



Photochemical grid model implementation of VOC, NO<sub>x</sub>, and O<sub>3</sub> source apportionment

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# Photochemical grid model implementation of VOC, NO<sub>x</sub>, and O<sub>3</sub> source apportionment

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## Abstract

For the purposes of developing optimal emissions control strategies, efficient approaches are needed to identify the major sources or groups of sources that contribute to elevated ozone ( $O_3$ ) concentrations. Source based apportionment techniques implemented in photochemical grid models track sources through the physical and chemical processes important to the formation and transport of air pollutants. Photochemical model source apportionment has been used to estimate impacts of specific sources, groups of sources (sectors), sources in specific geographic areas, and stratospheric and lateral boundary inflow on  $O_3$ . The implementation and application of a source apportionment technique for  $O_3$  and its precursors, nitrogen oxides ( $NO_x$ ) and volatile organic compounds (VOC), for the Community Multiscale Air Quality (CMAQ) model are described here. The Integrated Source Apportionment Method (ISAM)  $O_3$  approach is a hybrid of source apportionment and source sensitivity in that  $O_3$  production is attributed to precursor sources based on  $O_3$  formation regime (e.g., for a  $NO_x$ -sensitive regime,  $O_3$  is apportioned to participating  $NO_x$  emissions). This implementation is illustrated by tracking multiple emissions source sectors and lateral boundary inflow.  $NO_x$ , VOC, and  $O_3$  attribution to tracked sectors in the application are consistent with spatial and temporal patterns of precursor emissions. The  $O_3$  ISAM implementation is further evaluated through comparisons of apportioned ambient concentrations and deposition amounts with those derived from brute force zero-out scenarios, with correlation coefficients ranging between 0.58 and 0.99 depending on specific combination of target species and tracked precursor emissions. Low correlation coefficients occur for chemical regimes that have strong non-linearity in  $O_3$  sensitivity, which demonstrates different functionalities between source apportionment and zero-out approaches, depending on whether sources of interest are either to be accounted for pollutant levels in a given scenario, or to be perturbed to invoke alternate scenarios.

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## 1 Introduction

Regulatory programs have been in place in the United States for more than 50 years to reduce ambient exposure to ozone ( $O_3$ ) which has harmful effects on human health and vegetation (Bell et al., 2004; US Environmental Protection Agency (EPA), 2009; National Research Council, 1991). Nevertheless, many areas continue to exceed the national ambient air quality standard (NAAQS) for ozone, and uncertainty remains in both the local and distant sources that contribute to exceedances of the NAAQS. The EPA has set a NAAQS for  $O_3$  of 75 parts per billion (ppb), where compliance with the NAAQS is determined as the three year average of the 4th highest daily maximum 8 h average  $O_3$ . In areas that violate the NAAQS, the states and tribes must develop plans to attain the NAAQS by reducing emissions of  $O_3$  precursors, including volatile organic compounds (VOC) and nitrogen oxides ( $NO_x$ ). Additionally, Sect. 110(a) (2) (D) of the Clean Air Act requires states, in part, to eliminate significant contribution to nonattainment of the NAAQS in other states. To develop effective  $O_3$  attainment plans, it is important to understand the sources of ozone that contribute to violations of the NAAQS. Sources of  $O_3$  can include local sources, long-range transport (Zhang et al., 2008, 2009; Lin et al., 2012), stratospheric intrusion (Langford et al., 2009), and photochemical production of  $O_3$  ( $PO_3$ ) from a wide variety of biogenic and anthropogenic VOC and  $NO_x$  precursors (Haagen-Smit, 1954; Lefohn et al., 2014). For air quality managers who are tasked with developing the most expeditious and cost effective emissions control strategies, it is useful to have methods to identify the relative importance of sources that contribute to high  $O_3$  concentrations, and to predict how  $O_3$  will respond to reductions in VOC and  $NO_x$  precursor emissions. Specifically, it is useful to quantify the relative amount of  $O_3$  originating from specific VOC and  $NO_x$  emissions sources (or groups of sources, such as an emissions sector), as well as to distinguish locally produced  $O_3$  from  $O_3$  that is transported from upwind sources. Source sensitivity and apportionment approaches have been used to estimate intercontinental ozone contribution (Anenberg et al., 2010; Sudo and Akimoto, 2007; Zhang et al., 2009), contribution from specific

