 from each hypothetical source emitting 1000 TPY of  $NO_x$  are shown in Fig. 2. The supporting information includes similar plots of impacts from other precursors and emission rates. These spatial plots of maximum contribution to each downwind grid cell show highest impacts nearest the source. Studies of single source  $O_3$  impacts using finer grid resolution suggest there can sometimes be titration of  $O_3$  due to  $NO_x$  emissions at very close proximity (less than 12 km) to the source (Cohan et al., 2006; Baker and Kelly, 2014; Kelly et al., 2015). Negative  $O_3$  impacts are not estimated from these sources because source apportionment only apportions emissions sources to  $O_3$  production and not  $O_3$  destruction (Baker and Kelly, 2014; Kwok et al., 2015). Downwind impacts vary directionally from each of the sources due to differences in meteorology and the chemical environment near the source. Fig. 3 shows an aggregate of maximum daily 8-hr  $O_3$  impacts for all 24 hypothetical sources as a function of distance from the source. Figs. 2 and 3 show impacts typically decrease as distance from the source increases. For these sources and areas, peak  $O_3$  impacts from VOC emissions fall below 1 ppb (less than 40% of peak impact) at distances 50 km from the

**Table 1**Compilation of 8-hr O<sub>3</sub> impacts (ppb) from NO<sub>x</sub> emissions (tpd) reported in literature and in this study.

Reference	Location	Time period modeled	Year modeled	Type of source	Method used	Model resolution	Stack height (m)	Annual emissions (tpy)	8-hr O <sub>3</sub> delta (ppbv)
ENVIRON, 2005	Houston, TX	Summer episodes	1999 & 2000	Single – EGU	CAMx brute force	4 km	Not known	8468 NO <sub>x</sub>	9.4–24.3
ENVIRON, 2005	Houston, TX	Summer episodes	1999 & 2000	Single – EGU	CAMx brute force	4 km	Not known	14 235 NO <sub>x</sub>	8.9–32.7
ENVIRON, 2005	Houston, TX	Summer episodes	1999 & 2000	Single – EGU	CAMx brute force	4 km	Not known	11 972 NO <sub>x</sub>	5.7–10.2
ENVIRON, 2005	Houston, TX	Summer episodes	1999	Single – EGU	CAMx brute force	4 km	Not known	2665 NO <sub>x</sub>	0.9
Castell et al., 2010	Spain	Summer episodes	2003 & 2004	Single – EGU	CAMx brute force	2 km	65	1789 NO <sub>x</sub>	1.9–5.1
ENVIRON, 2012a	New Mexico	Full year	2005	Single – EGU	CAMx APCA	4 km	115.8	41 743 NO <sub>x</sub>	13
ENVIRON, 2012a	New Mexico	Full year	2005	Single – EGU	CAMx APCA	4 km	121.9	26 809 NO <sub>x</sub>	9.6
ENVIRON, 2012a	New Mexico	Full year	2005	Single – EGU	CAMx APCA	4 km	137.2	3797 NO <sub>x</sub>	6.1
ENVIRON, 2012a	New Mexico	Full year	2005	Single – EGU	CAMx APCA	4 km	36	151 NO <sub>x</sub>	1.2
ENVIRON, 2012a	New Mexico	Full year	2005	Single – EGU	CAMx APCA	4 km	85	4 NO <sub>x</sub>	0.01
ENVIRON, 2012a	Utah and Colorado	Full year	2006	Single – EGU	CAMx APCA	12 km	182.9	18 829 NO <sub>x</sub>	12.8
ENVIRON, 2012a	Utah and Colorado	Full year	2006	Single – EGU	CAMx APCA	12 km	182.9	11 130 NO <sub>x</sub>	7.4
ENVIRON, 2012a	Utah and Colorado	Full year	2006	Single – EGU	CAMx APCA	12 km	52.4	3703 NO <sub>x</sub>	4.1
ENVIRON, 2012a	Utah and Colorado	Full year	2006	Single – EGU	CAMx APCA	12 km	134.4	28 911 NO <sub>x</sub>	16.9
ENVIRON, 2012a	Utah and Colorado	Full year	2006	Single – EGU	CAMx APCA	12 km	19.8	302 NO <sub>x</sub>	0.7
ENVIRON, 2012a	Utah and Colorado	Full year	2006	Single – EGU	CAMx APCA	12 km	76.2	105 NO <sub>x</sub>	0.05
ENVIRON, 2012a	Utah and Colorado	Full year	2006	Single – EGU	CAMx APCA	12 km	182.9	7348 NO <sub>x</sub>	7
ENVIRON, 2012a	Utah and Colorado	Full year	2006	Single – EGU	CAMx APCA	12 km	182.9	17 801 NO <sub>x</sub>	10.9
ENVIRON, 2012a	Utah and Colorado	Full year	2006	Single – EGU	CAMx APCA	12 km	142.6	657 NO <sub>x</sub>	1.1
ENVIRON, 2012a	Utah and Colorado	Full year	2006	Single – EGU	CAMx APCA	12 km	65.5	1751 NO <sub>x</sub>	4.9
ENVIRON, 2012a	Utah and Colorado	Full year	2006	Single – EGU	CAMx APCA	12 km	145.7	34 744 NO <sub>x</sub>	12.6
ENVIRON, 2012a	Utah and Colorado	Full year	2006	Single – EGU	CAMx APCA	12 km	1.1	13 NO <sub>x</sub>	0.2
ENVIRON, 2012a	Utah and Colorado	Full year	2006	Single – EGU	CAMx APCA	12 km	12.2	86 NO <sub>x</sub>	0.98
This work	eastern US	Full year	2011	Hypothetical Source	CAMx OSAT	12 km	1	500 NO <sub>x</sub>	0.7–4.5
This work	eastern US	Full year	2011	Hypothetical Source	CAMx OSAT	12 km	1 and 90	1000 NO <sub>x</sub>	1.3–7.5
This work	eastern US	Full year	2011	Hypothetical Source	CAMx OSAT	12 km	90	3000 NO <sub>x</sub>	2.6–14.7
Kelly et al., 2015	California	Summer and winter episodes	2007	Hypothetical Source	CMAQ brute force & DDM	4 km	1 and 90	100 NO <sub>x</sub>	0.04–1.3
Kelly et al., 2015	California	Summer and winter episodes	2007	Hypothetical Source	CMAQ brute force & DDM	4 km	1 and 90	500 NO <sub>x</sub>	0.16–3.6
Kelly et al., 2015	California	Summer and winter episodes	2007	Hypothetical Source	CMAQ brute force & DDM	4 km	90	2000 NO <sub>x</sub>	2.8–5.6
U.S. Environmental Protection Agency, 2015	Detroit, MI	Full year	2007	Hypothetical Source	CMAQ brute force	4 km	1	100 NO <sub>x</sub>	0.67
U.S. Environmental Protection Agency, 2015	Detroit, MI	Full year	2007	Hypothetical Source	CMAQ brute force	4 km	1	300 NO <sub>x</sub>	1.7
U.S. Environmental Protection Agency, 2015	Atlanta, GA	Full year	2007	Hypothetical Source	CMAQ brute force	4 km	1	100 NO <sub>x</sub>	0.74
U.S. Environmental Protection Agency, 2015	Atlanta, GA	Full year	2007	Hypothetical source	CMAQ brute force	4 km	1	300 NO <sub>x</sub>	2.0

