

## RESEARCH ARTICLE

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## Key Points:

- Observed and modeled ozone seasonal cycles can be quantified by fitting sine curves
- Models tend to overestimate ozone in Northern Hemisphere midlatitude marine boundary layers
- Fundamental and second harmonic terms are not always well simulated by models

## Supporting Information:

- Supporting Information S1

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## Interhemispheric differences in seasonal cycles of tropospheric ozone in the marine boundary layer: Observation-model comparisons

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**Abstract** Marine boundary layer ozone seasonal cycles have been quantified by fitting the sum of two sine curves through monthly detrended observations taken at three stations: Mace Head, Ireland, and Trinidad Head, California, in the Northern Hemisphere and Cape Grim, Tasmania, in the Southern Hemisphere. The parameters defining the sine curve fits at these stations have been compared with those from a global Lagrangian chemistry-transport model and from 14 Atmospheric Chemistry Coupled Climate Model Intercomparison Project chemistry-climate models. Most models substantially overestimated the long-term average ozone levels at Trinidad Head, while they performed much better for Mace Head and Cape Grim. This led to an underestimation of the observed (North Atlantic inflow–North Pacific inflow) difference. The models generally underpredicted the magnitude of the fundamental term of the fitted seasonal cycle, most strongly at Cape Grim. The models more accurately reproduced the observed second harmonic terms compared to the fundamental terms at all stations. Significant correlations have been identified between the errors in the different models' estimates of the seasonal cycle parameters; these correlations may yield further insights into the causes of the model-measurement discrepancies.

### 1. Introduction

Ozone is widely recognized as an important air pollutant with widespread impacts on human health, crops, and vegetation [Monks *et al.*, 2015]. It is the focus of much policy-making activity, the aim of which is to reduce ozone exposures to meet air quality standards, guidelines, or criteria by reducing emissions of its precursors, oxides of nitrogen (NO<sub>x</sub>), and volatile organic compounds. Although many policy questions can be answered using observational networks, models are important tools in the policy formulation process for ozone. Regional-scale chemistry transport or air quality models are in widespread use in the policy-making process to assess and promulgate strategies to achieve satisfactory air quality.

As the intensity and frequency of ozone episodes fall in both North America and Europe, there is an increasing focus by policy makers on the intercontinental transport of ozone [Hemispheric Transport of Air Pollution (HTAP), 2010; Clifton *et al.*, 2014; Cooper *et al.*, 2015; Doherty, 2015]. In Europe, there are concerns that the progress achieved by the reduction of regional-scale ozone levels has been offset by a growth in the hemispheric ozone levels [Collins *et al.*, 2000] that has been attributed both to anthropogenic and natural (e.g., stratosphere-troposphere exchange) [Neu *et al.*, 2014] sources. Although episodic peak ozone levels monitored at the European stations with the highest mean ozone levels have declined markedly since 1980, these episodic peak levels at the stations with the lowest mean ozone have not [Derwent and Hjellbrekke, 2012]. This has been explained by the influence of the hemispheric scale transport of ozone. In North America, global-scale chemistry models [Emery *et al.*, 2012; Fiore *et al.*, 2002; Zhang *et al.*, 2011] are utilized to calculate hemispheric scale ozone concentrations transported into regions where exceedances of the United States National Ambient Air Quality Standards are documented. This is the so-called "Policy Relevant Background" [U.S. Environmental Protection Agency, 2014] or "North American Background," and further details are given in Lefohn and Cooper [2015].

While the use of regional-scale air quality models in policy formulation is long-standing, the use of global models is relatively recent [HTAP, 2010]. If such models are to provide reliable future guidance for intercontinental policy formulation, then we must have confidence in their performance. Currently, this confidence is

established through comparison with observations. However, it has not been possible, so far, to explain the origins of any shortcomings found other than to suspect the adequacy and completeness of any emission inventories employed, as well as chemical mechanisms, boundary layer mixing and convection, deposition, stratosphere-troposphere exchange, and lightning [Wild, 2007]. It has not been possible either to reconcile good agreement in one part of the model against poor agreement found elsewhere in these complex models.

Here we focus on the seasonal cycle in ozone in both models and observations and attempt a detailed examination of both, using techniques that are described in previous work [Parrish *et al.*, 2016]. Our aim is to understand which observed features of the seasonal cycle in ozone are faithfully reproduced by models and which features disagree. Our focus is on the marine boundary layer (MBL) because it receives relatively little in the way of emissions from human activities, because it is isolated from the rest of the troposphere and because it suffers much less from nocturnal depletion under shallow boundary layers. In this way, the process representation in chemistry transport models should be somewhat more reliable compared with that for continental areas. Furthermore, the marine environments upwind of North America and Europe have played an important role in the identification of the global rise in ozone baseline levels and the importance of intercontinental ozone transport [Parrish *et al.*, 2016]. A potential difficulty, however, is the accurate representation in models of the entrainment of ozone-rich free tropospheric air into the MBL.

Parrish *et al.* [2016] compared observed seasonal cycles at 11 MBL sites with the results from three global chemistry-climate models. They found similar seasonal cycles between sites within hemispheric scale regions. Here we consider observations from only three sites that are representative of different hemispheric scale regions, chosen so that there are a pair of stations to reflect the gradient between the Northern and Southern Hemispheres and a pair to reflect North Pacific inflow versus North Atlantic inflow. We compare results across a much larger number of models in order to obtain a more robust evaluation of the abilities of current models to correctly reproduce the seasonal cycle of ozone in the MBL. The models include a global Lagrangian chemistry-transport model STOCHEM-CRI [Derwent *et al.*, 2015], which has increased chemical complexity to treat range of emitted hydrocarbons [Utembe *et al.*, 2010] and the set of 14 models that took part in the Atmospheric Chemistry Coupled Climate Model Intercomparison Project (ACCMIP) exercise [Young *et al.*, 2013], see the supporting information attached to this paper.