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geographic areas (Tong and Mauzerall, 2008), emissions sectors (Fann et al., 2013; Wang et al., 2009; Ying and Krishnan, 2010), and single sources (Bergin et al., 2008). The Integrated Source Apportionment Method (ISAM) for PM<sub>2.5</sub> was previously implemented in the Community Multiscale Air Quality (CMAQ) model (Kwok et al., 2013).

Here, the ISAM implementation is extended to analysis of O<sub>3</sub> source apportionment. This implementation is compared to methods used in other photochemical air quality models and compared directly with source sensitivity apportionment approaches to provide confidence in the implementation.

## 2 Review of ozone source apportionment methods

Various methods have been applied to characterize and quantify the relationship between emission sources and ozone concentrations including statistical methods, model sensitivity simulations, and model source apportionment approaches (Cohan and Napelenok, 2011). Statistical approaches using ambient data trends (Porter et al., 2001) or ambient data paired with emissions source characteristics (Kenski et al., 1995; Scheff and Wadden, 1993) have been used in the past as methods for ozone source attribution. Receptor-based approaches such as the chemical mass balance (CMB) or positive matrix factorization (PMF) receptor models provide information about source attribution to ozone precursors, but not directly to ozone (Buzcu and Fraser, 2006; Chung et al., 1996; Kim et al., 2005; Scheff et al., 1996; Tong et al., 2005). Statistical correlation analyses of the regional ozone pattern and time-lagged correlation analyses have also been used to analyze transport effects (Guinnup and Collom, 1997; Husar and Renard, 1997). These studies concluded that transport of O<sub>3</sub> and precursors could occur over the distance of 300–600 km, but did not clearly differentiate the specific origins of transported ozone or the confounding effects of meteorological factors (Guinnup and Collom, 1997).

Air quality model sensitivity simulations have been widely used to predict how O<sub>3</sub> responds to changes in specific sources of emissions of VOC and NO<sub>x</sub> (Russell and

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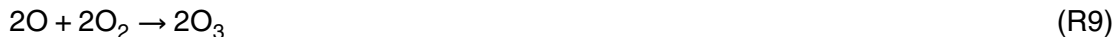
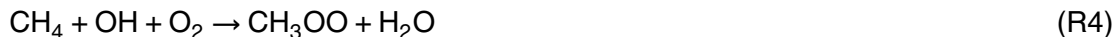
Dennis, 2000). Source sensitivity approaches include photochemical model “brute force” simulations, in which a single emission source is reduced or removed, and also model extensions that in a single simulation track multiple emissions sensitivities forward (decoupled direct method, DDM) (Dunker et al., 2002) or backward (adjoint) (Mesbah et al., 2012). Model sensitivity approaches have limitations when used for total source culpability, however, because of the nonlinear dependence of O<sub>3</sub> on concentrations of VOC and NO<sub>x</sub>. This is especially problematic for evaluating contributions of NO<sub>x</sub> because O<sub>3</sub> can have negative sensitivity to NO<sub>x</sub> in situations where the ratio of VOC to NO<sub>x</sub> is low. Therefore, summing the O<sub>3</sub> change in response to sensitivity simulations for multiple emissions sources can result in difficulty interpreting the cumulative effect of those emissions on O<sub>3</sub>.