source. The peak impacts from NO<sub>x</sub> emissions of 500 and 1000 TPY fall below 1 ppb (less than 40% of peak impact) at distances approximately 150 km from the source and at approximately 200 km from the source for the group of 3000 TPY NO<sub>x</sub> sources.

Fig. 4 shows daily maximum 8-hr O<sub>3</sub> impacts from sources included in this analysis and hypothetical sources simulated and post-processed similarly to this study from other projects (Kelly et al., 2015; U.S. Environmental Protection Agency, 2015). The distance of maximum downwind impact for the hypothetical sources are shown in the top panels of Fig. 4. Peak impacts for the sources included in this assessment and from other similarly processed studies (Kelly et al., 2015; U.S. Environmental Protection Agency, 2015) are typically closer than 50 km downwind from the source but rarely in the same grid cell as the source. Peak impacts are compared with annual precursor emission rates for this work and similar studies in the bottom panels of Fig. 4. The differences in peak impacts between areas are expected because of differences in chemical regimes where each of the hypothetical sources are located. For the assessments shown in Fig. 4, peak impacts of 8-hr

average O<sub>3</sub> are not notably different when emissions are released near the surface or aloft. Single source ozone impacts generally increase as emissions of NO<sub>x</sub> or VOC increase. Peak daily maximum 8-hr O<sub>3</sub> impacts over all hypothetical sources with different stack release and emissions perturbations range up to ~15 ppb from these NO<sub>x</sub> sources and ~3 ppb from these VOC sources. O<sub>3</sub> impacts are higher for NO<sub>x</sub> emissions released at the Shafter, California location compared to similar levels of VOC emissions from the same source and the opposite occurs for the hypothetical source placed in Riverside, California. This behavior is due to differences in ozone formation regimes between these areas where the hypothetical sources were placed. Riverside is NO<sub>x</sub>-rich due to large emissions just upwind in the Los Angeles region whereas Shafter is in a NO<sub>x</sub> limited part of the San Joaquin Valley (Kelly et al., 2015).

A broader review of literature that includes precursor emission rates and downwind O<sub>3</sub> impacts provides additional context to the results presented here even though many differences in model application and impact aggregation are reasonably anticipated. The majority of single source impact evaluations in available literature

**Table 2**  
Compilation of PM<sub>2.5</sub> impacts ( $\mu\text{g}/\text{m}^3$ ) from SO<sub>2</sub> and NO<sub>x</sub> emissions (tpd) reported in literature and in this study.

Reference	Location	Time period modeled	Year modeled	Type of source	Method used	Model resolution	Stack height (m)	Annual emissions (tpy)	Max 24-hr PM <sub>2.5</sub> sulfate ion ( $\mu\text{g}/\text{m}^3$ ) <sup>a</sup>	Max 24-hr PM <sub>2.5</sub> nitrate ion ( $\mu\text{g}/\text{m}^3$ ) <sup>a</sup>	Max annual average PM <sub>2.5</sub> sulfate ion ( $\mu\text{g}/\text{m}^3$ )	Max annual average PM <sub>2.5</sub> nitrate ion ( $\mu\text{g}/\text{m}^3$ )	Notes
National Association of Clean Air Agencies (2011)	Minnesota	Full Year	2005	Single – EGU	CAMx/BF	12 km + 200 m	198	13 273 NO <sub>x</sub> + 14 954 SO <sub>2</sub> + 1.8 NH <sub>3</sub> + 28 PM <sub>2.5</sub>	0.207	0.002			Urban
National Association of Clean Air Agencies (2011)	Minnesota	Full year	2005	Single – EGU	CAMx/BF	12 km + 200 m PiG	61	401 NO <sub>x</sub> + 532 SO <sub>2</sub> + 17 PM <sub>2.5</sub>	0.055	0.002			Highest ambient NH <sub>3</sub> of four cases presented
National Association of Clean Air Agencies (2011)	Minnesota	Full year	2005	Single – EGU	CAMx/BF	12 km + 200 m PiG	74	4475 NO <sub>x</sub> + 2257 SO <sub>2</sub> + 0.3 NH <sub>3</sub> + 8 PM <sub>2.5</sub>	0.248				Urban
National Association of Clean Air Agencies (2011)	Minnesota	Full year	2005	Single – EGU	CAMx/BF	12 km + 200 m PiG	35	1488 NO <sub>x</sub> + 472 SO <sub>2</sub> + 356 PM <sub>2.5</sub>	0.63	0.393			Lowest ambient NH <sub>3</sub> of four cases presented
Baker and Foley, 2011	eastern U.S.	Full year	2005	Multiple – EGUs	CAMx/PSAT	12 km	N/A	NO <sub>x</sub> >7000 + SO <sub>x</sub> >20 000 + PM <sub>2.5</sub> > 1100			0.385	0.018	
ENVIRON, 2012a	eastern U.S.	Full year	2006	Single – EGU	CAMx/PSAT	12 km	183	18 829 NO <sub>x</sub> + 7338 SO <sub>2</sub> + 33 NH <sub>3</sub> + 27 PM <sub>2.5</sub>	0.53	3.44	0.05	0.11	
Baker and Kelly, 2014	Central Tennessee	Summer episode	1999	Single – EGU	CMAQ, CAMx/BF, DDM, PSAT	4 km	193	42 435 NO + 4745 NO <sub>2</sub> + 8395 SO <sub>2</sub> + 1460 PM <sub>2.5</sub>	0.0–1.5				
This work	Eastern U.S.	Full year	2011	Hypothetical source	CAMx/PSAT	12 km	1	500 NO <sub>x</sub>		0.1–0.4			
This work	Eastern U.S.	Full year	2011	Hypothetical source	CAMx/PSAT	12 km	1	500 SO <sub>2</sub>		0.0–2.0			
This work	Eastern U.S.	Full year	2011	Hypothetical source	CAMx/PSAT	12 km	1 and 90	1000 NO <sub>x</sub>		0.1–0.7			
This work	Eastern U.S.	Full year	2011	Hypothetical source	CAMx/PSAT	12 km	1 and 90	1000 SO <sub>2</sub>		0.1–5.0			
This work	Eastern U.S.	Full year	2011	Hypothetical source	CAMx/PSAT	12 km	90	3000 NO <sub>x</sub>		0.2–1.1			
This work	Eastern U.S.	Full year	2011	Hypothetical source	CAMx/PSAT	12 km	90	3000 SO <sub>2</sub>		1.0–8.0			