## 2. Techniques

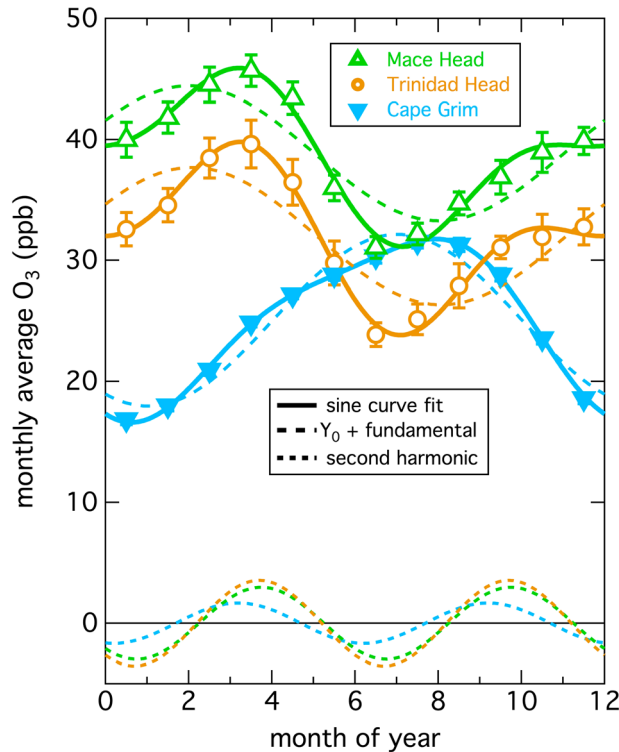
In this study, seasonal cycles of ozone were defined by least squares fits of sine functions to observed or model monthly mean ozone mixing ratios, as follows:

$$y = Y_0 + A_1 \sin(\theta + \phi_1) + A_2 \sin(2\theta + \phi_2) \quad (1)$$

where  $Y_0$  is the annual average ozone mixing ratio over the entire set of observations or model results,  $A_1$  and  $A_2$  are amplitudes,  $\phi_1$  and  $\phi_2$  are phase angles, and  $\theta$  is a time variable that spans 1 year period in  $2\pi$  radians. The second and third terms on the right-hand side of equation (1) are the fundamental and second harmonic terms of the fitted ozone seasonal cycle. In previous work [Parrish *et al.*, 2016], we have shown how the five parameters,  $Y_0$ ,  $A_1$ ,  $A_2$ ,  $\phi_1$ , and  $\phi_2$ , represented all of the statistically significant information regarding the average seasonal cycle in the observations or model results. The observation-model comparisons in this study are based on the analysis of these five parameters.

Full details of the sources of the observations and model results, together with the estimation procedures, are given in the supporting information, and only a brief summary is given here. Attention was focused on three marine boundary layer (MBL) baseline stations that have relatively long measurement records: Mace Head, Ireland (1989–2014), and Trinidad Head, California, United States of America (1990–2010), in the Northern Hemisphere and Cape Grim, Tasmania (1982–2010), in the Southern Hemisphere. The ozone observations employed for Mace Head and Trinidad Head have been carefully filtered to remove local influences but retain baseline levels as described in Parrish *et al.* [2016]. In all cases, ozone concentrations are consistently expressed as mixing ratios in units of nmol ozone per mol air, referred to as parts per billion.

Model ozone seasonal cycles were taken from a global Lagrangian chemistry-transport model STOCHEM-CRI and from the set of 14 chemistry-climate models that took part in the ACCMIP exercise. The model seasonal cycles were based on monthly mean ozone levels, including all hours of the day and night for the lowest model layers of the model grid cells containing the observing stations. The thickness of the lowest model layers and the



**Figure 1.** Sine curve fitted ozone seasonal cycles (solid lines) to observations from Mace Head, Ireland (26 years), Trinidad Head, California (21 years), and Cape Grim, Tasmania (29 years), together with the fundamental and second harmonic fits (dashed lines). The symbols give average monthly ozone concentrations over the entire data records with error bars indicating 2 sigma confidence limits (some error bars are obscured by the size of the symbols).

average ozone mixing ratio for each station has been added to each fitted fundamental curve to facilitate comparison with the observations. The observations and sine function fits overlap almost exactly at all sites. The fitted curves pass through the 2 sigma confidence limits for each monthly mean at all sites, and the root-mean-square deviations between the fits and the monthly means are 0.7, 0.5, and 0.2 ppb for Mace Head, Trinidad Head, and Cape Grim, respectively.

The observed and fitted seasonal cycles for the Northern Hemisphere Mace Head and Trinidad Head stations exhibited peaks in April and minima in July to August. The fundamental fits, in contrast, exhibited peaks in early March with minima 6 months later (September). The second harmonic fit showed two peaks, one in April and the other 6 months later (October). The observed and fitted seasonal cycles for the Southern Hemisphere Cape Grim station peaked in August and showed a minimum in January. The fundamental fit for Cape Grim exhibited a peak in August. The second harmonic fit showed the same two peaks as in the Northern Hemisphere (April and October).

In this manner, it has been possible to quantify using five parameters,  $Y_0$ ,  $A_1$ ,  $\phi_1$ ,  $A_2$ , and  $\phi_2$ , the observed seasonal cycles for the three MBL stations without loss of features and details or distortions. The fitted parameters and their confidence limits are presented in the supporting information. Notably, all parameters derived here from the observations at the three stations are consistent with the values reported in Table 2 of Parrish *et al.* [2016]; comparison of future model results can simply use these tabulated values without directly accessing and analyzing the monthly mean data themselves. An examination of model seasonal cycles now follows using the same sine curve fitting procedures.

### 3.2. Comparison of the Observed and Modeled Seasonal Cycles

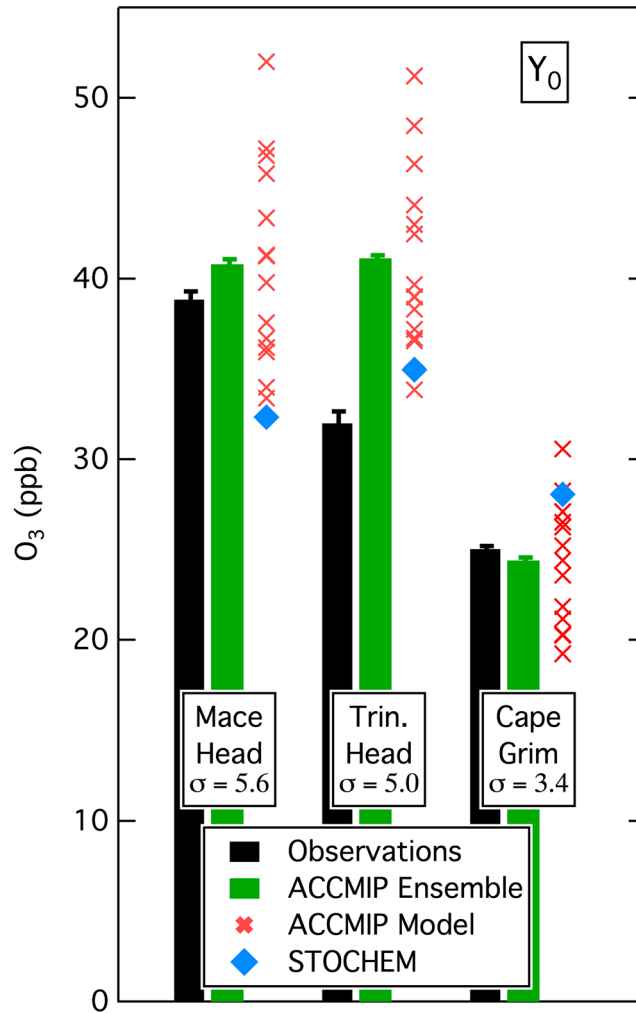
In this section, the fitted sine curves to the seasonal cycles in the observations and models are compared using the five parameters:  $Y_0$ ,  $A_1$ ,  $\phi_1$ ,  $A_2$ , and  $\phi_2$ , defined above in equation (1). The aim is to ascertain how well the models are

