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# Adjoint-based computation of U.S. nationwide ozone exposure isopleths

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## HIGHLIGHTS

- We create $O_3$ exposure isopleths everywhere in the US using adjoint sensitivities.
- $NO_x$ emissions lower $O_3$ for 51% of the year on average at 29% of locations in 2006.
- The isopleth ridge line VOC/$NO_x$ ratio is 9.2 ppbC/ppb on average across grid cells.
- Ozone-neutral VOC/$NO_x$ emission ratios are 0.01–1.9 ppbC/ppb across grid cells.

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## ABSTRACT

Population exposure to daily maximum ozone is associated with an increased risk of premature mortality, and efforts to mitigate these impacts involve reducing emissions of nitrogen oxides ($NO_x$) and volatile organic compounds (VOCs). We quantify the dependence of U.S. national exposure to annually averaged daily maximum ozone on ambient VOC and $NO_x$ concentrations through ozone exposure isopleths, developed using emissions sensitivities from the adjoint of the GEOS-Chem air quality model for 2006. We develop exposure isopleths for all locations within the contiguous US and derive metrics based on the isopleths that quantify the impact of emissions on national ozone exposure. This work is the first to create ozone exposure isopleths using adjoint sensitivities and at a large scale. We find that across the US, 29% of locations experience VOC-limited conditions (where increased $NO_x$ emissions lower ozone) during 51% of the year on average. VOC-limited conditions are approximately evenly distributed diurnally and occur more frequently during the fall and winter months (67% of the time) than in the spring and summer (37% of the time). The VOC/$NO_x$ ratio of the ridge line on the isopleth diagram (denoting a local maximum in ozone exposure with respect to $NO_x$ concentrations) is 9.2 ppbC/ppb on average across grid cells that experience VOC-limited conditions and 7.9, 10.1 and 6.7 ppbC/ppb at the three most populous US cities of New York, Los Angeles and Chicago, respectively. Emissions that are ozone exposure-neutral during VOC-limited exposure conditions result in VOC/$NO_x$ concentration ratios of 0.63, 1.61 and 0.72 ppbC/ppb at each of the three US cities respectively, and between 0.01 and 1.91 ppbC/ppb at other locations. The sensitivity of national ozone exposure to $NO_x$ and VOC emissions is found to be highest near major cities in the US. Together, this information can be used to assess the effectiveness of $NO_x$ and VOC emission reductions on mitigating ozone exposure in the US, determine where they will be counterproductive, and quantify the optimal $NO_x$/VOC reduction ratio.



## 1. Introduction

Population exposure to ozone has been quantitatively associated with an increased risk of premature mortality and morbidity (Bell, 2004; Jerrett et al., 2009; WHO, 2008). In the US, premature mortality due to ozone in 2005 has been estimated at 4700 – 19,000 early deaths by Fann et al. (2012) and 10,000 early deaths by Caiazzo et al. (2013). Efforts to mitigate ozone impacts have focused on emissions reduction measures such as the Clean Air Act (USEPA, 2011), $NO_x$ cap-and-trade policies such as in the eastern US (Mesbah et al., 2013) and other state-based emission controls (e.g.

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Cohan et al., 2006).

Ozone forms via photochemical reactions of oxides of nitrogen ($NO_x$) with volatile organic compounds (VOCs) (Seinfeld and Pandis, 2006; Sillman, 1999). Variations in emissions of these precursors as well as meteorological factors affecting the photochemistry (e.g. cloud cover) can result in nonlinear changes in $O_3$ concentrations with respect to emissions (Ainslie and Steyn, 2006; Sillman, 1999). For instance, increased ozone concentrations in cities were observed when larger reductions in $NO_x$ relative to VOC emissions occurred during the weekend due to a reduction in diesel vehicular traffic into cities (Cleveland and McRae, 1978; Heuss et al., 2003; Lebron, 1975). In addition, the response of ozone concentrations to changes in electricity generation emissions (Mesbah et al., 2013) and future anthropogenic emissions in the US (Tao et al., 2007) have also been shown to vary with location and time.

The nonlinear dependence of $O_3$ concentrations on $NO_x$ and VOC is commonly captured by an ozone isopleth diagram [e.g. Fig. 6.10 in Seinfeld and Pandis (2006)]. The isopleth diagram depicts the response of maximum ozone concentrations with respect to $NO_x$ and VOC concentrations and is useful in assessing the potential outcome of proposed changes in $NO_x$ and/or VOC emissions. The ozone ridge line on the isopleth diagram identifies the local maximum in ozone with respect to $NO_x$ concentration at each VOC level. In regions where the VOC/$NO_x$ ratio is lower than that of the ridge line (denoted as 'VOC-limited'), reducing $NO_x$ emissions increases $O_3$ concentrations whereas reducing VOC emissions lowers ozone. In regions of higher VOC/$NO_x$ ratios than that of the ridge (denoted as '$NO_x$-limited'), reducing $NO_x$ emissions decreases $O_3$ while VOC emissions have little effect on $O_3$.