<sup>a</sup> Impacts estimated for the National Association of Clean Air Agencies (2011) represent 98th percentile fully neutralized sulfate and nitrate.

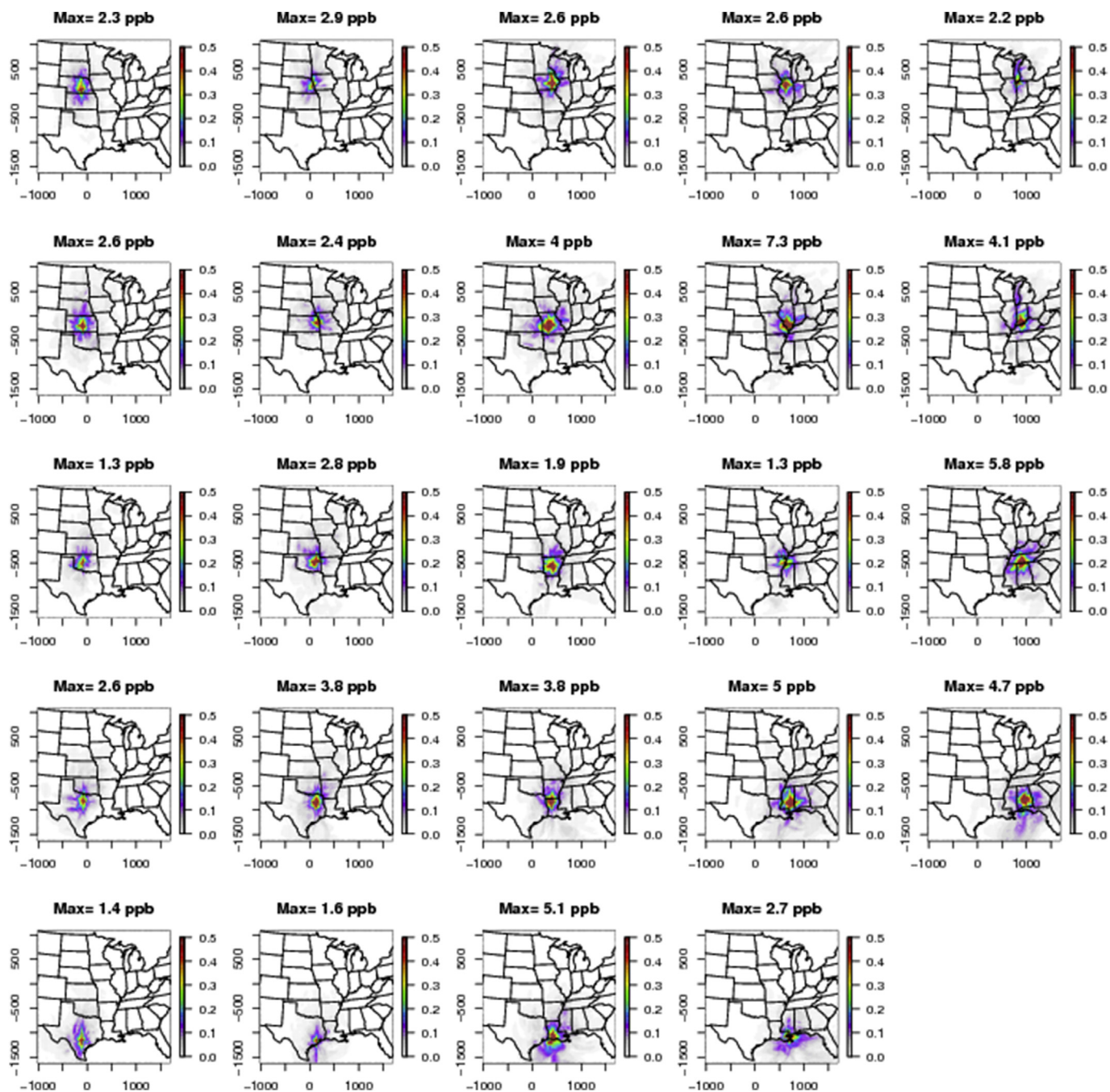


Fig. 2. Annual peak daily maximum 8-hr average O<sub>3</sub> contribution (ppb) from 24 different hypothetical sources of 1000 TPY of NO<sub>x</sub> emissions with an "elevated" release point.