dimensions of the grid squares containing the three MBL stations varied enormously, and no attempt was made to harmonize these differences by interpolation. Uncertainty is introduced into the comparisons discussed below through the spatial mismatch between the observations made at a single point and the model calculations that were effectively an average over single grid cell in the model. This issue for the three MBL stations is discussed in some detail in Parrish *et al.* [2016]. Details of the 14 models from ACCMIP are given elsewhere [Lamarque *et al.*, 2013; Naik *et al.*, 2013a; Young *et al.*, 2013].

## 3. Results

### 3.1. Observed Ozone Seasonal Cycles

The seasonal cycles in ozone at the three selected MBL stations: Mace Head and Trinidad Head in the Northern Hemisphere and Cape Grim, Tasmania, in the Southern Hemisphere are illustrated in Figure 1 for the observations and the sine function fits. The annual



**Figure 2.** Comparison of the observed and model values of the average ozone mixing ratio over the entire data set,  $Y_0$ , in parts per billion for the STOCHM-CRI model, the ACCMIP members, and their ENSEMBLE. Error bars indicate 2 sigma confidence limits for the observations and ACCMIP ensemble. The standard deviations of the results of the ACCMIP members are annotated for the three sites.

Trinidad Head station by 2 to 19 ppb and that this discrepancy is the largest among the three stations.

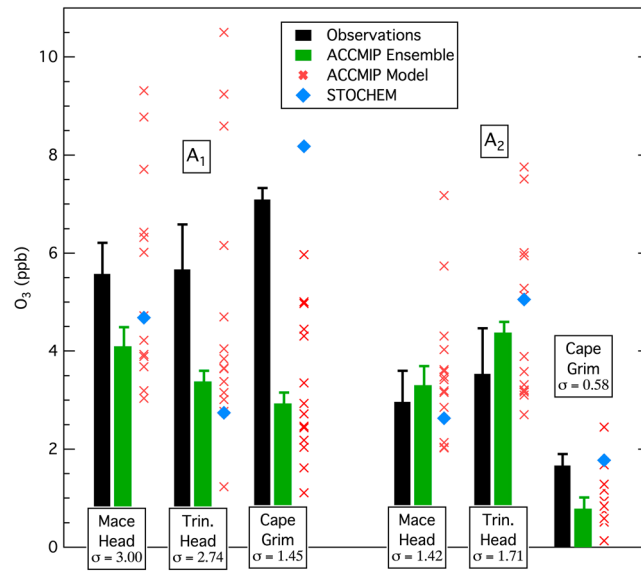
The STOCHM-CRI model calculated  $Y_0$  values in the order: Cape Grim,  $28.1 \pm 0.8$  ppb; Mace Head,  $32.3 \pm 2.1$  ppb, and Trinidad Head,  $35.0 \pm 1.8$  ppb, respectively, which gave the incorrect order for the North Pacific—inflow versus the North Atlantic—inflow stations. A similar problem was found for the ACCMIP models, with the predicted  $Y_0$  values for the ENSEMBLE: Cape Grim,  $24.4 \pm 0.2$  ppb; Mace Head,  $40.8 \pm 0.3$  ppb, and Trinidad Head,  $41.1 \pm 0.2$  ppb. If account were taken of the  $2\sigma$  error bars, then STOCHM-CRI and the ACCMIP-ENSEMBLE both gave Mace Head minus-Trinidad Head differences that were statistically indistinguishable from zero. In contrast, the observed Mace Head-Trinidad Head differences were highly statistically significant,  $6.8 \pm 0.8$  ppb. This difference was first recognized by Parrish et al. [2009] who reported  $7 \pm 2$  ppb higher ozone in all seasons arriving at European baseline stations versus those in North America, in close agreement with the current estimate. Parrish et al. [2009] could not provide an explanation for this difference, and none of the models was able to reproduce it.

Using tagged tracers in the STOCHM-CRI model [Derwent et al., 2015], the  $Y_0$  value for ozone undergoing intercontinental transport to Trinidad Head was  $24.8 \pm 1.6$  ppb compared with  $35.0 \pm 1.8$  ppb for ozone from all sources. The corresponding STOCHM-CRI  $Y_0$  values for Mace Head were  $29.7 \pm 2.2$  ppb and  $32.3$

able to quantify the seasonal cycles across the three MBL stations which have been chosen so that there are a pair of stations to reflect the gradient between the Northern Hemisphere versus the Southern Hemisphere and a pair to reflect North Pacific Ocean inflow versus North Atlantic Ocean inflow. Bar graphs of the observations and model ACCMIP ensemble mean (ENSEMBLE) results, with the STOCHM-CRI and individual ACCMIP member results included as points are used to examine whether the models are able to account for the range in the observed seasonal cycle parameters between the three MBL stations. The detailed values of all parameters are tabulated in the supporting information.

**3.2.1. Long-Term Average Ozone Levels,  $Y_0$**

The long-term average ozone levels,  $Y_0$ , are compared at the three MBL stations in Figure 2. The observed values of  $Y_0$  were, in ascending order, Cape Grim,  $25.0 \pm 0.2$  ppb; Trinidad Head,  $32.0 \pm 0.7$  ppb, and Mace Head,  $38.9 \pm 0.4$ , where the quoted uncertainty ranges are  $2\sigma$  or 95% confidence limits. All the models gave Cape Grim the lowest  $Y_0$ , but they disagreed about which station had the highest  $Y_0$ . The models typically show Cape Grim < Mace Head < Trinidad Head. Further, Figure 2 shows that the models overestimate the observations for the



**Figure 3.** Comparison of the observed and model values of the fundamental and second harmonic amplitudes,  $A_1$  and  $A_2$ , in parts per billion for the STOCHEM-CRI model, the ACCMIP members, and their ENSEMBLE. Error bars indicate 2 sigma confidence limits for the observations and ACCMIP ENSEMBLE. The standard deviations of the results of the ACCMIP members are annotated for both amplitudes at the three sites.

+6.83 ppb, with the ENSEMBLE at  $-0.33$  ppb. These should be compared with the observed difference of  $+6.8 \pm 0.8$  ppb. Only one of the ACCMIP models gave a reasonable estimate of the Mace Head-Trinidad Head difference of  $+6.83$  ppb, but then only by overestimating both  $Y_0$  values by substantial amounts, of the order of 7 ppb.

