

## Establishing Policy Relevant Background (PRB) Ozone Concentrations in the United States

Elena C. McDonald-Buller,<sup>†</sup> David T. Allen,<sup>†,\*</sup> Nancy Brown,<sup>‡</sup> Daniel J. Jacob,<sup>§</sup> Daniel Jaffe,<sup>||</sup> Charles E. Kolb,<sup>⊥</sup> Allen S. Lefohn,<sup>#</sup> Samuel Oltmans,<sup>∇</sup> David D. Parrish,<sup>∇</sup> Greg Yarwood,<sup>○</sup> and Lin Zhang<sup>§</sup>

<sup>†</sup>University of Texas at Austin, Austin Texas

<sup>‡</sup>Lawrence Berkeley National Laboratory, Berkeley, California

<sup>§</sup>Harvard University, Cambridge, Massachusetts

<sup>||</sup>University of Washington, Bothell, Washington

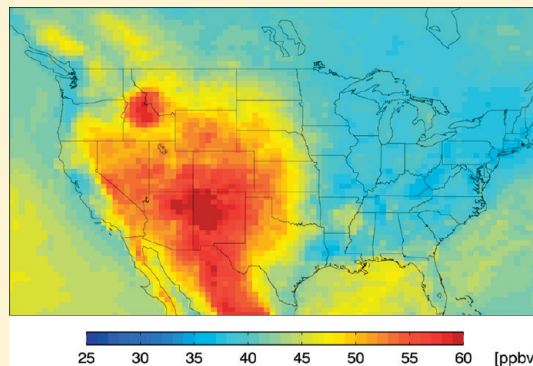
<sup>⊥</sup>Aerodyne Research, Inc., Billerica, Massachusetts

<sup>#</sup>ASL & Associates, Helena, Montana

<sup>∇</sup>National Oceanic and Atmospheric Administration, Boulder, Colorado

<sup>○</sup>ENVIRON International, Novato, California

**ABSTRACT:** Policy Relevant Background (PRB) ozone concentrations are defined by the United States (U.S.) Environmental Protection Agency (EPA) as those concentrations that would occur in the U.S. in the absence of anthropogenic emissions in continental North America (i.e., the U.S., Canada, and Mexico). Estimates of PRB ozone have had an important role historically in the EPA's human health and welfare risk analyses used in establishing National Ambient Air Quality Standards (NAAQS). The margin of safety for the protection of public health in the ozone rulemaking process has been established from human health risks calculated based on PRB ozone estimates. Sensitivity analyses conducted by the EPA have illustrated that changing estimates of PRB ozone concentrations have a progressively greater impact on estimates of mortality risk as more stringent standards are considered. As defined by the EPA, PRB ozone is a model construct, but it is informed by measurements at relatively remote monitoring sites (RRMS). This review examines the current understanding of PRB ozone, based on both model predictions and measurements at RRMS, and provides recommendations for improving the definition and determination of PRB ozone.



### INTRODUCTION

Among the most ubiquitous air quality problems that affect the U.S. are enhanced concentrations of ground-level ozone, which is a secondary pollutant formed by the photochemical reactions of its precursors that include oxides of nitrogen ( $\text{NO}_x$ ) and volatile organic compounds (VOC). Exposure to ozone has been associated with adverse human health effects, including decreased lung function, exacerbation of asthma and respiratory conditions, premature mortality, natural and agricultural ecosystem injury and loss, and deterioration of the built (i.e., materials) environment.<sup>1–8</sup>

Primary and secondary National Ambient Air Quality Standards (NAAQS) for ozone have been established to protect public health and public welfare, respectively. Review of the criteria and standards, by the U.S. Environmental Protection Agency (EPA), is required at five-year intervals by Section 109(d)(1) of the Clean Air Act. As a result of this process, the primary and secondary NAAQS for ground-level ozone have become increasingly stringent over the past several decades,

with significant changes in averaging time, level, and form. In March 2008, the EPA established primary and secondary NAAQS of 0.075 ppm for ozone concentrations averaged over 8 h.<sup>9</sup> During a reconsideration of these standards, in January 2010 the EPA proposed to strengthen the primary NAAQS to an 8 h averaged ozone concentration in the range of 0.060 and 0.070 ppm and to establish a new cumulative, seasonal secondary standard in the range of 7–15 ppm-hours.<sup>10</sup> In September 2011, the EPA's draft ozone NAAQS, which it had submitted for review to the President's Office of Management and Budget on July 11, 2011, were withdrawn.<sup>11</sup> Future rulemaking is to be based on EPA's<sup>12</sup> new periodic review of the air quality criteria and standards for ozone to be completed in 2013. The components of the periodic review consist of an Integrative

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Review Plan (IRP; an outline of the review process and key science-policy questions), an Integrative Science Assessment (ISA; an evaluation and integration of the policy-relevant science), the Risk and Exposure Assessments (REAs; quantitative estimates of health and welfare exposures and risks associated with current ambient levels and current and alternative regulatory air quality standards), and Policy Assessment (PA; a presentation of the scientific basis for the policy options for consideration by the EPA Administrator prior to establishing proposed and final rules).<sup>12</sup>

The determination of background ozone concentrations has important implications for the ozone rulemaking process. Background ozone concentrations used to inform decisions about setting the primary and secondary NAAQS are referred to as Policy Relevant Background (PRB) ozone concentrations.<sup>8</sup> For the review completed in March 2008, the EPA<sup>8,13,14</sup> defined PRB ozone concentrations as those that would occur in the United States in the absence of anthropogenic emissions in continental North America (i.e., the United States (U.S.), Canada, and Mexico). In this context, PRB concentrations represent levels that are not controllable by regulations either in the U.S. or through agreements with the neighboring North American countries.<sup>8,13,14</sup> Sources that contribute to PRB ozone concentrations include natural sources globally and anthropogenic sources from outside of North America. Processes that contribute to PRB ozone concentrations include photochemistry associated with natural emissions of volatile organic compounds (VOCs), nitrogen oxides (NO<sub>x</sub>), and carbon monoxide (CO) from sources such as biogenic emissions (not including agricultural activities), wildfires, lightning, the long-range transport of ozone and its precursors from outside of North America, and stratospheric-tropospheric exchange (STE) of ozone.<sup>8,13,14</sup>

The approach the EPA has used to establish PRB ozone concentrations has changed over time. For the review completed in 1997, the EPA<sup>15,16</sup> estimated an annual average ozone background concentration near sea level in the U.S. to be in the range of 0.020–0.035 ppm, which included a stratospheric contribution of 0.005–0.015 ppm and a 0.01 ppm contribution from the photochemical oxidation of methane and carbon monoxide. In addition, the natural ozone background concentration for a 1 h daily maximum at sea level during the summer in the U.S. was estimated to be 0.03–0.05 ppm.<sup>15</sup> These estimates were based on observations at sites in the continental U.S. with low maximum hourly average ozone concentrations that appeared to be relatively isolated from anthropogenic sources.<sup>15,16</sup> The EPA<sup>17</sup> adopted a constant value of 0.04 ppm for PRB ozone.