fall within two groups: estimating the O<sub>3</sub> effects of NO<sub>x</sub> emissions changes from large point sources (ENVIRON, 2005a; Vijayaraghavan et al., 2006; Bergin et al., 2008; Carreras-Sospedra et al., 2010; Castell et al., 2010; Yarwood et al., 2011; ENVIRON, 2012b; ENVIRON, 2012a; Baker and Kelly, 2014) and the O<sub>3</sub> effects of large, short-duration (1 and 2 h) releases of highly reactive volatile organic compounds from sources such as petroleum refineries (Nam et al., 2006; Kimura et al., 2008; Vizuete et al., 2008). The results for single source VOC releases show very high variability in maximum downwind O<sub>3</sub> impacts due to large differences in ozone forming potential and OH reactivity of the VOC released. Maximum 8-hr O<sub>3</sub> impacts presented in literature and those estimated here are shown in Fig. 5 and Table 1. Overall, peak 8-hr

average O<sub>3</sub> impacts reported in literature range up to ~33 ppb. This peak reported impact was modeled from a large NO<sub>x</sub> source (~14 000 TPY) using 4 km grid resolution over multiple high ozone episodes in the eastern Texas–Louisiana area (ENVIRON, 2005a). Limited information exists about how impacts presented in literature were estimated but a comparison is still useful to put the results of the current study into context. The emission rates used here are generally lower than in the assessments compiled with the literature review, but the impacts from these sources on daily maximum 8-hr ozone are generally consistent with what has been reported for similar types (e.g. emission rates) of sources elsewhere (ENVIRON, 2005b; Castell et al., 2010; ENVIRON, 2012a; Kelly et al., 2015; U.S. Environmental Protection Agency, 2015). Measurements

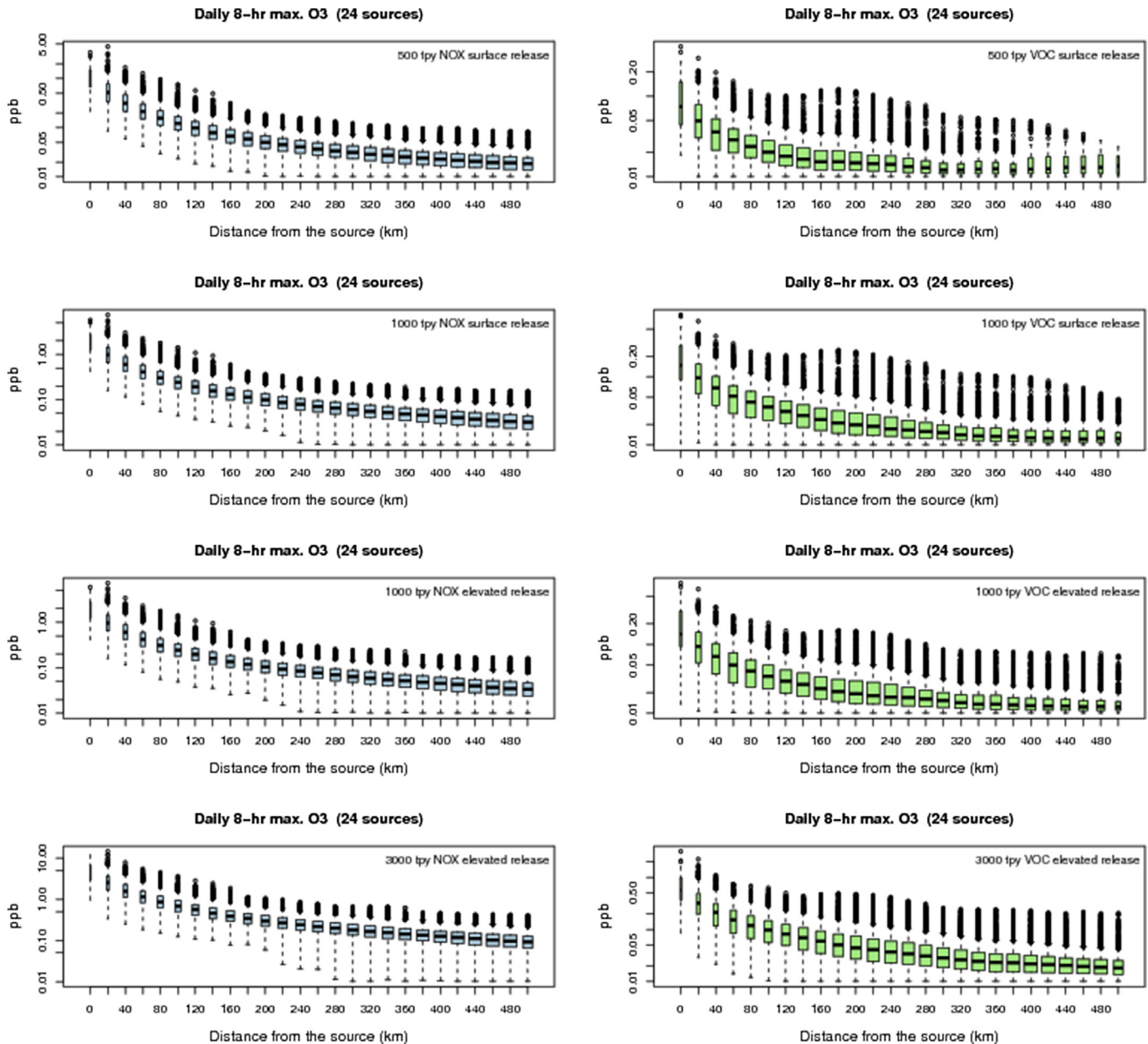


Fig. 3. Annual peak daily maximum 8-hr average O<sub>3</sub> impacts from 24 different hypothetical sources shown by distance from the source. Precursor emission rates are shown in the upper right corner.

of O<sub>3</sub> enhancements made as part of in-plume aircraft transects for very large single sources of NO<sub>x</sub> (Luria et al., 2003; Springston et al., 2005) show similar impacts as those in Fig. 5 although direct comparability is cautioned since it is not clear that the in-plume measurements captured downwind peak O<sub>3</sub> levels from these sources.

