



Direct ozone production rate measurements and their use in assessing ozone source and receptor regions for Houston in 2013



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HIGHLIGHTS

- We directly measure ozone production rates at two areas in the Houston region.
- September production rates are low, consistent with ambient ozone levels.
- An advection analysis indicates ozone source and receptor regions.

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ABSTRACT

Mitigating ozone pollution involves reducing ozone production and relies on complex air-quality models to design reduction strategies and determine their effectiveness. However, modeled ozone does not always agree with observations. A complementary approach is to measure the ozone production rate directly, leading to the development of the Measurement of Ozone Production Sensor (MOPS). Two improved second-generation MOPSV2s were deployed for NASA's DISCOVER-AQ field campaign in September 2013 at the University of Houston, 5 km south of downtown, and Smith Point, at the mouth of the Houston Ship Channel. Median September $P(O_3)$ was low, consistent with the observed ambient ozone. The MOPSV2s provided statistically similar results when they were compared for 8 day sat the University of Houston. October measurements yielded a median ozone production rate of 27 ± 11 ppbv hr^{-1} , falling within the range of calculated $P(O_3)$ from prior Houston field campaigns in 2006 and 2009. Additionally, diurnal patterns are similar to model-derived ozone production from these previous campaigns. An advection analysis for a high ozone event on 25 September 2013 indicates that the Houston site was in a local ozone source region, while Smith Point ozone was likely enhanced by transport from other areas.

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1. Introduction

Ozone (O_3) is an atmospheric pollutant that damages both plant life and human respiratory systems (Baird and Cann, 2008). Its absorption in plants can damage growth and agricultural yields (Dumont et al., 2014), while its inhalation in humans can impair pulmonary function (Berman et al., 2012). Medical science has shown that ozone effects on humans are worse than previously thought (Bell et al., 2004) with recent Environmental Protection Agency (EPA) estimates suggesting that short-term ozone exposure

can cause thousands of human cardiovascular and respiratory deaths each year (US EPA, 2013). Additionally, overall higher ozone exposure for urban inhabitants versus more rural inhabitants can create environmental inequity gaps, as residents with lower socioeconomic status tend to reside in or near highly-polluted urban areas (O'Neill et al., 2003).

To address these health concerns, the EPA has proposed to lower the current 8-h National Ambient Air Quality Standard (NAAQS) for ozone from 75 ppbv (2008) to 65–70 ppbv (US EPA, 2014b). While EPA regulations have reduced ozone pollution, millions of people still live in areas that exceed this NAAQS (US EPA, 2010, 2014a). The Houston–Galveston–Brazoria region remains in non-attainment with ozone standards despite decreases in vehicular emissions

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(Parrish, 2006).

Ozone mitigation strategies rely on reducing ozone precursors, NO_x [the sum of nitrogen dioxide (NO_2) and nitric oxide (NO)] and volatile organic compounds (VOCs). Air quality models are used to determine effective ozone reduction strategies, to monitor progress, and to predict ozone events. However, uncertainties in model emissions inventories, chemical mechanisms, and meteorology often reduce confidence in this approach. Independently-derived emissions inventories can create $\text{P}(\text{O}_3)$ inconsistencies among models (Luecken et al., 2007). Further, $\text{P}(\text{O}_3)$ calculated from modeled HO_2 is lower than that from measured HO_2 , underestimating $\text{P}(\text{O}_3)$ at high NO (Martinez et al., 2003; Ren et al., 2013). Significant uncertainties in chemical product yields and reaction rate coefficients can also create $\text{P}(\text{O}_3)$ 1σ uncertainties up to 40% during morning hours when pollution is developing, and can even reverse $\text{P}(\text{O}_3)$ sensitivity to NO_x and VOCs (Chen and Brune, 2012). Finally, uncertainty in mixing layer height and other meteorological parameters in planetary boundary layer schemes can create significant uncertainty in forecasts of ozone exceedances and their locations (Cuchiara et al., 2014).

1.1. Ozone chemistry

Changes in ambient ozone concentrations in a well-mixed boundary layer are dependent upon net photochemical production, entrainment from the free troposphere, surface deposition, and transport processes:

$$\frac{\partial[\text{O}_3]}{\partial t} = P(\text{O}_3) + \frac{w_e \Delta \text{O}_3 - u_d[\text{O}_3]}{H} - \nabla \cdot (\mathbf{v}[\text{O}_3]), \quad (1)$$

where $\partial[\text{O}_3]/\partial t$ is the local O_3 rate of change; $P(\text{O}_3)$ is the instantaneous net photochemical production rate; $(w_e \Delta \text{O}_3 - u_d[\text{O}_3])/H$ is the ozone transport rate across the mixing layer boundary; and $\nabla \cdot (\mathbf{v}[\text{O}_3])$ is the ozone transport rate within the mixing layer by horizontal advection and vertical turbulent eddies. Specifically, w_e is the entrainment velocity; ΔO_3 is the ozone difference between the free troposphere and the top of the mixing layer, H ; u_d is the ozone deposition velocity; and \mathbf{v} is the wind velocity. Although $\partial[\text{O}_3]/\partial t$ is easily derived, it does not indicate the source of ozone. Distinguishing factors contributing to ambient ozone and determining the relationship between ozone and its precursors are key issues for air quality modelers.