In source apportionment approaches, the objective is to identify the amount of O<sub>3</sub> produced by particular emissions sources rather than determining the sensitivity of O<sub>3</sub> to those sources. This distinction is important in cases where O<sub>3</sub> has a non-linear sensitivity or negative sensitivity to changes in emissions. Source apportionment methods also have the benefit of estimating contributions from many different VOC and NO<sub>x</sub> source categories in a single model simulation. To describe the different approaches used in source apportionment methods, it is helpful to review the chemistry of O<sub>3</sub> formation. In the troposphere, O<sub>3</sub>, nitrogen oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) react rapidly in a photo-stationary state (PSS) null cycle, shown in Reactions (R1)–(R3), which has no net effect on ambient O<sub>3</sub> concentrations:



Photochemical formation of O<sub>3</sub> (PO<sub>3</sub>) in the troposphere occurs almost exclusively by the oxidation of VOC (Finlayson-Pitts and Pitts, 1986), as illustrated in Reactions (R4)–(R7) using methane (CH<sub>4</sub>) reactions. While O<sub>3</sub> is not formed directly, Reactions (R5) and (R7) provide alternate pathways to convert NO to NO<sub>2</sub> without the loss of O<sub>3</sub>

in Reaction (R1), thereby allowing O<sub>3</sub> to accumulate as shown in Reaction (R10):



Net reaction:



10 Because multiple families of precursors participate in the photochemical formation of O<sub>3</sub> (*PO*<sub>3</sub>), including NO<sub>x</sub>, VOC and free radicals (HO<sub>x</sub> = OH+HO<sub>2</sub>+RO<sub>2</sub>), the developer of a mass apportionment method for sources of *PO*<sub>3</sub> must determine which precursor is of primary interest for source apportionment. For example, *PO*<sub>3</sub> can be apportioned only on the basis of the NO<sub>x</sub> emissions sources, or VOC emissions sources, or sources  
15 of HO<sub>x</sub> that contribute to *PO*<sub>3</sub> in Reactions (R4)–(R7). Alternatively, a hybrid approach can be used that combines attribution to multiple families of precursors, in which *PO*<sub>3</sub> is attributed to either VOC or NO<sub>x</sub> sources depending on whether *PO*<sub>3</sub> occurs under VOC- or NO<sub>x</sub>-sensitive conditions.

Ozone source apportionment approaches have been implemented in a number of  
20 regional air quality models including the Comprehensive Air-quality Model with Extensions (CAMx) (ENVIRON, 2013), the Model for Ozone and Related chemical Tracers (MOZART-4) (Emmons et al., 2012), the Weather Research and Forecasting with Chemistry (WRF-Chem) model (Pfister et al., 2013), and the Community Multiscale Air Quality (CMAQ) model version 4.6 (Arunachalam, 2010; Ying and Krishnan, 2010).

25 Each of the above approaches augments the model by adopting a system of tracer species to track the sources of ozone and its precursor species for selected groupings

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of emissions categories and geographical regions. It is useful to define the “bulk” concentration as the model simulated concentration of a given species in the unaugmented model, where the bulk concentration should be identical to the sum of the tracers, e.g.:

$$C_{\text{bulk},\text{O}_3}^{i,j,k} = \sum_{n=1}^N C_{\text{O}_3,n}^{i,j,k} \quad (1)$$

$$C_{\text{bulk},\text{VOC}}^{i,j,k} = \sum_{n=1}^N C_{\text{VOC},n}^{i,j,k} \quad (2)$$

$$C_{\text{bulk},\text{NO}_x}^{i,j,k} = \sum_{n=1}^N C_{\text{NO}_x,n}^{i,j,k} \quad (3)$$

where  $N$  represents the number of tracers needed to represent all sources that contribute to the bulk species concentration, and  $i, j, k$  represent cells within the 3-dimensional grid. While each of the models identified above is augmented with a set of tracers, there are significant differences used in source apportionment for these models that are summarized below.