Relatively remote monitoring sites (RRMS) are sites that are not strongly influenced by but not necessarily free from the effects of nearby pollution sources.<sup>8</sup> The estimate of PRB ozone concentrations at remote locations, such as Trinidad Head (CA), Mt. Bachelor Observatory (OR), Gothic (CO), and Yellowstone National Park (WY), have provided important insights regarding the relative importance of processes that contribute to PRB ozone concentrations.<sup>18,19</sup> However, for the review completed in March 2008,<sup>8,13,14,17</sup> the EPA determined that PRB ozone concentrations could not be derived solely from measurements of ozone at RRMS because of long-range transport from anthropogenic source regions within North America. Instead, estimates of PRB ozone concentrations were established based on predictions of the global chemical transport model, GEOS-Chem, described in Fiore et al.<sup>20</sup> for the 2001 April to September season. At the time, GEOS-Chem was

the only model documented in the literature for estimating PRB ozone. In addition to a standard simulation including anthropogenic and natural sources of emissions, Fiore et al.<sup>20</sup> conducted a simulation in which North American anthropogenic emissions were set to zero (North American background or PRB) and a simulation in which global anthropogenic emissions were set to zero and methane was set to its 700 ppbv preindustrial value (natural background). Differences between the PRB and natural ozone simulations reflected the contributions of intercontinental pollution influences and anthropogenic methane. GEOS-Chem predictions indicated that PRB ozone concentrations varied with season, altitude, and meteorological conditions. The EPA determined that 4 h average PRB ozone concentrations at the surface were generally in the range of 0.015–0.035 (0.025 ± 0.010) ppm in the afternoon, but were actually lower under meteorological conditions conducive to high ozone episodes (i.e., concentrations >0.084 ppm). PRB ozone concentrations were estimated to be highest during spring, due to contributions from hemispheric pollution and stratospheric intrusions, and were predicted to decline into summer.<sup>8,13,14,17</sup> The stratospheric contribution to surface ozone was estimated to typically be below 0.020 ppm and was more frequently enhanced at high altitude than low altitude sites.<sup>8,13,14,17</sup>

In the existing regulatory framework for review of the NAAQS described above,<sup>12</sup> PRB ozone estimates are established in the ISA and have a crucial role in the REAs. Risks are only estimated for ambient ozone concentrations that exceed PRB levels, which EPA<sup>17</sup> considers most relevant for policy decisions. For the review completed in March 2008, the EPA used estimates of PRB ozone concentrations for 12 urban areas (Atlanta, Boston, Chicago, Cleveland, Washington DC, Detroit, Houston, Los Angeles, New York, Philadelphia, Sacramento, and St. Louis) to calculate human health risks.<sup>17</sup> Risk assessments reflected two different types of human studies (i.e., controlled human exposure and epidemiological).<sup>17</sup> For its controlled human exposure risk analyses, the EPA calculated the following to estimate risk associated with hourly ozone concentrations in excess of PRB: (1) the expected risk given the personal exposures associated with ambient ozone concentrations; (2) the expected risk given the personal exposures associated with estimated PRB ambient ozone concentrations; and (3) subtracted the latter from the former. For its epidemiological risk analyses, the EPA used different exposure metrics, including the 24-h average and the daily 1 h and 8 h maximum ozone concentrations. As an example, for the concentration–response function relating daily mortality to daily 1-h maximum ozone concentrations, the daily changes in 1 h maximum ozone concentrations were calculated. For the epidemiology-based risk assessment associated with levels of ozone above PRB levels, the following steps were implemented: (1) using monitor-specific input streams of hourly ozone concentrations for a specific year, the 1 h maximum ozone concentration for each day was calculated; (2) using the stream of hourly PRB ozone concentrations, the 1 h maximum PRB ozone concentration for each day was calculated; and (3) for each day, the latter was subtracted from the former.

Sensitivity analyses performed by the EPA<sup>17</sup> relating varying PRB ozone concentrations to risk estimates demonstrated its importance in the REA process. Estimates assuming lower PRB ozone levels resulted in increased estimates of nonaccidental mortality incidence per 100 000 that were often 50–100% greater than the base case estimates.<sup>17</sup> Similarly, estimates

assuming higher PRB ozone levels resulted in decreased estimates of nonaccidental mortality incidence per 100 000 that were  $\geq 50\%$  less than the base case estimates.<sup>17</sup> The EPA's sensitivity analyses illustrated that changing estimates of PRB ozone concentrations have a progressively greater impact on estimates of mortality risk as more stringent standards are considered.<sup>17</sup>

In March 2011, the EPA<sup>21</sup> released the first external review draft of the ISA for the ongoing periodic review. The draft ISA includes relevant emerging studies conducted after the release of the 2006 criteria documents,<sup>8,13,14</sup> among these are studies by Cooper et al.,<sup>22</sup> Zhang et al.,<sup>23</sup> Oltmans et al.,<sup>24</sup> Parrish et al.,<sup>25</sup> Langford et al.,<sup>26</sup> Kaynak et al.,<sup>27</sup> and Wang et al.<sup>28</sup> Future drafts of the ISA will incorporate other research as it becomes available. In April 2011, the EPA issued its plans for the health risk and exposure assessment<sup>29</sup> for the ongoing periodic review. Among the changes from the review completed in March 2008, the EPA plans to model population exposures to ambient ozone in three or more of the 12 urban areas modeled, as well as in a high-elevation area such as Denver.<sup>29</sup> The GEOS-Chem model with  $0.5^\circ \times 0.67^\circ$  ( $\sim 50 \times 50 \text{ km}^2$ ) horizontal resolution over North America as described by Zhang et al.<sup>30</sup> is expected to be used to derive PRB ozone estimates with multiple scenarios including a base case or current atmosphere scenario, for which a model performance evaluation will be conducted using surface and satellite measurements, and three additional emissions scenarios isolating the contributions of internationally transported air pollutants to U.S. ozone concentrations.<sup>29</sup>

The primary objectives of the review presented here are to examine the current understanding of PRB ozone, based on both model predictions and measurements at RRMS and to provide recommendations for improving the definition and determination of PRB ozone. The review is based on both information available in the literature and information presented at a workshop held on March 30–April 1, 2011 at The University of Texas at Austin: (<http://www.utexas.edu/research/ceer/prb/>). The workshop, entitled *Workshop on Policy Relevant Background Ozone Concentrations in the United States*, included 10 invited participants (all of the authors of this paper with the exception of Dr. Lin Zhang) with expertise in global and regional chemical-transport models, remote/rural ambient surface and airborne monitoring, satellite data retrievals, and emissions inventory development and analysis. On March 30, 2011, the first day of the workshop, the participants made presentations and responded to questions in their areas of expertise. These presentations were open to the public on The University of Texas at Austin campus and were broadcast live over the web, drawing a national audience. The findings and recommendations were initially formulated by the participants at closed sessions during March 31 and April 1, 2011. They were refined through a series of analyses performed in response to reviewer comments, following the workshop. All of the authors participated in this process. In addition to the authors, the discussions also involved Dr. Joseph Pinto as an active participant from the U.S. EPA. The workshop was sponsored by the American Petroleum Institute, for which two representatives attended as observers only.

Our review is organized into a series of five topics that address the definition of PRB ozone, spatial and temporal variations across the U.S., the application and performance of models used to determine PRB, the role of measurements, and the potential implications of sources of PRB ozone for attainment demonstrations and the SIP

development process. Each section includes major findings followed by policy and/or research recommendations.

## ■ THE CONTEXT OF PRB OZONE: DEFINING BACKGROUND AND BASELINE OZONE CONCENTRATIONS

National and international activities have attempted to distinguish between the terms “background” and “baseline” ozone concentrations in the context of understanding the long-range transport of air pollution. The Task Force on Hemispheric Transport of Air Pollution (TF HTAP), created in December 2004 by the Convention on Long-range Transboundary Air Pollution (LRTAP Convention), acknowledged that the terms global or hemispheric background concentrations and baseline concentrations are often used interchangeably.<sup>31</sup> TF HTAP<sup>31</sup> defined baseline concentrations of a pollutant as “...an observation made at a site when it is not influenced by recent, locally emitted or produced pollution.”, and global or hemispheric background concentrations as “...a model construct that estimates the atmospheric concentration of a pollutant due to natural sources only.” In the context of baseline concentrations, the Task Force<sup>31</sup> stated that neither a strict definition of recently produced local sources of anthropogenic pollution, nor a means to eliminate traces of local pollution emitted many days earlier and well-mixed with other air masses, exist. For ozone and other pollutants that have longer lifetimes, models are required to determine global or hemispheric background concentrations at sites where naturally occurring concentrations are well mixed with anthropogenic sources.<sup>31</sup> The TF HTAP further recognized the terms “urban background” and “rural or regional background” in the literature, which are based on observations. Urban background concentrations were described as those “...observed in urban areas away from the direct influence of heavily-trafficked roads and chimney stacks.” Rural or regional background concentrations were described as “...those observed at locations where there is little influence from urban sources of pollution.”<sup>31</sup>

The Committee on the Significance of International Transport of Air Pollutants of the National Research Council<sup>32</sup> acknowledged EPA's definition of PRB ozone as a model construct, but noted that it was unclear whether the PRB included tropospheric ozone from North American sources that have already traveled around the globe. The Committee<sup>32</sup> described the term “background O<sub>3</sub>” as ambiguous, hypothetical, and not directly measurable and the term would always have to be qualified. Baseline ozone was used by the Committee<sup>32</sup> to “describe a measurable quantity, the statistically defined lowest abundances of ozone in the air flowing into a country, which is typical of clean-air, remote marine sites at the same latitude.” The Committee<sup>32</sup> recognized that baseline ozone varies with location and season in the Northern Hemisphere and can change over time. In addition, regional and continental emissions of ozone precursors “...will also contribute to an increasingly diffuse background that is indistinguishable from baseline O<sub>3</sub> in most urban airsheds and beyond local control.”<sup>32</sup>

In an overview of the role of background ozone on air quality issues, Reid et al.<sup>33</sup> noted that “different interpretations in the understanding of what constitutes background widen the uncertainty in reported values”. In their context, the ozone background concentration is the lowest level that can be achieved in a jurisdiction. It has implications for both local air quality policy and the contribution to health and ecosystem impacts.