Photochemical simulations using a matrix of different combinations of VOC and $NO_x$ emissions have been used to generate isopleth diagrams. Kinosian (1982) employed the Empirical Kinetic Modeling Approach (EKMA) together with the ozone isopleth plotting package (OZIP) to generate city-specific isopleths for a city in the Central Valley of California and the South Coast Air Basin. Other studies have calculated the ozone response to a range of emission perturbations at specific locations using multiple runs of 3-dimensional chemistry transport models (CTMs) (Milford et al., 1989; Reynolds et al., 2004; Sierra et al., 2013; Wagner et al., 1992; Zavala et al., 2009) and box models (Chameides et al., 1992; Menut et al., 2000). Menut (2003) showed isopleths of ozone as a function of meteorological parameters (wind speed, reaction rate, atmospheric stability and temperature) and emissions ($NO_x$ and VOC) over Paris using multiple runs of a CTM. Apart from simulations, ozone isopleths have also been constructed based on measured VOC, $NO_x$ and $O_3$ concentrations at a rural and urban site in Italy (Thielmann et al., 2001).

Hakami et al. (2004) employed the higher-order decoupled direct method (HDDM) to compute third-order source-oriented sensitivities of ozone with respect to domain-wide $NO_x$ and VOC emissions. They used the sensitivities together with a third-order Taylor expansion to construct ozone isopleths assuming $NO_x$ and VOC emissions perturbations of $\pm 70\%$ in the San Joaquin Valley in central California. A similar approach was used to create an ozone isopleth in the Houston region (Estes et al., 2008). The HDDM method was also applied by Cohan et al. (2005) to characterize ozone response to large perturbations in emissions over Georgia.

Studies have been conducted to parameterize the ozone isopleth based on a dimensional scaling analysis (Ainslie and Steyn, 2006) and non-linear regression (Chang and Rudy, 1993) and were found to compare well with simulated ozone concentrations.

Here we develop isopleths of national population exposure to ozone as a function of ambient VOC and $NO_x$ concentrations using emissions sensitivities from the adjoint of the GEOS-Chem air quality model (Henze et al., 2007). Adjoint sensitivities are receptor-oriented, meaning that they relate, in this case, the integrated ozone exposure to emissions at every location and time. Adjoint methods have been extensively used to constrain sources of emissions using measurements of atmospheric concentrations (e.g. Chai et al., 2009; Kopacz et al., 2009; Zhu et al., 2013) and also to calculate the dependence of ozone and aerosols on precursor emissions (e.g. Henze et al., 2009, 2007; Parrington et al., 2012; Walker et al., 2012). They have been applied in the context of aviation's air quality impact (Ashok et al., 2014; Gilmore et al., 2013; Koo et al., 2013), sectoral attribution of emissions impacts (e.g. Dedoussi and Barrett, 2014; Pappin and Hakami, 2013a, 2013b), vegetative exposure to ozone in the US (Lapina et al., 2014) and optimal air quality management strategies (e.g. Hakami et al., 2006; Mesbah et al., 2013, 2012).

We develop ozone exposure isopleths for every location in the US and use them to calculate three metrics that quantify the impact of emissions on national ozone exposure: duration of the year that VOC-limited conditions occur, the VOC/$NO_x$ ratio of the ridge line on the isopleth diagram and the ozone exposure-neutral VOC/$NO_x$ concentration ratio. The ozone exposure-neutral ratio is the ratio of VOC/$NO_x$ concentrations that neither increases nor decreases ozone exposure during VOC-limited conditions. These metrics may be used together with measured or modeled $NO_x$ and VOC to determine the prevailing exposure regime (i.e. VOC-limited or $NO_x$-limited) and if emissions from a particular source will increase or decrease national population exposure to ozone.

This work is the first to generate ozone exposure isopleths using sensitivities from the adjoint of an air quality model to calculate national-level exposure to ozone concentrations. The adjoint method overcomes a limitation of the previous studies in that multiple model simulations with emissions perturbations were required to calculate the sensitivity of ozone to $NO_x$ and VOC emissions. Furthermore, the adjoint method provides sensitivities to emissions at every location and time, and a single simulation is sufficient to calculate isopleths of national ozone exposure for every location in the domain, instead of one simulation per location (e.g. the HDDM approach). In this work, we also create ozone exposure isopleths at a large scale, i.e. for all locations nationwide. Ozone exposure isopleths have been researched in prior literature (Hayes et al., 1991; Wagner et al., 1992), though they have been created only for specific locations or regions of emissions. By calculating population exposure to ozone in the U.S., we account for the spatial distribution of ozone and assess the human health implications of changing $NO_x$ or VOC emissions at every location.

The paper is organized as follows: section 2 presents the methods used to calculate ozone exposure isopleths, including adjoint air quality modeling and the steps taken to generate the ozone exposure isopleth and quantify emissions impacts on ozone exposure. Section 3 discusses our results, where we present ozone exposure isopleths for the three largest cities in the US as well as the spatial distribution of the three isopleth metrics and emission sensitivities.

## 2. Methods

In this section, we present the methods we use to calculate ozone exposure isopleths. First, we discuss the air quality model used to calculate adjoint sensitivities of 1-h daily maximum ozone exposure to $NO_x$ and VOC emissions. Next, we describe the computation of ozone exposure isopleths from the adjoint sensitivities and modeled $NO_x$ and VOC mixing ratios. Finally, we present three quantitative metrics based on the exposure isopleths that are used to describe the ozone response to changes in $NO_x$ and VOC emissions.