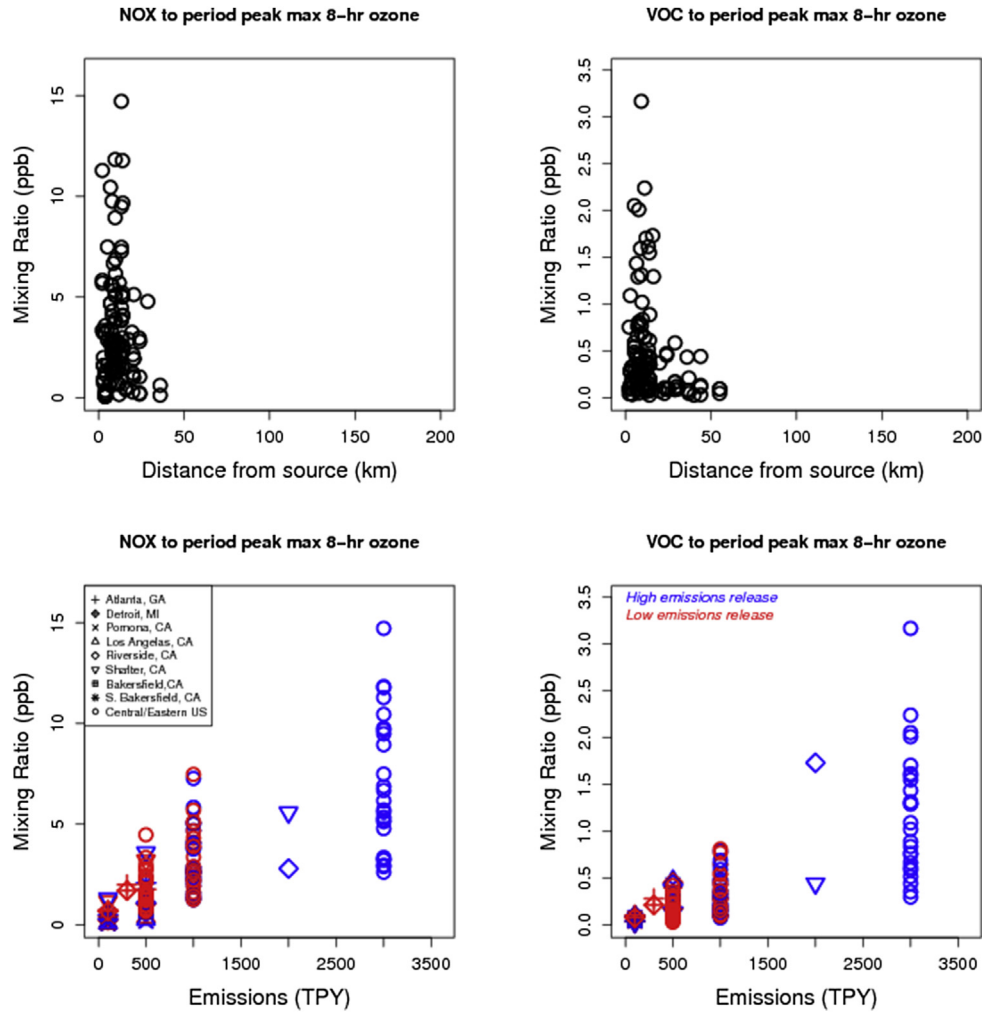
### 3.2. PM impacts from single sources

The contribution of hypothetical source emissions of SO<sub>2</sub> to PM<sub>2.5</sub> sulfate ion and NO<sub>x</sub> to PM<sub>2.5</sub> nitrate ion maximum 24-hr average impact in each grid cell over all modeled days in 2011 are shown in Fig. 6 and S12. The supporting information includes similar plots of impacts from other precursors and emission rate combinations. Impacts for both tend to be highest near the source with notable variability in impacts directionally from the source

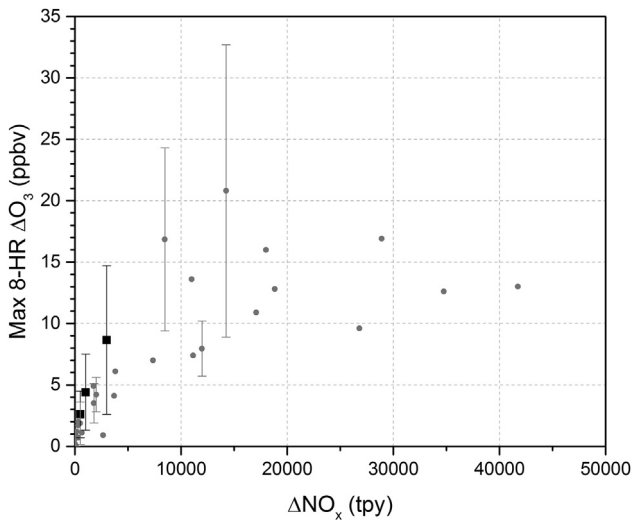
related to meteorology and the nearby chemical environment. The highest daily average PM<sub>2.5</sub> sulfate and PM<sub>2.5</sub> nitrate ion impacts from all hypothetical sources included in this analysis are shown by distance from the source in Fig. 7. Impacts for both sulfate and nitrate tend to decrease as distance from the source increases. PM<sub>2.5</sub> nitrate ion impacts are below 1.0 µg/m<sup>3</sup> (less than 50% of the peak impact) by 50 km from these sources in these areas. PM<sub>2.5</sub> sulfate ion impacts are also below 1.0 µg/m<sup>3</sup> (less than 40% of the peak impact) by 50 km from the 500 and 1000 TPY sources and below 1.0 µg/m<sup>3</sup> (less than 20% of the peak impact) by 100 km for the 3000 TPY sources.