It is obvious that the definitions and use of the terms background and baseline ozone concentrations vary widely and can be subject to ambiguities across the air quality scientific and regulatory communities. While this review cannot remove this ambiguity, for clarity it is necessary to precisely define the meanings of these terms that will be used in this review. Here, a baseline ozone concentration is defined as an observation made at a site when it is not influenced by recent nationally emitted or produced pollution. In practice, the determination of the absence of recent pollution is based upon measurements of short-lived tracer species (e.g., radon or  $\text{NO}_x$ ) or transport modeling. Since there is no practical method for determining if national emissions have perhaps been circulated globally, well-aged and well-mixed national influences are necessarily included in baseline concentrations. This definition is consistent with that of the TF HTAP, but explicitly recognizes that U.S. generated pollution should be excluded on all spatial scales (local, regional, etc.) to the extent possible in the determination of baseline ozone concentrations. This definition does not define baseline ozone concentrations as necessarily the lowest ozone concentration measured at a site, nor does it represent baseline ozone concentrations as a single value. This review recognizes PRB ozone concentrations as a model construct in accordance with EPA's definition. Differences between PRB and baseline ozone concentrations can be quantified by evaluating the models used to construct PRB ozone concentrations against observations at sites used to determine baseline ozone concentration. These differences will reflect North American pollution contributions to transported midlatitude ozone, unrecognized U.S. pollution contributions, and errors in the models.

We note that although EPA has established a relatively specific regulatory definition of PRB ozone concentrations,<sup>8,13,14</sup> ambiguities in this definition and its application still exist. These are largely associated with the question of whether emissions sources could be subject to control or not. For example, uncertainties surround the inclusion of fires that are natural versus anthropogenic in origin, of agricultural emissions, of ocean-going vessels and air transport operations, and of North American anthropogenic methane emissions.

**Findings.** Inconsistencies exist in the use of the terms “background” and “baseline” ozone concentrations.

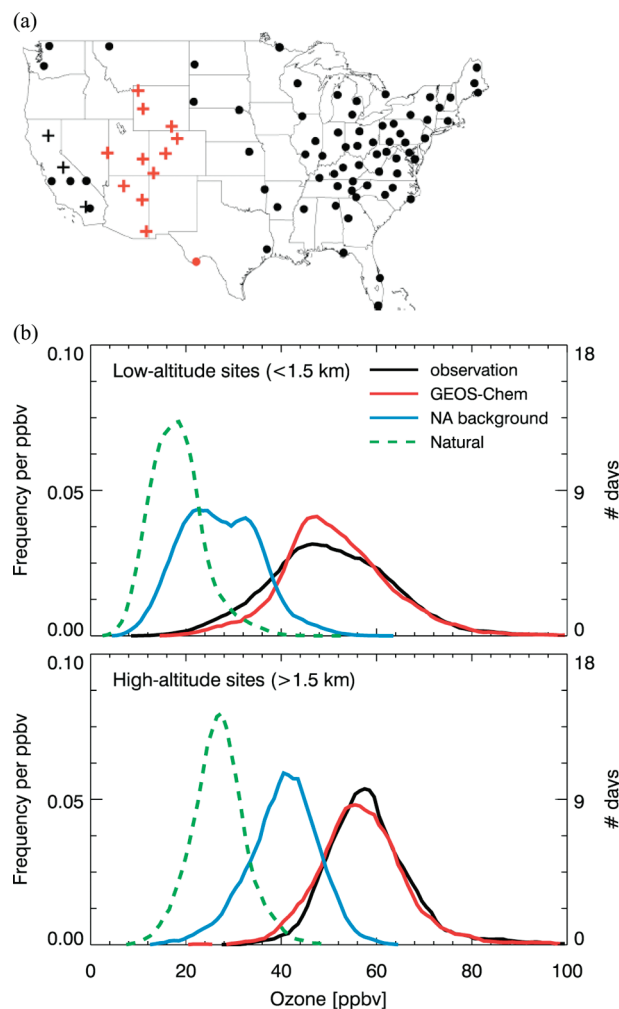
The EPA has established a relatively specific regulatory definition of PRB ozone, but ambiguities in the definition and its application still exist.

**Policy Recommendations.** The definitions and applications of the terms “background” and “baseline” ozone concentrations in the scientific, risk and exposure, and policy assessment air quality communities and among air quality managers should be harmonized.

Further clarity is required in the regulatory definition of PRB ozone recognizing the contributions and uncertainties surrounding biomass burning, biogenic emissions related to agriculture, ocean-going vessels and air transport operations, and North American anthropogenic methane emissions.