The CAMx Ozone Source Apportionment Technology (OSAT) includes tracers for  $\text{O}_3$  and for the families of reactive  $\text{NO}_x$  and VOC species. The ratio of production of hydrogen peroxide to nitric acid ( $\text{PH}_2\text{O}_2/\text{PHNO}_3$ ) is used to determine if  $\text{PO}_3$  occurs in either a  $\text{NO}_x$ - or VOC-sensitive chemical regime ( $\text{PH}_2\text{O}_2/\text{PHNO}_3$  above or below 0.35, respectively; Sillman, 1995). If  $\text{PO}_3$  occurs in a  $\text{NO}_x$ -sensitive regime, the  $\text{NO}_x$  tracers are used to attribute  $\text{PO}_3$  proportionally to the emissions sources that contributed to the  $\text{NO}_x$  concentration. Alternatively, if  $\text{PO}_3$  occurs in a VOC-sensitive regime, the VOC tracers are used to attribute  $\text{PO}_3$  to the emissions source that contributed to the VOC concentration. CAMx OSAT does not include tracers for individual VOC species. Instead, to reduce computational cost, the source attribution is based on a VOC family tracer, defined as the reactivity weighted sum of the emissions of individual VOC species for each source category. The VOC tracer decays based on an estimate of its reactivity with OH, and the VOC tracer’s contribution to  $\text{PO}_3$  is estimated based on its maximum incremental reactivity (MIR) (Carter, 1994). The adjustment using MIR also accounts for increased  $\text{PO}_3$  from highly reactive VOC, such as aldehydes and

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aromatics, which can also act as sources of OH radicals (Jeffries and Tonnesen, 1994).  $O_3$  production and destruction reactions operate simultaneously within the chemical mechanism, so the net change in ozone during a chemistry solver time step in the model simulation is the sum of production and loss:

$$\Delta O_3 = PO_3 + DO_3 \quad (4)$$

where  $DO_3 \leq 0$  indicates chemical destruction of  $O_3$ . In CAMx OSAT,  $PO_3$  is estimated as the net change in  $O_3$  during the chemistry time step combined with amount of chemical destruction of  $O_3$ :

$$PO_3 = \Delta O_3 - DO_3 \quad (5)$$

$PO_3$  is used to update the  $O_3$  tracers attributed to VOC and  $NO_x$  emissions sources, and in a separate step the  $O_3$  tracers are reduced by  $DO_3$ . CAMx OSAT does not consider the reaction of  $O_3$  with NO as chemical destruction, because this reaction occurs as part of the PSS null cycle in Reactions (R1)–(R3) that neither produces nor destroys  $O_3$ . Finally, it should be noted that CAMx OSAT adopts tracers that are updated at each chemistry time step based on chemical reaction rates, but these tracers are not added to the chemical mechanism and therefore do not increase the computational cost of the numerical chemistry algorithm.

In contrast to CAMx OSAT, the MOZART and WRF-Chem models both adopt a source apportionment method that augments the chemical mechanism with additional species and duplicative reactions that act as tracers of emissions sources of  $NO_x$ .  $O_3$  tracers are updated based only on their attribution to  $NO_x$ . These adaptations are primarily appropriate at the global scale, where  $PO_3$  is primarily  $NO_x$ -limited, and tagging  $NO_x$  was an appropriate choice for that purpose (Emmons et al., 2012). However, the MOZART and WRF-Chem source apportionment approach treats Reaction (R1) as chemical destruction of  $O_3$ , so that when a stratospheric or boundary condition (BC)  $O_3$  molecule reacts with anthropogenic NO molecule via Reaction (R1), the  $O_3$  that is subsequently formed in Reactions (R2) and (R3) is considered anthropogenic.

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Because the PSS null cycle does not result in any net  $PO_3$ , the approach used in MOZART and WRF-Chem could artificially convert tracers of stratospheric and BC  $O_3$  to anthropogenic  $O_3$  and overestimate the contribution of anthropogenic  $NO_x$  to  $O_3$ .

Ying and Krishnan (2010) implemented a source apportionment algorithm in CMAQ that relies on a set of additional species and duplicative reactions that act as tracers of  $O_3$  produced from individual VOC species. In this case, the model developers were primarily concerned with  $O_3$  attribution to anthropogenic and biogenic VOC in the urban ozone non-attainment area, and therefore tracers were only evaluated for VOC species. The algorithm used the  $NO_2$  production rates in Reactions (R5) and (R7) to represent  $PO_3$ , so this method has the benefit of representing total photochemical production of odd oxygen ( $O_x$ ) which is defined as the sum of  $O_3$ ,  $NO_2$  and other species that act as a reservoir of atomic oxygen. However, this approach does not consider the effects that highly reactive VOC species have on production of new radical species which also affects the  $PO_3$ . Therefore, this approach may underestimate the contribution of high reactivity VOC and overestimate the contribution of low reactivity to  $PO_3$ . Additionally, because of the large number of additional tracer species and reactions included in the photochemical mechanism, and the resulting increased computational cost, only one VOC emissions source category could be included in each simulation.