Fig. 8 shows maximum daily 24-hr PM<sub>2.5</sub> sulfate and PM<sub>2.5</sub> nitrate ion impacts from all sources included in this analysis and hypothetical sources simulated as part of other projects that were simulated and post-processed similarly to those presented here (Kelly et al., 2015; U.S. Environmental Protection Agency, 2015).





**Fig. 4.** Single source impacts from hypothetical sources presented here and in similar studies. The daily maximum 8-hr avg O<sub>3</sub> impacts are shown for each hypothetical source matched with the distance downwind from the source of the maximum impact (top panels) and by precursor emission rate (bottom panels). The contribution from hypothetical source NO<sub>x</sub> to O<sub>3</sub> impacts are shown on the left and VOC to O<sub>3</sub> impacts on the right.



**Fig. 5.** Relationship between change in daily maximum 8-hr average O<sub>3</sub> and change in NO<sub>x</sub> precursor emissions (tpy). Impacts shown as squares represent the 24 sources presented here and circles represent impacts presented elsewhere.

Peak PM<sub>2.5</sub> sulfate ion impacts for the sources included in this assessment and from other similarly processed studies (Kelly et al., 2015; U.S. Environmental Protection Agency, 2015) are typically closer than 50 km downwind from the source but rarely in the same grid cell as the source. Single source impacts on PM<sub>2.5</sub> sulfate ion generally increase with increasing SO<sub>2</sub> emissions. The near-surface plume release point often resulted in higher PM<sub>2.5</sub> sulfate ion impacts than the elevated releases. PM<sub>2.5</sub> nitrate ion impacts from NO<sub>x</sub> emissions generally increase with increasing emissions. The emission release height has less impact on PM<sub>2.5</sub> nitrate ion at these locations compared with PM<sub>2.5</sub> sulfate ion. The highest daily average PM<sub>2.5</sub> sulfate ion impact from SO<sub>2</sub> emissions from these sources is ~8 μg/m<sup>3</sup>. The highest daily average PM<sub>2.5</sub> nitrate ion impact from NO<sub>x</sub> emissions from these sources is ~1 μg/m<sup>3</sup>.

A number of studies examine the effect of regional scale emissions on PM<sub>2.5</sub> concentrations (Simon et al., 2012). Fewer studies (see Table 2) have attempted to quantify the effects of single sources on downwind PM<sub>2.5</sub> concentrations, and fewer still that report estimated secondary PM<sub>2.5</sub> enhancements from these single sources (Baker and Foley, 2011; Baker and Kelly, 2014; ENVIRON, 2012a; National Association of Clean Air Agencies, 2011). The Minnesota case study presents predicted PM<sub>2.5</sub> sulfate and nitrate

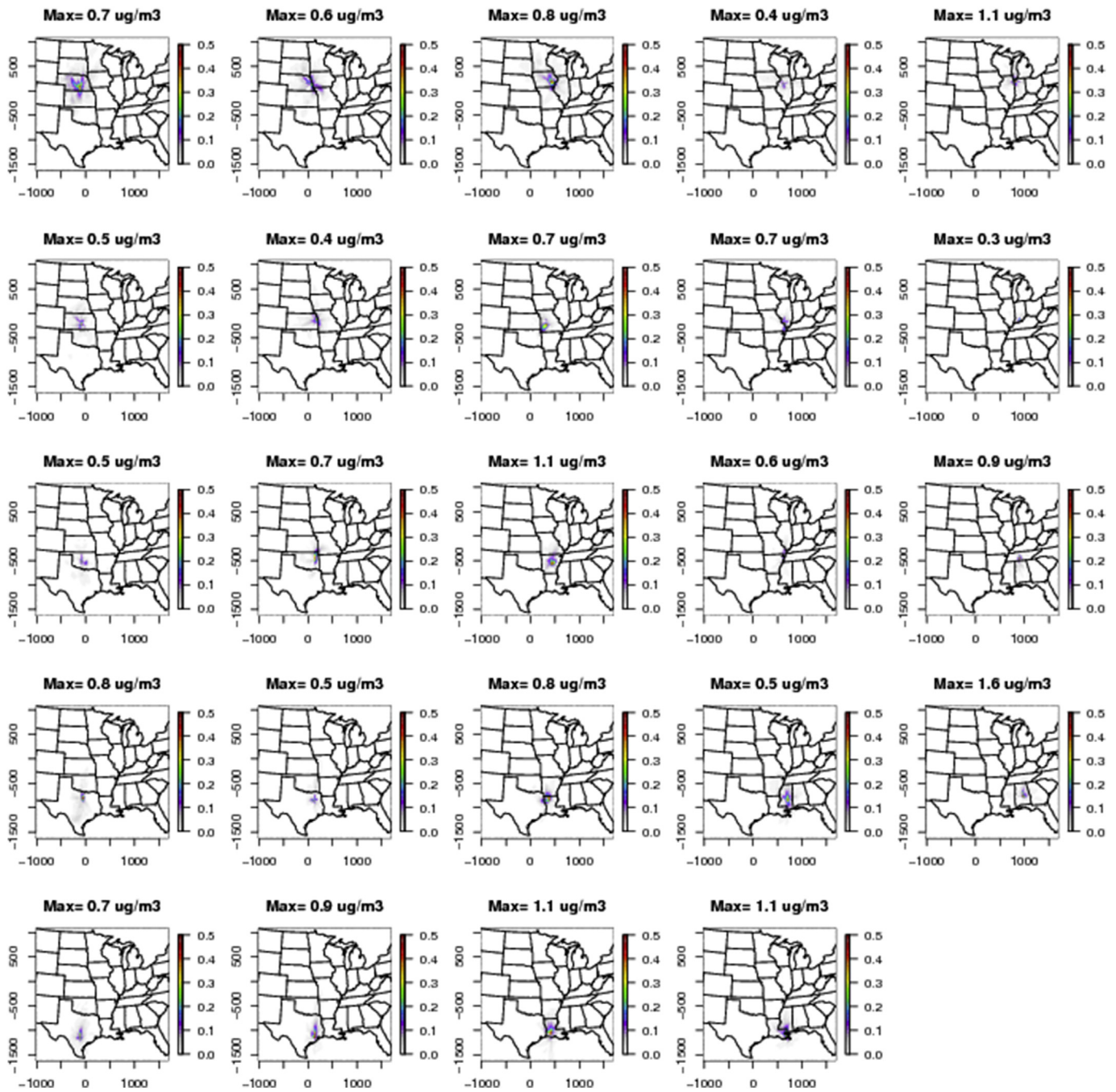


Fig. 6. Annual peak daily average  $PM_{2.5}$  sulfate ion contribution ( $\mu g/m^3$ ) from 24 different hypothetical sources of 1000 TPY of  $SO_2$  emissions with an “elevated” release point.