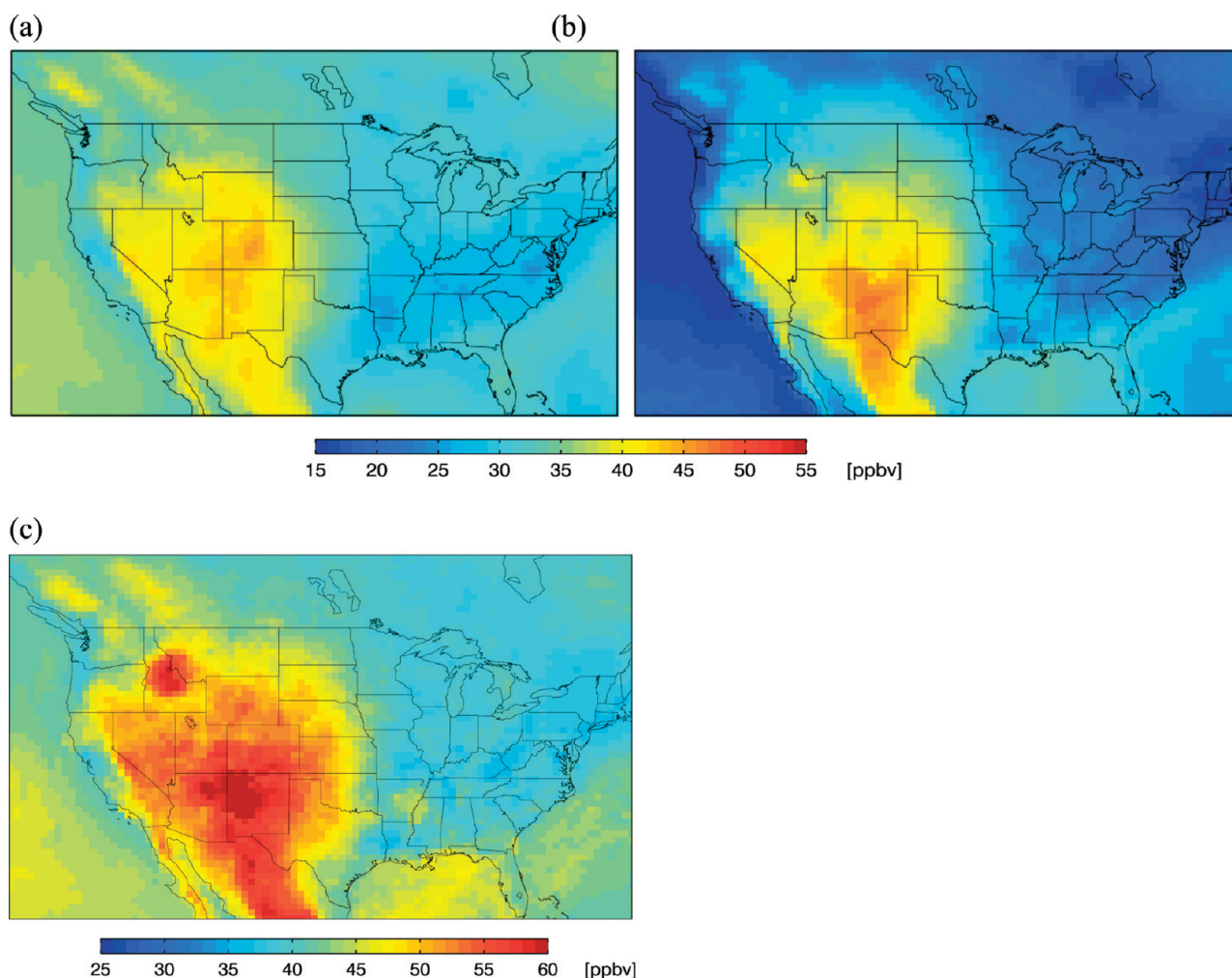
## ■ SPATIAL AND TEMPORAL VARIATIONS IN PRB OZONE

Global and regional chemical transport models<sup>20,30,34</sup> as well as measurements of baseline ozone concentrations<sup>35</sup> at RRMS have demonstrated that PRB ozone concentrations vary spatially and temporally across the U.S. Temporal and spatial variations



**Figure 1.** (a) CASTNet ozone monitoring sites in the continental United States in 2006 from Zhang et al.<sup>30</sup> Sites in the intermountain west are indicated in red. Pluses denote sites above 1.5 km altitude. (b) Frequency distributions of maximum daily 8-h averaged (MDA8) ozone concentrations in March–August 2006 for the ensemble of low-altitude (<1.5 km) and high-altitude CASTNet sites in the U.S. from Zhang et al.<sup>30</sup> Model results (red) are compared to observations (black). Also shown are frequency distributions for the North American (PRB) background (solid blue) and natural background (dashed green).

can arise from regional differences in PRB ozone sources, such as fires, long-range transport, synoptic-scale meteorological variability, and STE, or from differences in ozone removal processes including deposition and chemical destruction. Figure 1 shows the frequency distributions of maximum daily 8 h averaged (MDA8) ozone concentrations observed at the ensemble of Clean Air Status and Trends Network (CASTNet) low altitude (<1.5 km) and elevated (>1.5 km) sites during 2006. These observations are compared with GEOS-Chem predictions, sampled at the appropriate pressure level, by Zhang et al.,<sup>30</sup> and natural and North American (i.e., PRB ozone) background ozone concentrations. GEOS-Chem predictions of the natural background were determined by zeroing global anthropogenic  $\text{NO}_x$ , nonmethane volatile organic compounds (NMVOC), and CO emissions and setting methane concentrations to a preindustrial value of 700 ppbv. North American (PRB) ozone background concentrations were determined by



**Figure 2.** GEOS-Chem mean PRB MDA8 ozone concentrations (ppb) for the (a) spring (March/April/May) and (b) summer (June/July/August) of 2006, and (c) annual 4th highest GEOS-Chem PRB MDA8 ozone concentrations for 2006–2008 from Zhang et al.<sup>30</sup>

zeroing anthropogenic  $\text{NO}_x$ , NMVOC, and CO emissions in continental North America. Figure 1 indicates that the variation in PRB ozone concentrations is in part attributable to their tendency to increase with altitude. All elevated sites are located in the western U.S.; PRB ozone is generally higher in the mountainous western U.S. than in the eastern U.S. Mean PRB values for the U.S. in spring-summer (6-month average) are  $27 \pm 8$  ppbv at low altitude sites (<1.5 km) and  $40 \pm 7$  ppbv at high-altitude sites. These values were 9–13 ppbv higher than the natural background due to intercontinental pollution including anthropogenic methane and were on average 4 ppbv higher than those reported in earlier studies with GEOS-Chem by Fiore et al.<sup>20</sup> and Wang et al.;<sup>28</sup> the differences were attributed to a combination of increasing Asian emissions, higher model lightning, and higher model resolution. In another recent study using the Community Multiscale Air Quality (CMAQ) regional model, Mueller and Mallard<sup>34</sup> examined the relative roles of natural emissions (including biogenic, oceanic, geogenic, and fires) and background sources (i.e., model boundary conditions established from the GEOS-Chem simulations of Fiore et al.<sup>36</sup>) on ozone concentrations at CASTNet sites for the year 2002. MDA8 ozone concentrations due to boundary and natural sources were higher in the western than the eastern U.S.<sup>34</sup>

Time scales of systematic temporal variation in PRB ozone range from hourly (i.e., diurnal profiles), to seasonal to interannual.<sup>30</sup> Figure 2 shows seasonal mean GEOS-Chem predictions of PRB ozone concentrations during 2006 and annual GEOS-Chem predictions of the fourth highest PRB ozone concentrations during 2006–2008 from Zhang et al.<sup>30</sup> Figure 2 demonstrates the strong geographic and seasonal variations that exist in PRB ozone concentrations across the U.S. In some regions, PRB concentrations could approach 60–70 ppb, a range previously under consideration for revisions to the ozone NAAQS.

**Finding.** Strong spatial and temporal variability exists in PRB ozone across the U.S.

**Policy Recommendation.** The EPA should consider the spatial and temporal variability of PRB ozone in the periodic review of the air quality criteria and standards for ozone, in particular recognizing differences that may exist between populated high- and low- elevation areas and between years and seasons.

**Research Recommendation.** The scientific communities associated with global and regional modeling and measurements at relatively remote sites that are used to inform estimates of PRB ozone should continue to establish and assess the distributions of

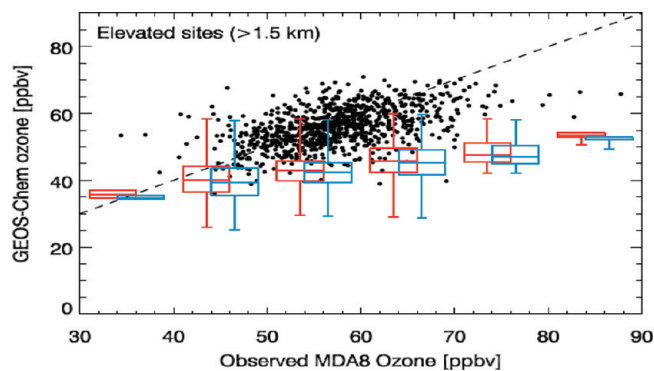
PRB ozone concentrations in the U.S. To the extent possible, coordination between the scientific and policy communities should occur in the definition and use of relevant terminology, in the study of key processes that affect PRB ozone estimates, and in the compilation of measurement and modeling data reflecting the state of the science. Coordination should occur within the time frame needed to support the periodic review process.

### MODELING OF PRB OZONE

The lifetime of ozone in the troposphere can be as long as months,<sup>37</sup> comparable to the time scale for hemispheric mixing. The relatively long lifetime of ozone and the EPA's current regulatory definition of PRB ozone necessitate a reliance on global-scale chemical transport models.