Ozone source attribution analysis can also be performed using the process analysis and integrated reaction rate outputs in the CMAQ and CAMx models. Each model has the option to store hourly mass throughput for each reaction in the chemical mechanism, and post processing can be performed to attribute ozone to VOC and  $NO_x$  precursors when these processes are coupled with tools such as Lagrangian trajectory models to track source specific transport (Henderson et al., 2011). While these approaches are useful for analyzing chemical production terms within selected grid cells, it is computationally challenging to use this approach for source attribution to specific emissions sources across the full model domain.

Evaluating the accuracy of source apportionment model results is challenging, because source contribution of secondary pollutants cannot be assessed independently

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based on monitoring data. Previous PM<sub>2.5</sub> source apportionment implementations have been evaluated by comparing source contributions to changes in PM<sub>2.5</sub> using brute force source model sensitivity simulations and by evaluating conservation of mass in the source apportionment results (Kwok et al., 2013; Wang et al., 2009). Source apportionment and brute force source sensitivity methods should provide similar results when O<sub>3</sub> has a linear or nearly linear sensitivity to changes in precursors' emissions. Therefore, comparisons to sensitivity simulations can be useful for evaluating source apportionment methods. However, in cases where O<sub>3</sub> has a strong non-linear dependence on precursors, such as the sensitivity to NO<sub>x</sub> under radical limited conditions, source apportionment and sensitivity approaches can provide different results. For example, Emmons et al. (2012) found differences of a factor of 2–4 when comparing the MOZART O<sub>3</sub> source apportionment method to 20% perturbations in precursor NO<sub>x</sub> emissions. Dunker et al. (2002) compared CAMx O<sub>3</sub> source attributions using OSAT and DDM sensitivity simulations and found that the two methods gave similar spatial distributions and that DDM sensitivity simulations explained about 70% of the modelled O<sub>3</sub> concentration. Zhang et al. (2005) compared CAMx OSAT, DDM and Process Analysis methods and also found that each method provided generally consistent assessments of source contributions to O<sub>3</sub>, with the exception of urban areas in which O<sub>3</sub> had negative sensitivity to NO<sub>x</sub>. In each of the studies described above, small emissions reductions or first-order DDM sensitivities do not account for non-linearity in the O<sub>3</sub> response to precursors and may not provide a reliable test for evaluating source apportionment approaches. Tonnesen (1999) found that model sensitivity analyses using small emissions changes did not accurately characterize the effect of uncertainty in model inputs on O<sub>3</sub> attainment strategies and recommended that large emissions changes should be used to assess model sensitivity. Therefore, similar to previous studies, ISAM O<sub>3</sub> contributions are compared here with model sensitivity simulations to determine if ISAM provides generally consistent results. However, instead of using small emissions changes, we use brute force zero-out scenarios of emissions sectors to account more reliably for non-linearity in the O<sub>3</sub> response to changes in precursors.

While we expect that there will be some differences in the sensitivity and source apportionment results, especially for strongly non-linear  $\text{NO}_x$  sensitivity in urban areas, we believe this approach to be useful for evaluating the accuracy of ISAM  $\text{O}_3$  source attributions for conditions that do not have strongly non-linear sensitivities.