### 3.2.2. Amplitudes of the Fundamental, $A_1$

The detailed values of  $A_1$  are shown on the left side of Figure 3. The observed amplitudes of the fundamentals,  $A_1$ , were found to be Mace Head,  $5.6 \pm 0.6$  ppb; Trinidad Head,  $5.7 \pm 0.9$  ppb, and Cape Grim,  $7.1 \pm 0.2$  ppb. The  $A_1$  values for the two Northern Hemisphere stations were statistically indistinguishable, with that for the Southern Hemisphere station significantly greater. The observed order of the stations was therefore: Mace Head  $\approx$  Trinidad Head  $<$  Cape Grim.

Model performance for this parameter was generally poor. STOCHEM-CRI gave reasonable estimates for  $A_1$  at Mace Head,  $4.7 \pm 3.0$  ppb, and Cape Grim,  $8.2 \pm 1.2$  ppb, but that for Trinidad Head was too low by a wide margin,  $2.8 \pm 2.6$  ppb. The results for this model were outside the  $\pm 10\%$  range, and the stations were ordered differently than the observations: Trinidad Head  $<$  Mace Head  $<$  Cape Grim.

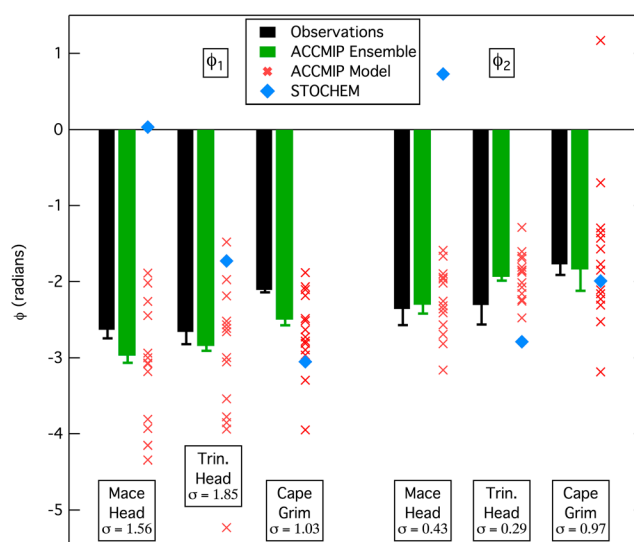
Agreement for the amplitudes from the ACCMIP models was also poor overall. The ENSEMBLE gave its lowest  $A_1$  value for Cape Grim,  $2.9 \pm 0.2$  ppb, next highest for Trinidad Head,  $3.4 \pm 0.2$  ppb and highest for Mace Head,  $4.1 \pm 0.4$  ppb. Again, the stations were ordered differently than the observations: Cape Grim  $<$  Trinidad Head  $<$  Mace Head. Of all the ACCMIP models, only one gave an  $A_1$  value for Mace Head within  $\pm 10\%$  of the observed and one (though not the same model) for Trinidad Head. There were no ACCMIP predictions of  $A_1$  within  $\pm 10\%$  of that observed for Cape Grim because generally all simulated amplitudes were gross underestimations, see Figure 3.

The Northern Hemisphere-Southern Hemisphere difference as indexed by the Mace Head-Cape Grim difference was found to be  $-1.5 \pm 0.6$  ppb in the observations. This difference was reported to be  $-3.5 \pm 1.6$  ppb in STOCHEM-CRI which, although it was of the correct sign, was found to be a substantially overestimated, as shown by the gradients in Figure 3. The ACCMIP ENSEMBLE gave a difference of  $+1.2 \pm 0.4$  ppb, which although approximately of the correct magnitude had the incorrect sign.

STOCHEM-CRI and most ACCMIP models underestimated the  $A_1$  values for the Trinidad Head station. When taken with the overestimation problem with the  $Y_0$  values for the same station described in section 3.2.1 above, the underestimation problem with the  $A_1$  values may point to a common issue across the models.

$\pm 2.1$  ppb, which suggested a smaller local ozone contribution than for Trinidad Head. This difference in behavior suggested a larger local North American contribution at Trinidad Head compared with the local European contribution at Mace Head in the STOCHEM-CRI chemistry transport model.

Of the 14 ACCMIP models, only one model in addition to STOCHEM-CRI (see Figure 2) gave a  $Y_0$  value for Trinidad Head that fell within  $\pm 10\%$  of the observations. The remaining 13 models gave substantially larger  $Y_0$  values. This left the ENSEMBLE average substantially larger also. For Mace Head, the ACCMIP models performed much better such that several models and the ENSEMBLE gave results that fell within  $\pm 10\%$ . However, the Mace Head-Trinidad Head differences were found to lie within the range from  $-3.21$  to



**Figure 4.** Comparison of the observed and model values of the fundamental and second harmonic phase angles,  $\phi_1$  and  $\phi_2$ , in radians for the STOCHM-CRI model, the ACCMIP members, and their ENSEMBLE. The  $\phi_1$  values for the Northern Hemisphere stations have been shifted by  $-\pi$  radians to allow direct comparison with the Southern Hemisphere station. Error bars indicate 2 sigma confidence limits for the observations and ACCMIP ENSEMBLE. The standard deviations of the results of the ACCMIP members are annotated for both phase angles at the three stations.

adjustment, fundamental phase angles overlapped corresponding to a spring maxima in both hemispheres in both observations and models.  $\phi_1$  values were found to be less negative (peak earlier in the spring) for the observations at Cape Grim,  $-2.10 \pm 0.03$  rad, and more negative (peak later in the spring) at the two Northern Hemisphere stations: Trinidad Head,  $-2.66 \pm 0.16$  rad and Mace Head,  $-2.63 \pm 0.06$  rad. The two Northern Hemisphere stations had  $\phi_1$  values that were statistically indistinguishable. The average observed difference in  $\phi_1$  between the hemispheres ( $-0.54 \pm 0.16$  rad or  $31 \pm 9$  days) indicated that the maximum of the fundamental term occurred 1 month later in the Northern Hemisphere compared with the Southern Hemisphere. This difference may reflect the greater importance of photochemical ozone production in the Northern Hemisphere where the large majority of man-made ozone precursors are emitted.

The ACCMIP ENSEMBLE values of  $\phi_1$  for the three stations gave the same overall pattern as the observations, see Figure 4, with Cape Grim as less negative and the two Northern Hemisphere stations as more negative, that is, to say, earlier and later spring maxima, respectively. The observed phases of all stations were well reproduced by the ACCMIP ENSEMBLE, but the models exhibited substantial variability that was larger in the Northern Hemisphere. One of the ACCMIP models exhibited a phase angle at Trinidad Head that was up to 2.5 rad (5 months) later in the year compared with the observations. The STOCHM-CRI model did not accurately reproduce that phase at any station and was nearly completely out of phase at Mace Head.