The EPA's earlier and ongoing periodic reviews of the air quality criteria and standards for ozone have relied solely on successive generations of the GEOS-Chem model.<sup>20,30,38</sup> A number of other mature global models for tropospheric ozone, with different heritages, have been developed by the scientific community. The full diversity of these models has not been applied to estimate the distributions of PRB ozone either for the regulatory process or in the peer-reviewed literature. Model intercomparisons including evaluations with ozone observations have been reported by Reidmiller et al.,<sup>38</sup> the Intergovernmental Panel on Climate Change,<sup>39</sup> Atmospheric Composition Change—the European Network (ACCENT),<sup>40</sup> and the United Nations Economic Commission for Europe TF HTAP.<sup>41</sup> These intercomparisons have revealed large differences between simulations of ozone for specific sites and regions, even for models with comparable skills in their overall abilities to reproduce observations. Although community intercomparisons of global ozone models offer insights on model differences in global budgets and individual processes, these cannot be readily related to PRB estimates because of nonlinear chemistry and because of the detail needed for PRB values in policy applications. Application of multiple global models and model intercomparisons of PRB ozone estimates, including with observations at RRMS and aloft, are needed to provide a better appreciation of model uncertainty and understanding of the processes contributing to PRB ozone. The recent study by Mueller and Mallard<sup>34</sup> indicates the potential for a regional model such as CMAQ to also be used in the study of PRB, although a global model is still required to provide boundary conditions. The application of regional models and the nesting of finer-scale regional models within global models for estimating PRB ozone and for understanding how processes, such as fires, drought, and changes in emissions inventories, affect estimates of PRB ozone, should be explored more thoroughly in the future.

State-of-science global models of tropospheric ozone, such as GEOS-Chem, can reproduce monthly mean MDA8 ozone concentrations at RRMS typically within 5 ppb, and also provide a good simulation of synoptic-scale variability in MDA8 ozone.<sup>28</sup> In an evaluation of 15 global models and one hemispheric chemical transport model for the HTAP project, Reidmiller et al.<sup>38</sup> found that although wide variation existed between simulated maximum and minimum ozone concentrations, the ensemble mean represented observations at U.S. CASTNet sites in most regions and seasons well, with mean annual biases typically less than 5 ppbv. At RRMS, PRB ozone often accounts for a large fraction of total ozone and ozone variability, both in the model and in observational



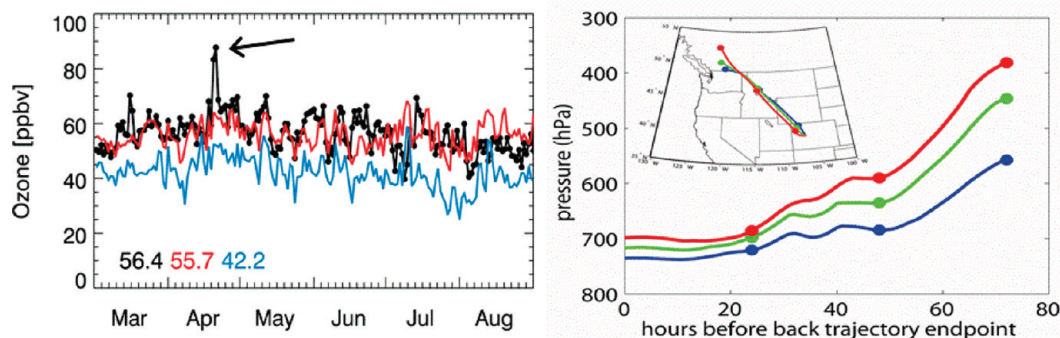
**Figure 3.** Comparison of GEOS-Chem predictions and observed MDA8 ozone concentrations at elevated (>1.5 km) CASTNet sites in the intermountain western U.S. during March-May 2006. Model results are from Zhang et al.<sup>30</sup> The vertical bars are model statistics of U.S. background ozone in red (obtained by zeroing U.S. anthropogenic emissions) and North American background (PRB) ozone in blue, as a function of observed ozone in 10 ppb bins. The statistics show minima, 25th percentile, medians, 75th percentiles, and maxima.

analyses that attempt to separate baseline from pollution influences. This provides some confidence that the models can provide reasonable estimates of monthly mean MDA8 PRB ozone ( $\pm 10$  ppb).

However, there are regions in the U.S. where global models show consistent biases that could be relevant to PRB ozone estimates. For example, models are generally unable to simulate the very low ozone concentrations observed at Gulf Coast sites in summer during onshore flow from the Gulf of Mexico.<sup>20,30,36,38,41</sup> which could reflect marine boundary layer chemistry or stratification that is not properly represented. Models generally find little ozone production in wildfire plumes for short aging times (days) because  $\text{NO}_x$  emissions are low and conversion to peroxyacetyl nitrate (PAN) is rapid.<sup>42–44</sup> In contrast, observations show large ozone production from at least some regional wildfires that may significantly elevate ozone at low altitude sites on a monthly basis.<sup>43,45–47</sup> and persist over long distances from the burned region.<sup>48,49</sup> Yet another difficulty for models is the complex topography in some regions of the U.S., which may promote external influences on surface ozone through fine-scale orographic flow and subsidence.<sup>50</sup>

GEOS-Chem and other global models also have difficulty representing the fine structures of ozone events observed at RRMS in the U.S., including events for which the contribution of PRB ozone is likely important. Stratosphere-troposphere exchange can contribute to PRB ozone at low altitude and, in particular, at elevated sites (Figure 3).<sup>18,19,26,45,51–56</sup> Fire plumes transported on intercontinental scales can contain very high ozone concentrations.<sup>48,57,58</sup> These plumes are generally transported in the free troposphere above the boundary layer, and have a strongly layered structure that is difficult to capture with Eulerian models because of numerical diffusion under stretched-flow conditions.<sup>59</sup> Numerical diffusion broadly affects the ability of models to capture observed maxima, particularly at mountain sites. The effect is expected to be less at surface sites due to dilution of the plumes during entrainment into the boundary layer.<sup>23,60</sup>

**Findings.** Several mature global models are available, but the full diversity of these models has not been applied to estimate the



**Figure 4.** Measured and modeled MDA8 ozone concentrations (left) for Gothic, Colorado (38.96°N, 106.99°W, 2926 m asl) during March 1, 2006–August 31, 2006. The black line shows the observed MDA8 ozone concentrations; the red line shows GEOS-Chem simulations from Zhang et al.;<sup>30</sup> the blue line shows the PRB variations as calculated by GEOS-Chem. Numerical values in black, red and blue give the corresponding average MDA8 value for the entire period. Maximum MDA8 values for the year occurred on April 19th (83 ppbv) and 20th (88 ppbv), respectively, and were not captured by the GEOS-Chem model (black arrow). The right side shows HYSPLIT back-trajectories for April 20th, which indicate rapid descent from the upper troposphere (350–500 hPa). Trajectories were initialized at 300, 500, and 700 m above ground level. This rapid air mass descent is consistent with the 8 h average water vapor mixing ratio observed during the MDA8 period on April 20th of 1.5 g/kg compared to a mean of  $4.6 \pm 2.5$  g/kg (1 sigma) for all days during this entire period, consistent with a free tropospheric source.

distributions of PRB ozone either in the EPA's regulatory process or in the peer-reviewed literature.

Agreement between global model predictions and measurements of monthly mean MDA8 ozone at RRMS provides some confidence in the ability of global chemical transport models to predict PRB ozone in many parts of the U.S.

Global chemical transport models exhibit biases in monthly mean MDA8 ozone in some regions of the U.S., including the Gulf Coast, regions affected by fires, and regions with complex topography, which have implications for model estimates of PRB ozone. They also have difficulty representing the fine structures of ozone events at RRMS that include contributions from PRB ozone sources.

The application of regional models or the nesting of finer-scale regional models within global models for estimating PRB ozone has been only minimally explored.

**Research Recommendations.** Comparisons of multiple, independent global model predictions of the distribution of PRB ozone in the U.S. that can be performed on a time scale consistent with EPA's periodic review process for the ozone standards should be a high priority for the EPA and the global modeling community.

Models used to provide PRB ozone estimates should be extensively evaluated with surface, sonde, and satellite ozone observations. Consistent protocols for evaluation of global model performance should be developed, and among other requirements, should include an assessment of the strengths and weaknesses in the representation of key chemical and physical processes and thorough documentation and review of emissions inventories.

Research should focus on key processes that affect predictions of MDA8 ozone concentrations in the U.S. by global models. Priorities include fires, vertical transport in regions of complex topography, and physical and chemical processes in the marine boundary layer of the Gulf of Mexico.