from a photochemical grid model simulation (CAMx) applied at 12 km grid resolution with sub-grid plume treatment and 200 m sub-grid plume sampling (National Association of Clean Air Agencies, 2011). Four individual stacks over Minnesota were chosen to reflect varying emission scenarios and background conditions: emissions ranged from 400 to 13 000 TPY  $NO_x$  and 500 to 15 000 TPY  $SO_2$ , each with varying stack height. In these case study simulations all precursor emissions are co-emitted by each source (National Association of Clean Air Agencies, 2011). Over all cases, 98th percentile daily average concentrations of secondary formation  $PM_{2.5}$  were up to  $\sim 1 \mu g/m^3$ . These sources had stack release points well above ground level and had surface level peak impacts typically within 10 km.

Another single source assessment estimated secondary  $PM_{2.5}$  for the Hunter EGU emitting 18 800 TPY of  $NO_x$  and 7 300 TPY of  $SO_2$  in eastern Utah using the CAMx model applied with PSAT at 12 km resolution for an entire year (ENVIRON, 2012a). Predicted 24-h maximum values were  $3.44 \mu g/m^3$  and  $0.53 \mu g/m^3$  of  $PM_{2.5}$  nitrate ion and  $PM_{2.5}$  sulfate ion respectively. The highest secondary  $PM_{2.5}$  impacts tended to be closest to the source (ENVIRON, 2012a). An episodic assessment presented a case-study examining the impact of a single EGU on downwind  $SO_4^{2-}$  using several photochemical grid model based source impact assessment approaches applied with the CMAQ model: brute force emission adjustments, DDM, and PSAT (Baker and Kelly, 2014). This case study examines emissions from the TVA Cumberland facility (48 000 TPY  $NO_x$  and