### 3.2.4. Amplitudes of the Second Harmonics, $A_2$

The amplitudes of the second harmonics in the observations showed a regular progression across the three MBL stations (Figure 3): Cape Grim,  $1.7 \pm 0.2$  ppb; Mace Head,  $3.0 \pm 0.6$  ppb, and Trinidad Head,  $3.5 \pm 0.9$  ppb.

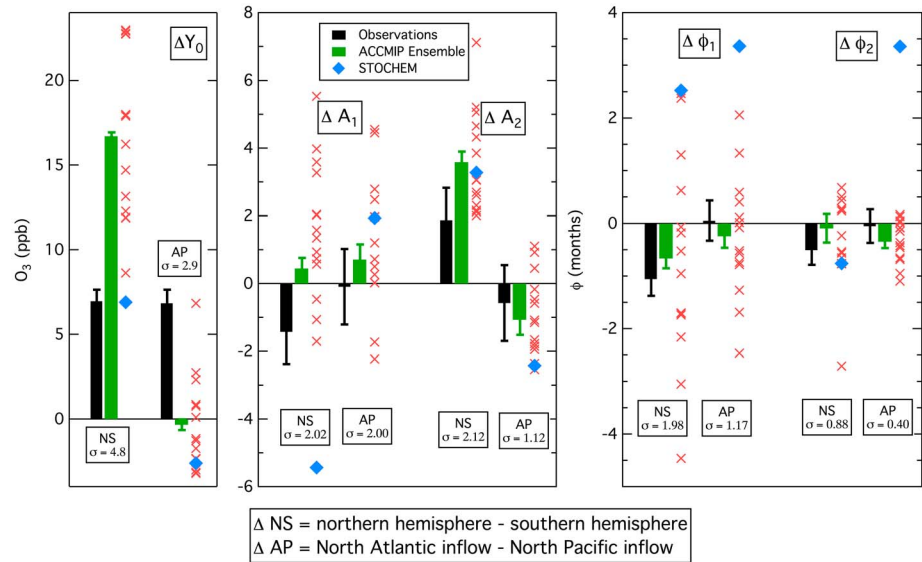
Figure 3 demonstrates that the models have significant skill in reproducing the broad spatial pattern in the observed second harmonic amplitudes. The amplitudes of the second harmonic in the STOCHM-CRI model were found within  $\pm 10\%$  for Cape Grim and Mace Head but overestimated the observed value for Trinidad Head by 45%. The ACCMIP ENSEMBLE indicated a steeper gradient across the three MBL stations, underestimating the observed second harmonic amplitude at Cape Grim by more than a factor of 2 and overestimating it at Trinidad Head by 25%.

A substantial number of the ACCMIP models gave second harmonic amplitudes that lay within  $\pm 10\%$ . However, it was not always the same ACCMIP members that performed well at each station. There was

The ACCMIP models also performed poorly for Cape Grim but, in contrast, STOCHM-CRI performed well at this station. The ACCMIP models significantly underestimated the strength of the fundamental amplitude of the seasonal cycle at Cape Grim compared with the observations. Whereas a marked seasonal cycle was observed, little was predicted. This may point to an underestimation by all models of photochemical ozone destruction or an overestimation of photochemical ozone production during the austral summer.

### 3.2.3. Phase Angles of the Fundamental, $\phi_1$

To facilitate comparison of the phase angles of the fundamentals of the observations and models between the Northern and Southern Hemispheres, Northern Hemisphere  $\phi_1$  values have been shifted by  $-\pi$  radians when plotted in Figure 4 and discussed below. With this



**Figure 5.** Comparison of the observed and model values of the differences in  $Y_0$  (ppb), the two amplitudes (ppb), and the two phase angles (months), for the STOCHEM-CRI model, the ACCMIP members, and their ENSEMBLE. The differences are between the Northern and Southern Hemispheres (calculated from Trinidad Head-Cape Grim) with  $\phi_1$  at Trinidad Head shifted by  $\pi$  radians so that a difference of 0 indicates both have the same seasonal cycle, but shifted by 6 months between hemispheres) and between the Atlantic and Pacific inflow (calculated from Mace Head-Trinidad Head). Error bars indicate 2 sigma confidence limits for the observations and ACCMIP ENSEMBLE. The standard deviations of the results of the ACCMIP members are annotated for all parameters at the three sites.

significant variability in the ACCMIP results, such that the amplitudes spanned nearly a factor of 3 from 2.7 to 7.8 ppb at Trinidad Head, from 2.0 to 7.2 ppb at Mace Head, and from 0.1 to 2.5 ppb at Cape Grim.

On the whole, the ACCMIP models reproduced the amplitude of the second harmonic better than that of the fundamental. Figure 3 shows closer accord of the absolute magnitudes for the ACCMIP ENSEMBLE for  $A_2$  than for  $A_1$  and the standard deviations of the ACCMIP members are smaller for  $A_2$  than  $A_1$ .

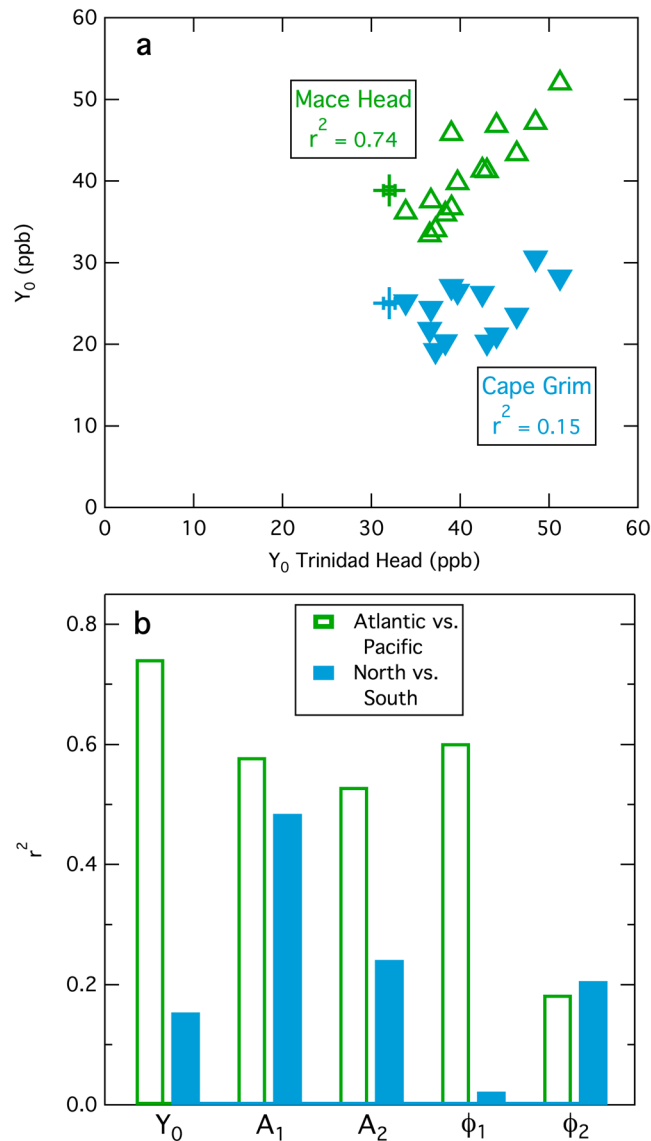
### 3.2.5. Phase Angles of the Second Harmonics, $\phi_2$