The difficulties Eulerian models encounter when simulating the fine structures of ozone events observed at RRMS and their effects on PRB ozone distributions should be evaluated. Specific questions that should be addressed during model evaluation are: (1) Do problems exist mainly at mountain sites or do they extend

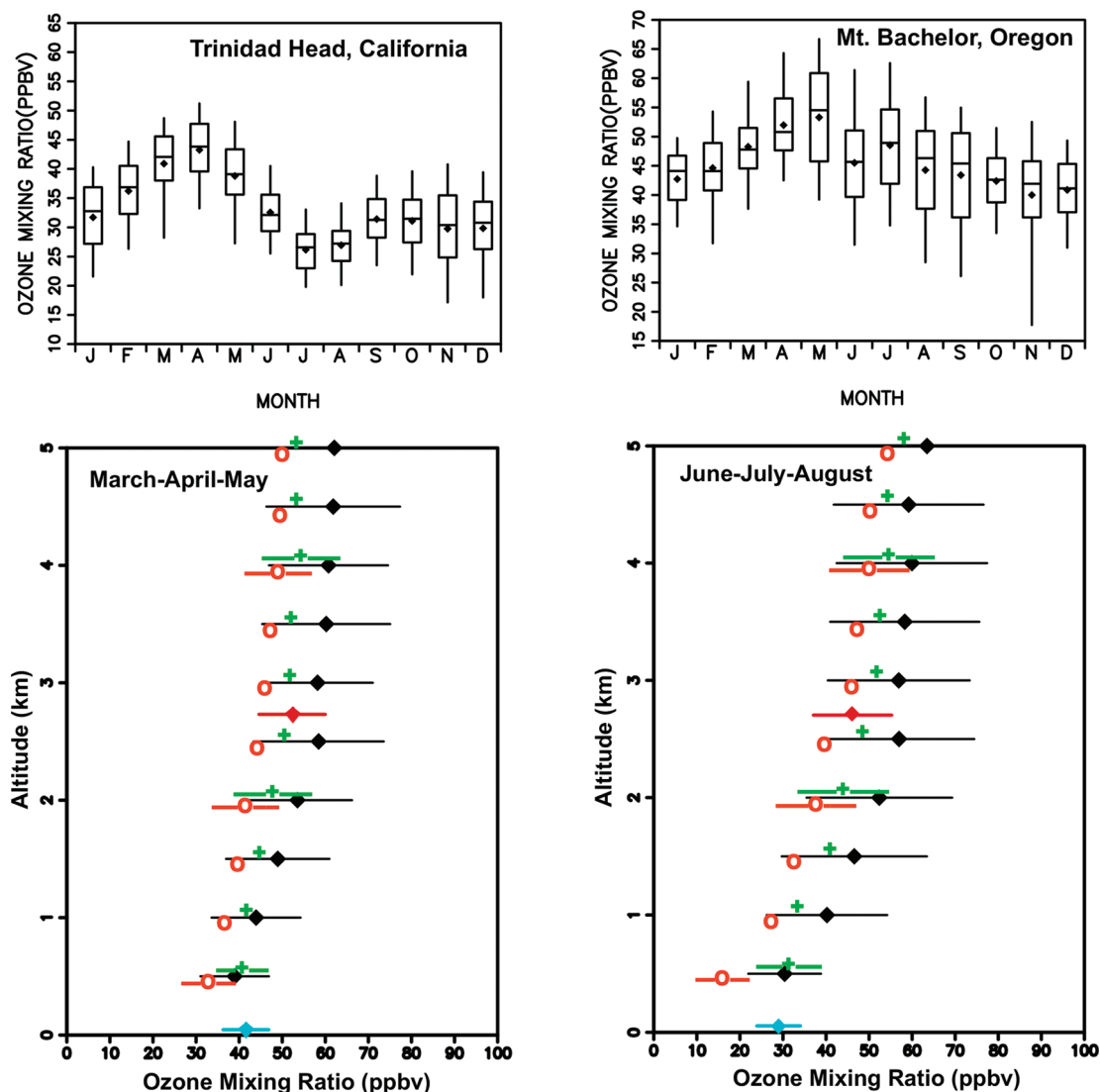
to low elevation sites? (2) Do enhanced ozone events that have their origins in PRB sources significantly affect the enhancements in the overall ozone distribution, and if so, can the models identify these patterns? (3) Can model limitations in simulating the fine structure of the ozone event distribution be overcome? and (4) Can model limitations be overcome by blending model and observational approaches?

Research should explore the application of regional models and the nesting of finer-scale regional models within global models for estimating PRB ozone and for understanding how processes, such as fires, STE, drought, and changes in emissions inventories, affect estimates of PRB ozone.

## THE ROLE OF MEASUREMENTS IN THE DETERMINATION OF PRB OZONE

PRB ozone is a model construct that must be informed by and evaluated based on observational data. The current regulatory definition of PRB includes certain sources of ozone and excludes others. Global models can distinguish estimates of PRB ozone from total predicted ozone, but comparable source apportionment of measured ambient ozone generally is not possible because emissions from multiple, disparate sources interact to form ozone in a highly nonlinear manner and unique source tracers are lacking. However, as described in the previous section, caution must be exercised in applying global models to estimate the distributions of PRB ozone. For example, Figure 3 indicates that GEOS-Chem overpredicts lower observed concentrations and does not capture observations greater than 65 ppb of MDA8 ozone concentrations at elevated (>1.5 km) CASTNet sites in the intermountain western U.S. during March–May 2006. Figure 4 shows similar results specifically for the Gothic Colorado site that experienced enhanced ozone concentrations during April 2006, likely from the descent of air from the upper troposphere, which was not replicated by the GEOS-Chem model.

Observations are essential to validate models and improve the confidence in their performance, to better understand the causes of enhanced ozone, to indicate geographic areas of strength and weakness, and to guide model improvements where needed. Measurements of baseline ozone at RRMS approximate PRB

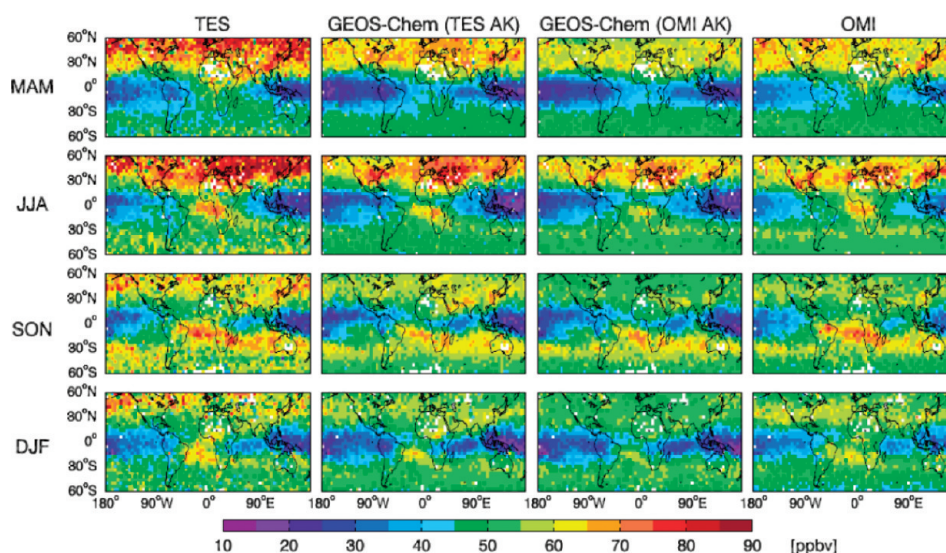


**Figure 5.** Hourly averaged surface ozone concentrations by month at Trinidad Head, California during the daytime (upper left panel) and for Mt. Bachelor, Oregon for free tropospheric sampling conditions (upper right panel) for 2004 through 2009. The diamond represents the mean, the horizontal bar represents the median, the box represents the 25th and 75th percentiles, and the whiskers represent the 5th and 95th percentiles. Average spring (March/April/May) ozone profiles derived from ozone sondes at Trinidad Head are shown in the bottom left panel for 1997 through 2010. These data represent averages over 500 m in altitude with  $\pm 1$  standard deviation. The symbols in blue are the seasonal surface ozone average at Trinidad Head and the symbol in red is the Mt. Bachelor seasonal average plotted at the altitude of the observatory. Profile results from the GEOS-Chem model for 2006 are shown as green pluses. The contribution from Policy Relevant Background in the model profile is shown by orange circles. Representative standard deviations at several altitudes for the model are shown. The bottom right panel shows ozone profiles during the summer months (June/July/August) at Trinidad Head and from the model. The model results are plotted slightly offset in altitude from the nominal altitude for clarity. The slight difference between the Trinidad Head sonde data and the Mt. Bachelor values is due to large scale differences in subsidence at the two locations.<sup>61</sup>