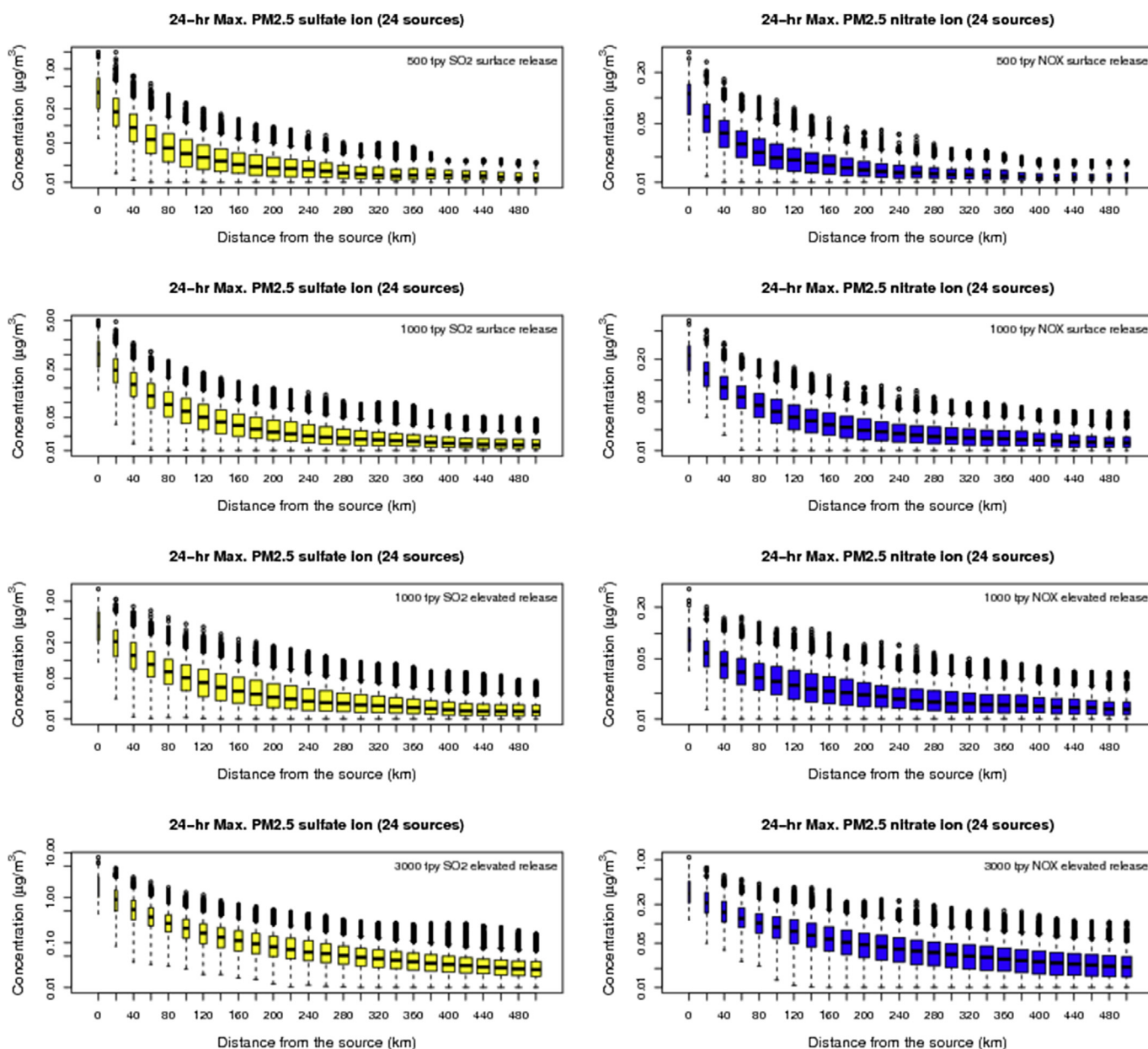


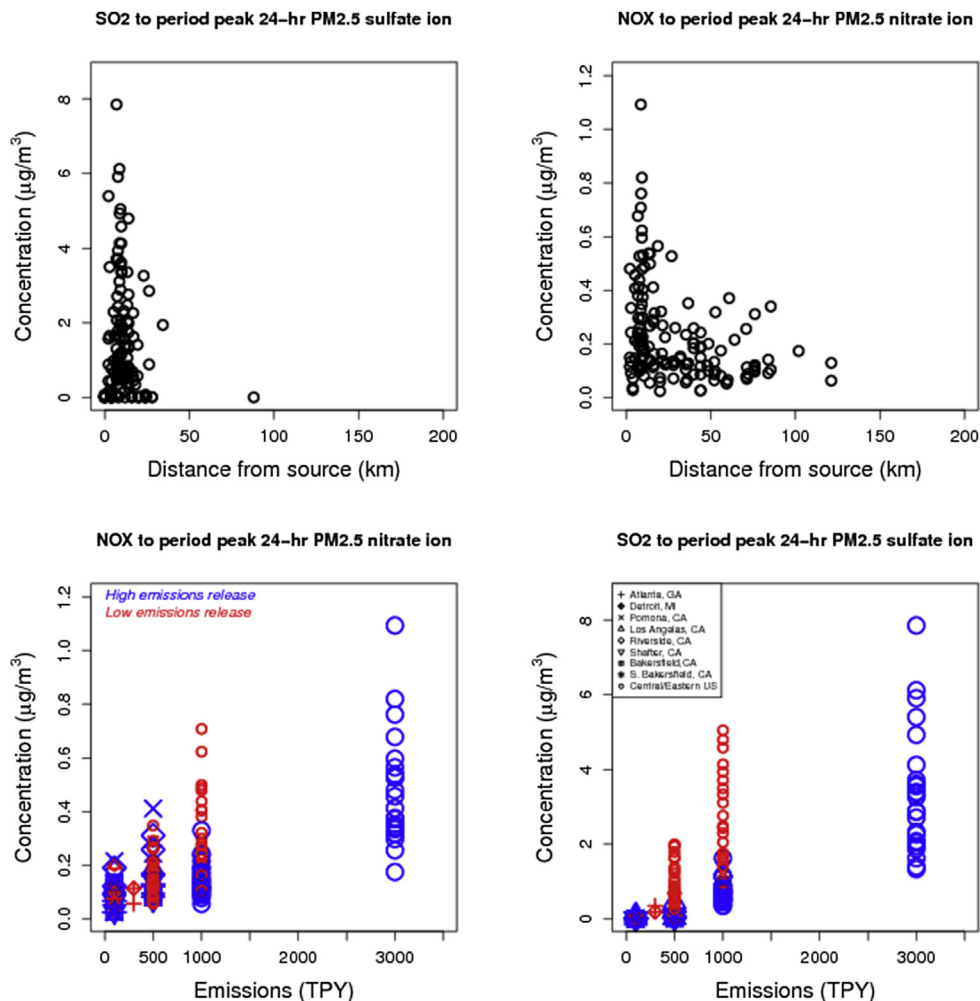
Fig. 7. Annual peak daily average  $PM_{2.5}$  sulfate and nitrate ion impacts from 24 different hypothetical sources shown by distance from the source. Precursor emission rates are shown in the upper right corner.

8 300 TPY  $SO_2$ ) during a high pollution episode focusing on July 6, 1999. These different source isolation approaches generally have similar spatial patterns with maximum enhancements that ranged up to  $\sim 1.5 \mu\text{g}/\text{m}^3 \text{SO}_4^{2-}$ . However, it is important to keep in mind these results are for a single day and impacts could be higher if more days were simulated.

#### 4. Future direction

Single source impacts on  $O_3$  and secondary  $PM_{2.5}$  are provided for a variety of sources covering a large geographic area of the central and eastern U.S. The geographic region where sources are located can be important because of general differences in temperature, actinic flux, biogenic emissions, oxidant concentrations, and terrain among other notable influences. Given the importance of providing robust single source impacts, the assessment

presented here for 24 hypothetical sources is supplemented with impacts reported for similarly configured studies of hypothetical sources in California, Detroit, and Atlanta. However, there remain gaps that limit the general applicability of these results. None of the published work related precursor emissions to  $O_3$  formed under wintertime conditions. Further investigation of various source attribution approaches and grid resolutions under a range of chemical and physical conditions is needed to fully assess variability in single source impacts. This could include additional modeled assessments using different modeling systems and chemical mechanisms. Finally, there is a need for additional systematic single source secondary pollutant impact estimates for a broader range of emission and stack parameters, regions, and chemical background environments to increase confidence in the generalizability in results from one area to another or support the need for more refined area and time specific assessments.



**Fig. 8.** Single source impacts from hypothetical sources presented here and in similar studies. Daily maximum 24-hr avg  $PM_{2.5}$  impacts are shown for each hypothetical source compared to the distance downwind from the source of the maximum impact (top panels) and by precursor emission rate (bottom panels). The contribution of hypothetical source  $SO_2$  to  $PM_{2.5}$  sulfate ion impacts are shown on the left and  $NO_x$  to  $PM_{2.5}$  nitrate ion impacts on the right.

## Disclaimer

Although this work was reviewed by EPA before publication, it may not necessarily reflect official Agency policy.

## Conflict of interest

The authors have no conflicts of interest to report.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.apr.2015.08.003>.

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