The phase angles of the second harmonics are presented in Figure 4, noting that no shifting by  $-\pi$  radians has been applied to the Northern Hemisphere stations as with  $\phi_1$ . The observed order of the  $\phi_2$  values was Mace Head  $\approx$  Trinidad Head and both more negative than Cape Grim with the phase angles of the two Northern Hemisphere stations statistically indistinguishable: Mace Head,  $-2.4 \pm 0.2$  rad and Trinidad Head,  $-2.3 \pm 0.3$  rad. The observed difference in phase angle between the Northern Hemisphere versus the Southern Hemisphere stations was small but statistically significant at  $-0.6 \pm 0.3$  rad (16  $\pm$  8 days later maxima in the Northern Hemisphere).

The ACCMIP ENSEMBLE estimated  $\phi_2$  values at Mace Head and Cape Grim with pinpoint accuracy, within 0.07 rad or 2 days but was  $0.37 \pm 0.03$  rad less negative or 11  $\pm$  1 days earlier at Trinidad Head. The ACCMIP ENSEMBLE was thus able to accurately reproduce the observed difference in phase angle between Mace Head in the Northern and Cape Grim in the Southern Hemisphere ( $-0.46 \pm 0.3$  rad). STOCHEM-CRI accurately reproduced the observed  $\phi_2$  values at Cape Grim but was  $0.44 \pm 0.26$  rad or 13  $\pm$  8 days early at Trinidad Head. However, this model was a long way out at Mace Head for this parameter.

There was a large range in the estimated second harmonic phase angles between the individual ACCMIP members, however. The Northern Hemisphere stations exhibited  $\phi_2$  values between  $-3.2$  and  $-1.3$  rad (23 days later to 30 days earlier), and the Southern Hemisphere values ranged between  $-3.2$  and 1.2 rad (41 days later to 85 days earlier) relative to the observations.

In accord with the behavior found for the amplitudes, the ACCMIP models reproduced the phase of the second harmonic better than that of the fundamental. Figure 4 shows good agreement on average for both phase angles, but the standard deviations of the ACCMIP members are smaller for  $\phi_1$  than for  $\phi_2$ . This is even more pronounced when the variability is considered in days compared to radians.



**Figure 6.** (a) Correlation of  $Y_0$  for Mace Head and Cape Grim with that for Trinidad Head. The triangles give the results derived by the 14 ACCMIP members, and the plus symbols with error bars (smaller than the symbols) indicate the observations. The square of the linear correlation coefficient is annotated for each set of results. (b) Comparison of the squares of the linear correlation coefficients for all five parameters derived from the 14 ACCMIP members. The correlations are for North Atlantic versus North Pacific inflow (i.e., Mace Head versus Trinidad Head) and Northern versus Southern Hemisphere (i.e., Cape Grim versus Trinidad Head).

Trinidad Head, each ACCMIP member tends to further overestimate  $Y_0$  at both of these Northern Hemisphere midlatitude stations by a similar amount, although the magnitude of this overestimation varies between the models. The correlation of the  $Y_0$  values between Cape Grim and Trinidad Head is much poorer ( $r^2 = 0.15$ ) with the ACCMIP models accurately reproducing the Cape Grim values, on average. A general positive bias of chemistry-climate models for lower tropospheric ozone has been discussed [e.g., Lamarque et al., 2012; Naik et al., 2013b; Parrish et al., 2014]; however, the correlations in Figure 6a suggest that such overestimates are found in all of the ACCMIP members at northern midlatitudes but are not a general global feature. Young et al. [2013] and Parrish et al. [2016] also found model overestimates at northern but not southern midlatitudes. If the bias is indeed limited to northern midlatitudes, this regional difference may help to diagnose the cause of the problem. In this case, the problem could arise from model treatment of anthropogenic

### 3.2.6. Variations in Interhemispheric Differences Between the ACCMIP Models

Direct examination of the interhemispheric differences can provide additional information that is not apparent from examination of model-observation differences at the separate stations. Figure 5 shows the interhemispheric differences for the five parameters discussed in the preceding sections. They are plotted between the Northern and Southern Hemispheres (NS), calculated from Trinidad Head and Cape Grim parameters and between the Atlantic and Pacific (AP) inflow stations, calculated from the Mace Head and Trinidad Head parameters. In Figure 5, the standard deviations of the results of the 14 ACCMIP members are annotated. A striking feature of these standard deviations is that in most cases the standard deviations of the differences are smaller than the standard deviations at the individual stations annotated in Figures 2–4. Propagation of error considerations leads to the expectation of larger standard deviations for the differences if the model errors at the individual stations are uncorrelated. Therefore, this feature indicates that the model errors are significantly correlated between the stations.

The correlation of the  $Y_0$  parameters derived from the separate ACCMIP members is examined in Figure 6a. The  $Y_0$  values are highly correlated between Mace Head and Trinidad Head ( $r^2 = 0.74$ ). This correlation indicates that in addition to an overall bias between Mace Head and



emissions (which are concentrated at northern midlatitudes) or model treatment of ozone deposition to continental surfaces (which are also concentrated in that region) or potential “dynamic” influences (weather patterns tend to be more complex and variable due to the more pronounced land-sea contrasts).

The correlations for all five parameters derived from the separate ACCMIP members are compared for NS and AP in Figure 6b, and the correlation plots for amplitudes and phase angles are included in the supporting information (Figures S1 and S2). The magnitudes of the fundamental of the seasonal cycles ( $A_1$ ) are significantly correlated between Mace Head and Trinidad Head ( $r^2 = 0.58$ ) and between Cape Grim and Trinidad Head ( $r^2 = 0.48$ ). These correlations indicate that about one half of the variance between the different models and between the models and the measurements is due to problems within each model that are common to all three sites, and the other half of the variance is due to model problems that differ between sites.