ozone, and provide powerful constraints for and evaluations of model-derived estimates of PRB ozone. A surface monitoring network designed specifically for informing PRB ozone estimates does not exist in the U.S. Ozone measurements at a number of relatively remote surface sites in the U.S. are regularly representative of baseline ozone concentrations. However, care must be taken when interpreting these measurements as approximating PRB ozone. Data from two of these sites, located near the U.S. west coast, the higher elevation Mt. Bachelor, Oregon site<sup>61</sup> and marine boundary layer location and ozone sonde launch site at Trinidad Head, California,<sup>24,62</sup> are shown in Figure 5, and data from these sites have been used widely to gain an observational perspective on western U.S. PRB ozone levels. At Mt. Bachelor,

multiple constituents are measured that provide markers indicative of possible PRB sources that contribute to measured (enhanced) ozone events at NAAQS thresholds.<sup>19,23,61</sup> When interpreting such data, two considerations are important. First, baseline ozone and PRB ozone are not synonymous in that quantification of baseline ozone attempts to avoid recent local or regional influences, while PRB ozone includes some of these influences such as surface deposition and local and regional ozone production from natural sources such as biogenic emissions and wildfires. Second, determination of baseline ozone concentrations by filtering recent local and regional influences is a difficult and somewhat uncertain process. For example, mountain top site data are often filtered according to water vapor





**Figure 6.** Global tropospheric ozone distributions at 500 hPa from the TES and OMI satellite instruments for the different seasons of 2006. The central two columns show the GEOS-Chem model ozone fields smoothed by the different averaging kernels (sensitivities) of the two instruments, demonstrating that most of the differences between TES and OMI are due to different instrument sensitivities rather than bias. White areas indicate lack of data meeting the retrieval quality criteria. From Zhang et al.<sup>74</sup>

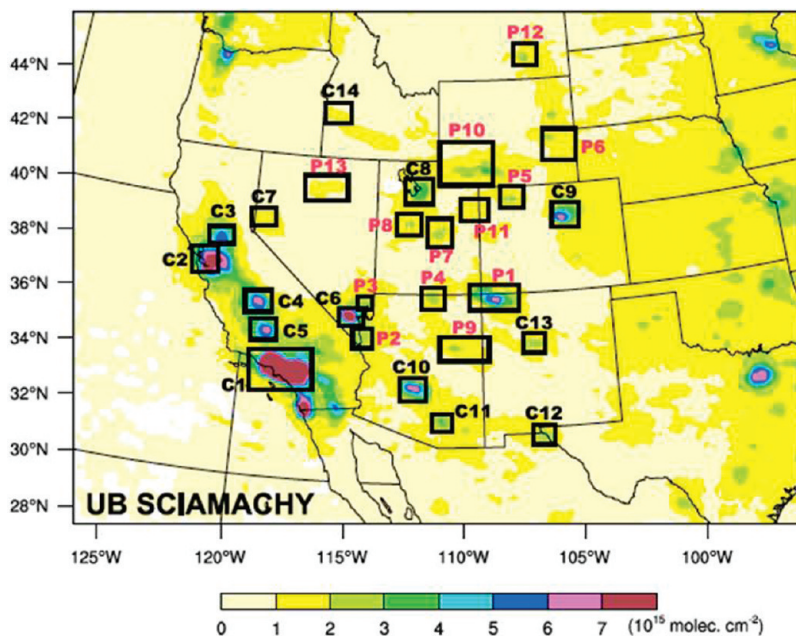
measurements, which are designed to eliminate all boundary layer influences and retain only free troposphere data,<sup>19,63</sup> and marine boundary layer data can be filtered according to tracers of continental influences (radon, CO<sub>2</sub> depletion, etc.),<sup>25,64</sup> wind sector selection,<sup>24,25</sup> or transport modeling.<sup>64</sup> Nevertheless, when these complications are properly considered, baseline measurements of ozone do provide observational data for testing the ability of models to diagnose PRB ozone contributions. The GEOS-Chem predictions of ozone profiles and the North American (PRB) background ozone over Trinidad Head are also shown in Figure 5 averaged over the spring and summer of 2006. The model under-predicts the sonde measurements in the free troposphere by about 5 ppbv, but agrees well with measurements at Mt. Bachelor. The PRB ozone is on average 5 ppbv lower in spring and 7 ppbv lower in summer, reflecting influences from the North American anthropogenic sources in the baseline ozone concentrations.

Interior continental surface sites that are generally free from local (<100 km) anthropogenic contributions of ozone can inform the understanding of PRB sources, including fires and STE and provide valuable information for evaluating global models as described above. Some of the existing CASTNet ozone monitoring sites qualify for that purpose. However, additional measurements of carbon monoxide (CO), chemically speciated fine particulate matter (PM), volatile organic compounds (VOCs), oxides of nitrogen (NO<sub>x</sub>) and total odd nitrogen (NO<sub>y</sub>) at a time resolution comparable to ozone measurements are required to provide stronger constraints on the model and aid in the diagnosis of model performance.

In recent years, ground-based and aircraft campaigns have been carried out along the west coast of North America that have provided information on the characteristics of air reaching the west coast of the U.S, including the baseline ozone distribution, sources that contribute to this baseline, and the impacts on continental interior ozone distributions.<sup>65–68</sup> These short-term studies have deployed advanced instrumentation that measure a large number of ozone precursors as well as other intermediate

species and secondary products (carbonyls, free radicals, aerosol composition). The resulting data sets provide not only stringent tests of model calculations, but also direct means to assess emission sources and to characterize atmospheric transformation and transport processes.<sup>65–68</sup> Commercial aircraft equipped with appropriate instrumentation can also be a reliable and cost-effective means of improving the vertical characterization of the troposphere, as demonstrated by the European MOZAIC program (1994–2010)<sup>69</sup> and expected by the recently initiated IAGOS (In-Service Aircraft for the Global Observing System; <http://www.iagos.org/>) program.

In its recently issued plans for the health risk and exposure assessment<sup>29</sup> for the ongoing periodic review of the air quality criteria and standards for ozone, the EPA noted that the performance evaluation of the GEOS-Chem model will be conducted using both surface and satellite measurements. Satellite-borne sensors have been used in the detection and quantification of the long-range transport of tropospheric ozone and its precursor species and aerosol pollution.<sup>32,70</sup> Detection of tropospheric ozone from satellites is challenging because of the larger stratospheric signal. In addition, stratospheric/tropospheric exchange events (folds) that transport stratospheric ozone into the free troposphere can be difficult to distinguish from pollution plumes entrained into the free troposphere, particularly if only ozone concentration fields are utilized.<sup>23,32,71</sup> Nonetheless, satellite data sets have provided unique large-scale views with repeat coverage that have allowed plumes from intense pollution episodes to be tracked around the northern hemisphere.<sup>32,72,73</sup> Validation and intercomparison of tropospheric ozone observations from the tropospheric emission spectrometer (TES) and ozone monitoring instrument (OMI) satellite sensors, operating in the IR and in the UV respectively, lends confidence in the use of satellite observations for testing models of tropospheric ozone.<sup>74</sup> Figure 6 from Zhang et al.<sup>74</sup> shows the global distributions of tropospheric ozone at 500 hPa from the TES and OMI sensors, along with comparisons to the GEOS-Chem model. In addition, satellite pollutant concentration field data sets coupled



**Figure 7.** Average  $\text{NO}_2$  columns over the western U.S. during the summer of 2005 derived from the SCIAMACHY satellite from Kim et al.<sup>80</sup> Boxes highlight emissions from some U.S. electrical power plants (labeled with P) and cities (labeled with C). Since  $\text{NO}_2$  has a short atmospheric lifetime (several hours), emission sources can be identified from their geographic position without confounding effects from transport.

with inverse model analyses of CO, nitrogen dioxide ( $\text{NO}_2$ ) and formaldehyde (HCHO) have been used to constrain emissions of CO,  $\text{NO}_x$ , and VOCs respectively.<sup>75–79</sup> For example, Figure 7 shows average  $\text{NO}_2$  columns due to  $\text{NO}_x$  emissions from electrical power plants and urban areas in the western U.S. during the summer of 2005 derived from the SCIAMACHY satellite.<sup>80</sup> However, all U.S. satellite sensors for measuring tropospheric composition are beyond their design lifetimes (including MODIS, MISR, MOPITT, AIRS, OMI, TES) and there is no plan for immediate successor systems to provide continuity. Serious degradation of the observation system from space is to be expected in the coming few years, only partly mitigated by the continuing European program (GOME-x, IASI sensors).