The instantaneous ozone production rate, $P(\text{O}_3)$, is summarized by Equation (2) as the difference between the net chemical ozone production (P_{chem}) and loss (L_{chem}) rates:

$$P(\text{O}_3) = P_{chem} - L_{chem}. \quad (2)$$

$$P_{chem} = k_{\text{NO}+\text{HO}_2}[\text{NO}][\text{HO}_2] + \sum_i k_{\text{NO}+\text{RO}_{2i}}[\text{NO}][\text{RO}_{2i}] \quad (3)$$

$$\begin{aligned} L_{chem} = & f_{\text{H}_2\text{O}}J_{\text{O}_3}[\text{O}_3] + k_{\text{OH}+\text{O}_3}[\text{OH}][\text{O}_3] + k_{\text{HO}_2+\text{O}_3}[\text{HO}_2][\text{O}_3] \\ & + P(\text{RONO}_2) + k_{\text{OH}+\text{NO}_2}[\text{OH}][\text{NO}_2] + L(\text{O}_3 + \text{alkenes}) \\ & + L(\text{O}_3 + \text{halogens}) \end{aligned} \quad (4)$$

Equation (3) describes the net photochemical ozone production as the formation of NO_2 molecules outside of the NO_x photostationary state (PSS) via reactions with NO and peroxy radicals (HO_2 and RO_2); k terms are reaction rate coefficients. Equation (4) describes the net chemical ozone loss through its photolysis where J_{O_3} and $f_{\text{H}_2\text{O}}$ are the O_3 photolysis frequency and fraction of $\text{O}(^1\text{D})$ atoms reacting with H_2O ; O_3 reactions with HO_x ; reactions between

OH and NO_2 ; the production of organic nitrates [$\text{P}(\text{RONO}_2)$] including net production of peroxyacyl nitrates; and O_3 reactions with alkenes and halogens.

The net production rate has been presented in several ways (Kleinman, 2005; Finlayson-Pitts and Pitts, 2000). As ozone can be destroyed directly or through loss of NO_2 to reservoir species, L_{chem} encompasses all possible ozone loss processes in different NO_x regimes.

Production pathways can vary with NO_x and VOC abundances. Two regimes are defined for $\text{P}(\text{O}_3)$ dependency on these precursors: one in which NO_x increases are more effective in producing ozone, called NO_x -sensitive, and one in which increasing VOCs is more effective in producing ozone, called VOC-sensitive (Kleinman, 2005). Knowing a region's dominant regime dictates the most cost-effective mitigation strategy.

1.2. Direct ozone production rate measurements

NO_x and VOCs directly influence $\text{P}(\text{O}_3)$. All other terms in Equation (1) are proportional to O_3 or NO_2 , which are related, or to the ozone gradient. Therefore, reducing $\text{P}(\text{O}_3)$ will reduce O_3 provided that it is not transported from other areas. Ozone production is traditionally determined from modeled or measured radicals: an alternative method is to measure it directly. These measurements are a useful tool for evaluating model photochemistry, determining the efficacy of ozone abatement strategies, and providing constraints for model chemical mechanisms. Direct measurements can help to distinguish NO_x -VOC sensitivity, and through Equation (1), ambient ozone sources can be attributed to either local production or transport from other areas.

A new instrument, the Measurement of Ozone Production Sensor (MOPS), measures $\text{P}(\text{O}_3)$ (Cazorla and Brune, 2010). The idea of a direct $\text{P}(\text{O}_3)$ measurement was first proposed by Jeffries (1971), but was never published in peer-reviewed literature.

The first version, MOPsv1, was deployed to Houston during the SHARP 2009 campaign as a first attempt to evaluate model-derived $\text{P}(\text{O}_3)$ (Cazorla et al., 2012). Measured $\text{P}(\text{O}_3)$ was found to be similar to calculated $\text{P}(\text{O}_3)$ from measured radicals, but peak values were shifted to later in the morning. Further, the MOPsv1 diurnal curve was similar to that calculated from modeled radicals, but $\text{P}(\text{O}_3)$ magnitudes were twice as large. These inconclusive findings, along with high measurement uncertainty, made it difficult to test model-derived $\text{P}(\text{O}_3)$. The MOPsv1 captured morning $\text{P}(\text{O}_3)$, but routinely measured negative $\text{P}(\text{O}_3)$ in the afternoon, which was thought to result from NO_2 wall loss in the MOPS chambers (Cazorla and Brune, 2010).

Since 2009, the MOPsv1 has been rigorously tested and deployed to Ft. Worth, TX in 2010, but further improvements were needed to quantitatively measure $\text{P}(\text{O}_3)$. This paper describes these improvements and the first $\text{P}(\text{O}_3)$ measurements obtained by two second-generation MOPsv2s during the 2013 Deriving Information on Surface conditions from Column and Vertically-resolved observations Relevant to Air Quality (DISCOVER-AQ) field campaign in Houston. Two MOPsv2s measured $\text{P}(\text{O}_3)$ in separate locations and were later compared while collocated. These measurements are discussed and surface advection rates are derived for a high ozone event in September.

2. Experimental methods

2.1. The Penn state Measurement of Ozone Production Sensor

The ozone production rate is found by measuring the difference in O_x ($\text{O}_3 + \text{NO}_2$) that is continuously sampled between a transparent sample chamber and a reference chamber that is covered

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