The errors for the ACCMIP members are significantly correlated for most of these parameters for both the NS and AP comparisons. These correlations all indicate that the ACCMIP models differ in important respects in their treatment of the processes that drive the ozone seasonal cycle throughout the troposphere, and the correlations can potentially provide diagnostic information regarding the causes of the errors within the individual ACCMIP models. One difficulty with such diagnosis is the limited precision possible for the determination of the seasonal cycle parameters with only a few years (5 to 10 years for the ACCMIP models and a single year for the STOCHEM-CRI model) of model simulations; the confidence limits of these parameter determinations (Tables S1–S3) are of the order of the model-measurement differences, which limits our ability to interpret the present results. Future examination of the correlations with improved precision could provide useful guidance for model improvement.

#### 4. Discussion and Conclusions

To understand the seasonal cycle of ozone in the MBL, a simple conceptual model has been employed as formulated in our previous study [Parrish *et al.*, 2016] in which ozone produced photochemically in the free troposphere or in the continental polluted boundary layer or injected from the stratosphere is entrained into or advected into the MBL. The late winter to early spring maximum and the corresponding late summer minimum is a reflection of the domination of the ozone seasonal cycle by net photochemical destruction in the MBL [Ayers *et al.*, 1992; Oltmans and Levy, 1994]. Faster destruction in summer versus winter accounts for the summertime minimum and wintertime maximum. Consequently, ozone maximizes in late winter to early spring, and this is the main driver of the fundamental harmonic term seen in Figure 1 at the three chosen MBL stations. There may also be contributions from seasonal cycles in the entrainment of ozone-rich free tropospheric air into the MBL. The observed seasonal cycles are not pure sine curves, and there is evidence for secondary maxima in late autumn and “shoulders” during the late winter, see Figure 1. This behavior is reflected in a large contribution from the second harmonic term as described by Parrish *et al.* [2016] who first recognized and quantified this term which they found to be a robust feature of observations and models for MBL stations. They argued that the second harmonic resulted from a second harmonic in the seasonal cycle of the photolysis rate coefficient of ozone which acts as the main photochemical destruction sink for ozone and provided a detailed discussion of this issue [see Parrish *et al.*, 2016, section 4.3].

In this study, we have extended the Parrish *et al.* [2016] work by analyzing the seasonal cycles of 14 ACCMIP models rather than the three models of Parrish *et al.* [2016], together with the STOCHEM-CRI model at three MBL stations: Mace Head, Trinidad Head, and Cape Grim. These three stations allowed us to focus on inter-hemispheric differences, that is, to say, Northern versus Southern Hemisphere and North Pacific versus North Atlantic. Our main finding was that we could accurately describe the seasonal cycles in the observations and all model results by fitting sine curves and deriving five parameters:  $Y_0$ ,  $A_1$ ,  $\phi_1$ ,  $A_2$ , and  $\phi_2$  in equation (1). The fundamental term,  $A_1 \sin(\theta + \phi_1)$ , described the majority of the seasonal variations in both observed and modeled ozone. However, a second harmonic term of the form  $A_2 \sin(2\theta + \phi_2)$  was required to generate an accurate fit to all sets of observations and model results. Together, the five parameters provided a convenient means of accurately quantifying observed and model seasonal cycles.

Armed with this analytical tool, a systematic assessment was made of the seasonal cycles produced by STOCHEM-CRI and the 14 ACCMIP members and their ensemble mean (ENSEMBLE). Compared to the fundamental, all models more accurately reproduced the observed second harmonic terms. This accurate

agreement both in amplitude and phase angle suggested that the second harmonic term arose from a cyclic phenomenon that was well simulated by all models. The cycle of the actinic flux and its control of the photochemical destruction of ozone is a strong candidate to explain the second harmonic term, as argued by Parrish *et al.* [2016]. However, despite the general agreement found between the observed and model terms,  $A_2$  and  $\phi_2$ , there was a large amount of variability between the results from the different ACCMIP members. The representation of the photochemical destruction sink for ozone should be straightforwardly represented in the ACCMIP models, and it is not at all clear why there should be such large variability. Further analysis was beyond the scope of this study.

Despite the large increase in chemical complexity in STOCHEM-CRI compared with the ACCMIP models, there did not appear to be much improvement in performance for the second harmonic parameters,  $A_2$  and  $\phi_2$ , versus observations. The STOCHEM-CRI and ACCMIP ENSEMBLE values for  $A_2$  agreed reasonably closely, except for Cape Grim, and those for  $\phi_2$ , except for Trinidad Head. The increase in chemical complexity in STOCHEM-CRI was entirely in the photochemical processes leading to ozone production. Because there was little or no increase in the complexity of the ozone destruction processes, it was reasonable that the second harmonic terms should be similar, assuming a similar level of treatment of the solar actinic fluxes. There was no significant improvement in the performance of STOCHEM-CRI with respect to  $A_1$  and  $\phi_1$  compared to the ACCMIP models, for reasons which are not clear without further detailed information of the formulation of the ACCMIP models.

The model treatments of the fundamental terms,  $A_1 \sin(\theta + \phi_1)$  and of the individual parameters,  $A_1$  and  $\phi_1$ , were in many cases in poor agreement with those of the observations. STOCHEM-CRI reproduced the observed fundamental amplitudes well at Mace Head and Cape Grim but underestimated them at Trinidad Head. The ACCMIP ENSEMBLE only performed well at Mace Head, in contrast, underestimating  $A_1$  at the other stations. The ACCMIP ENSEMBLE performed well for  $\phi_2$  at all stations in contrast to STOCHEM-CRI which only performed well at Mace Head.

Further work is required to work through the model discrepancies found here to ascertain candidate explanations and identify needed improvements in tropospheric ozone models. We have identified those features of the model seasonal cycles that appear to be reasonably well described, namely, the photochemical ozone sinks. Entrainment of free tropospheric air is expected to be an important factor controlling the concentrations and seasonality of MBL ozone; it will be important to investigate model treatment of this entrainment and degree of isolation of the MBL. We have also identified a particularly large extent of variability in the simulated ozone seasonal cycles between the ACCMIP members. Detailed analysis of ozone budget terms (including, for example, the possible importance of halogen chemistry) will be required over and above that already performed by Young *et al.* [2013] before the causes of the model variability and detailed discrepancies can be established. We have also identified significant correlations between the parameters derived from the individual ACCMIP models. For example, the models generally overestimate the long-term average ozone levels ( $Y_0$ ) at northern midlatitudes (but not in the Southern Hemisphere) and the overestimates of the different ACCMIP members correlate between Mace Head and Trinidad Head, possibly suggesting a model difficulty in treating anthropogenic emissions or surface deposition, and that this difficulty varies between models. Model errors in  $A_1$  correlate between all three stations, while model errors in  $A_2$  and  $\phi_1$  correlate between Mace Head and Trinidad Head, but not between the Northern and Southern Hemispheres. We suggest that future work further investigating these correlations in more detail may yield further insights into the causes of model-measurement discrepancies. Until these issues can be resolved, large uncertainties remain in tropospheric model simulations of ozone transported on intercontinental scales.