**Findings.** PRB ozone is a model construct that must be informed and validated by data from surface, airborne, and space-based measurements.

Surface and airborne measurements of species other than ozone will be required to identify and quantify PRB ozone sources and to constrain models for PRB ozone estimates.

Satellite-borne sensors have been used in the detection and quantification of the long-range transport of tropospheric ozone and its precursor species, and in the evaluation and constraint of emissions estimates of important ozone precursor species.

Many U.S. satellite sensors for measuring tropospheric composition are beyond their design lifetimes. Degradation or loss of these systems will be only partly mitigated by the continuing European programs.

**Research Recommendations.** Joint research teams composed of investigators with expertise in modeling of PRB ozone and measurements at relatively remote sites should develop integrated assessments of the distributions of PRB ozone in the U.S.

Existing, geographically dispersed remote monitoring sites throughout the U.S. should be enhanced by adding measurements of CO,  $\text{NO}_y$ , and PM mass.

Deployment of additional measurements including VOCs, halocarbons, mercury (Hg), chemically speciated fine PM, and  $\text{NO}_x$  should be considered at research sites to allow more refined chemical fingerprinting of air masses.

**Policy Recommendations.** The U.S. should consider instrumentation of U.S. commercial aircraft for long-term observations of atmospheric trace gases.

Current U.S. satellite sensors capable of characterizing and quantifying emissions and long-range transport of ozone and critical precursor species should be maintained as long as possible.

Planning and implementation of new U.S. atmospheric composition satellite missions should continue as vigorously as possible. Engagement in this process could provide attention to sensor specifications that may facilitate the collection of PRB relevant data. Two U.S. atmospheric composition missions are in their early planning phases, with expected launches in the 2020s, at the National Aeronautics and Space Administration (NASA); a geostationary air quality mission (GEO-CAPE) and a global atmospheric composition mission (GACM). Such a combination of geostationary (North America) and low-elevation orbit (global) perspectives would be of considerable value for better constraining estimates of PRB ozone.

## INFLUENCE OF SOURCES OF PRB OZONE ON ATTAINMENT DEMONSTRATIONS AND SIP DEVELOPMENT

The EPA provides guidance on the use of models and other analyses for ozone attainment demonstrations and State Implementation Plan (SIP) development.<sup>81</sup> The initial step in the recommended modeling procedure is the development of a conceptual description of ozone formation in the local area. Based on the results of the conceptual description, potential episodes or seasons to use for photochemical grid modeling are analyzed and eventually a time period for modeling is selected.

Conceptual descriptions are conducted based largely on observational data. The final steps of the modeling procedure include: (i) running the air quality model with basecase emissions to evaluate the performance and performing diagnostic tests to improve the model, as necessary, and (ii) performing future year modeling (including additional control strategies, if necessary) and applying the attainment test at each monitor.<sup>81</sup> The attainment test is based on a relative rather than absolute application of the model estimates, such that the ratio of the model's future to current (baseline) predictions or relative response factor (RRF) is considered. Future ozone concentrations for the attainment test are estimated at existing monitoring sites by multiplying the modeled relative response factor at locations near each monitor by the observation-based, baseline ozone design value for that site.<sup>81</sup> Resulting predicted future concentrations are compared to NAAQS. If these do not meet the attainment test, the future year modeling is typically repeated with the inclusion of one or a suite of emissions control strategies until the attainment test can be passed.

Many sources of PRB ozone do not yet have an explicitly acknowledged role in the development and evaluation of attainment demonstrations and SIPs. In some areas of the U.S., PRB ozone concentrations may provide a significant contribution on days identified as having high ozone, especially with a lower threshold that would accompany a more stringent NAAQS. Identifying and understanding the role of sources of PRB ozone relative to local, regional, or continental contributions to observations at monitoring sites during the development of a conceptual description may influence the selection of historical time periods for air quality modeling. The EPA does have a rule establishing criteria and procedures for use in determining whether air quality monitoring data have been influenced by exceptional events.<sup>82</sup> While the concept of exceptional events and elimination of certain types of events from air quality planning activities has been used for emission sources such as wildfires,<sup>83</sup> there is no precedent for its use for some of the sources of PRB ozone. Because of the nature of the approach for determining attainment, it is important that states understand the relative effects of sources of PRB ozone on model responsiveness (i.e., stiffness) to local and regional emissions control strategies under consideration.

**Finding.** Many sources of PRB ozone do not have an explicitly acknowledged role in the development and evaluation of ozone attainment demonstrations and State Implementation Plans, but may impact components of these processes.

**Policy Recommendations.** EPA should inform states about existing and emerging developments in the quantification of PRB ozone and assess the potential role of PRB ozone in attainment demonstrations.

## ■ SUMMARY PERSPECTIVES

PRB ozone concentrations<sup>8,13,14</sup> are defined by the EPA as those concentrations that would occur in the U.S. in the absence of anthropogenic emissions in continental North America (U.S., Canada, and Mexico). This review found that further clarity is required in the regulatory definition of PRB ozone and its application, recognizing the contributions and uncertainties surrounding biomass burning, biogenic emissions related to agriculture, ocean-going vessels and air transport operations, and North American anthropogenic methane emissions. Estimates of PRB ozone have had an important role historically in the

EPA's human health and welfare risk analyses used in establishing NAAQS. The margin of safety for the protection of public health in the ozone rulemaking process has been established from human health risks calculated based on PRB ozone estimates. Sensitivity analyses conducted by the EPA<sup>17</sup> have illustrated that changing estimates of PRB ozone concentrations have a progressively greater impact on estimates of mortality risk as more stringent standards are considered. Many sources of PRB ozone do not currently have a role in the development and evaluation of attainment demonstrations and SIPs, but may impact components of these processes as well.

As defined by the EPA, PRB ozone is a model construct, but it is informed by data from surface, airborne, and space-based measurements. Consequently, collaborative research teams with expertise spanning these areas are needed for integrated assessments of the distributions of PRB ozone. Strong spatial and temporal variability exists in the distributions of PRB ozone concentrations across the U.S. A recent assessment<sup>30</sup> with the GEOS-Chem model found 6-month mean PRB values for the U.S. in spring-summer of  $27 \pm 8$  ppbv at low altitude sites (<1.5 km) and  $40 \pm 7$  ppbv at high-altitude CASTNet sites. In some regions, PRB concentrations approach 60–70 ppb, a range previously under consideration for revisions to the ozone NAAQS. Several mature global models are available, but the full diversity of these models has not been applied to estimate the distributions of PRB ozone either in the EPA's regulatory process or in the peer-reviewed literature. Comparisons of multiple, independent global model predictions of the distribution of PRB ozone should be a high priority for the EPA and the global modeling community. Future research should focus on key processes that affect predictions of MDA8 ozone concentrations in the U.S. by global models, including fires, STE, vertical transport in regions of complex topography, physical and chemical processes in the marine boundary layer of the Gulf of Mexico, as well as replication of the fine structures of ozone events observed at RRMS.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*Phone: (512) 471-0049; fax: (512) 471-1720; e-mail: allen@che.utexas.edu.

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