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#### References

- Ayers, G. P., S. A. Penkett, R. W. Gillett, B. Bandy, I. E. Galbally, C. P. Meyer, C. M. Elsworth, S. T. Bentley, and B. W. Forgan (1992), Evidence for photochemical control of ozone concentrations in unpolluted marine air, *Nature*, *360*, 446–449.
- Clifton, O. E., A. M. Fiore, G. Correa, L. W. Horowitz, and V. Naik (2014), Twenty-first century reversal of the surface ozone seasonal cycle over the north-eastern United States, *Geophys. Res. Lett.*, *41*, 7343–7350, doi:10.1002/2014GL061378.
- Collins, W. J., D. S. Stevenson, C. E. Johnson, and R. G. Derwent (2000), The European regional ozone distribution and its links with the global scale for the years 1992 and 2015, *Atmos. Environ.*, *34*, 255–267.
- Cooper, O. R., A. O. Langford, D. D. Parrish, and D. W. Fahey (2015), Challenges of a lowered U.S. ozone standard, *Science*, *348*(6239), 1096–1097, doi:10.1126/science.aaa5748.
- Derwent, R. G., and A.-G. Hjellbrekke (2012), *Air Pollution by Ozone Across Europe, Handbook on Environ. Chem.*, vol. 163, Springer, Berlin.

- Derwent, R. G., S. R. Utembe, M. E. Jenkin, and D. E. Shallcross (2015), Tropospheric ozone production regions and the intercontinental origins of surface ozone over Europe, *Atmos. Environ.*, *112*, 216–224.
- Doherty, R. M. (2015), Ozone pollution from near and far, *Nat. Geosci., News Views*, 10 Aug.
- Emery, C., J. Jung, N. Downey, J. Johnson, M. Jimenez, G. Yarwood, and R. Morris (2012), Regional and global model estimates of policy relevant background ozone over the United States, *Atmos. Environ.*, *47*, 206–217.
- Fiore, A. M., D. J. Jacob, I. Bey, R. M. Yantosca, B. D. Field, and A. C. Fusco (2002), Background ozone over the United States in summer: Origin, trend and contribution to pollution episodes, *J. Geophys. Res.*, *107*(D15), 4275, doi:10.1029/2001JD000982.
- HTAP (2010), *Hemispheric Transport of Air Pollution 2010. Part A: Ozone and Particulate Matter, Air Pollut. Stud.*, vol. 17, U. N., Geneva, Switzerland.
- Lamarque, J. F., et al. (2012), CAM-chem: Description and evaluation of interactive atmospheric chemistry in the Community Earth System Model, *Geosci. Model Dev.*, *5*, 369–411, doi:10.5194/gmd-5-369-2012.
- Lamarque, J. F., et al. (2013), The Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP): Overview and description of models, simulations and climate diagnostics, *Geosci. Model Dev.*, *6*, 179–206, doi:10.5194/gmd-6-179-2013.
- Lefohn, A. S., and O. R. Cooper (2015), Introduction to the special issue on observations and source attribution of ozone in rural regions of the western United States, *Atmos. Environ.*, *109*, 279–281.
- Monks, P. S., et al. (2015), Tropospheric ozone and its precursors from the urban to the global scale from air quality to short-lived climate forcer, *Atmos. Chem. Phys.*, *15*, 8889–8973.
- Naik, V., et al. (2013a), Pre-industrial to present-day changes in tropospheric hydroxyl and methane lifetime from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP), *Atmos. Chem. Phys.*, *13*, 5277–5298.
- Naik, V., L. W. Horowitz, A. M. Fiore, P. Ginoux, J. Mao, A. M. Aghedo, and H. Levy (2013b), Impact of preindustrial to present-day changes in short-lived pollutant emissions on atmospheric composition and climate forcing, *J. Geophys. Res. Atmos.*, *118*, 8086–8110, doi:10.1002/jgrd.50608.
- Neu, J. L., T. Flury, G. L. Manney, M. L. Santee, N. J. Livesey, and J. Worden (2014), Tropospheric ozone variations governed by changes in stratospheric circulation, *Nat. Geosci.*, *7*, 340–344, doi:10.1038/ngeo2138.
- Oltmans, S. J., and H. Levy (1994), Surface ozone measurements from a global network, *Atmos. Environ.*, *28*, 9–24.
- Parrish, D. D., D. B. Miller, and A. H. Goldstein (2009), Increasing ozone in marine boundary layer inflow at the west coasts of North America and Europe, *Atmos. Chem. Phys.*, *9*, 1303–1323.
- Parrish, D. D., et al. (2014), Long-term changes in lower tropospheric baseline ozone concentrations: Comparing chemistry-climate models and observations at northern mid-latitudes, *J. Geophys. Res. Atmos.*, *119*, 5719–5736, doi:10.1002/2013JD021435.
- Parrish, D. D., et al. (2016), Seasonal cycles of O<sub>3</sub> in the marine boundary layer: Observation and model simulation comparisons, *J. Geophys. Res. Atmos.*, *121*, 538–557, doi:10.1002/2015JD024101.
- U.S. Environmental Protection Agency (2014), Policy assessment for the review of the ozone National Ambient Air Quality Standards, in *United States Environmental Protection Agency EPA-425/R-14-006*, North Carolina, US EPA, Research Triangle Park.
- Utembe, S. R., M. C. Cooke, A. T. Archibald, M. E. Jenkin, R. G. Derwent, and D. E. Shallcross (2010), Using a reduced Common Representative Intermediates (CRIV2-R5) mechanism to simulate tropospheric ozone in a 3-D Lagrangian chemistry transport model, *Atmos. Environ.*, *44*, 1609–1622.
- Wild, O. (2007), Modelling the global tropospheric ozone budget: Exploring the variability in current models, *Atmos. Chem. Phys.*, *7*, 2643–2660.
- Young, P. J., et al. (2013), Pre-industrial to end 21st century projections of tropospheric ozone from the Atmospheric Chemistry and Climate Model Intercomparison Project, *Atmos. Chem. Phys.*, *13*, 2063–2090.
- Zhang, L., D. J. Jacob, N. V. Downey, D. A. Wood, D. Blewitt, C. C. Carouge, A. van Donkelaar, D. B. A. Jones, L. Murray, and Y. Wang (2011), Improved estimates of the policy-relevant background ozone in the United States using the GEOS-Chem global model with 1/2° × 2/3° horizontal resolution over North America, *Atmos. Environ.*, *45*, 6769–6776.