## 3 Method

### 3.1 Implementation overview

The ISAM for  $\text{O}_3$  has been implemented in the CMAQ model, which was developed by the United States Environmental Protection Agency (EPA) and is used by EPA, other regulatory agencies, and academic institutions to characterize local to continental scale ozone formation and transport (Byun and Schere, 2006; Foley et al., 2010). The ISAM  $\text{O}_3$  source apportionment implementation is designed to track the contribution from user selected categories of  $\text{NO}_x$  and VOC emissions to model estimated  $\text{NO}_x$ , VOC, and ozone concentration and deposition. In addition to precursor emissions, the model tracks  $\text{O}_3$ ,  $\text{NO}_x$ , and VOC from the lateral boundary conditions, and initial conditions. Precursor emissions tracers can be defined geographically using an additional model input file that assigns the fractional area of each model grid cell to specified sub-regions (typically a State or Province). Precursor emissions tracers can also be defined by source sector (typically, major point sources, mobile sources, biogenic sources, etc.) or for specific point sources with a tag identification environment variable associated with each point source stack on the model ready input file. The user may also combine the emissions source sector and the specific geographic sub-region functionality. This implementation adds to the previous version of  $\text{PM}_{2.5}$  ISAM code and uses many of the same approaches that were presented in detail by Kwok et al. (2013). Only new ozone specific physical and chemical algorithms are described here.

The ozone source apportionment approach implemented in CMAQ is similar to the approach implemented in CAMx (ENVIRON, 2013), but uses tracers for individual

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nitrogen and VOC species, whereas CAMx uses two tracers to represent the families of  $\text{NO}_x$  and VOC. Ozone production is attributed to either VOC or  $\text{NO}_x$  emissions sources based on the ozone chemical formation regime that is estimated using the  $\text{PH}_2\text{O}_2/\text{PHNO}_3$  indicator ratio, similar to the implementation in CAMx. As described above, the bulk concentration of each VOC and  $\text{NO}_x$  species is equal to the sum of the tracers used to identify the sources of VOC and  $\text{NO}_x$ . The bulk  $\text{O}_3$  concentration in each model grid cell is equal to the sum of  $\text{O}_3$  tracers that were produced in either VOC- or  $\text{NO}_x$ -sensitive conditions:

$$\text{O}_{3,\text{bulk}} = \sum_{\text{tag}} \text{O}_3 V_{\text{tag}} + \sum_{\text{tag}} \text{O}_3 N_{\text{tag}} \quad (6)$$

where  $\text{O}_3 V_{\text{tag}}$  and  $\text{O}_3 N_{\text{tag}}$  are the VOC-sensitive and  $\text{NO}_x$ -sensitive  $\text{O}_3$  attributed to each tag source, respectively. The implementation described here is for the Carbon Bond, 2005 (CB05) photochemical mechanism that uses a reduced set of model VOC species (Yarwood et al., 2005). Tracers are defined for the CB05 VOC species contributing to ozone formation including acetaldehyde (ALD2), higher aldehydes (ALDX), ethene (ETH), ethane (ETHA), ethanol (ETOH), formaldehyde (FORM), internal olefin (IOLE), isoprene (ISOP), methanol (MEOH), olefin (OLE), paraffin (PAR), mono-terpene (TERP), toluene (TOL), and xylene (XYL) (Table 1). The nitrogen compounds in CB05 that participate in the  $\text{O}_3$  formation chemistry include NO,  $\text{NO}_2$ , nitrogen trioxide ( $\text{NO}_3$ ), dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ), nitrous acid (HONO), peroxyacyl nitrates (PAN), higher peroxyacyl nitrates (PANX), peroxyntiric acid (PNA), and organic nitrates (NTR).

ISAM apportions CMAQ-calculated wet and dry deposition to individual sources as done in the previous  $\text{PM}_{2.5}$  ISAM code.

In the CMAQ gas phase chemistry module, nitrogen species are updated by chemical sensitivity approach as in Kwok et al. (2013). Likewise, the explicit VOC tracers are

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entered into the same algorithm in a matrix solution:

$$[\text{VOC}_{j,\text{tag}}^{\text{new}}] = \left( \mathbf{I} - \frac{\Delta t}{2} \mathbf{J} \right)^{-1} \left( \mathbf{I} + \frac{\Delta t}{2} \mathbf{J} \right) [\text{VOC}_{j,\text{tag}}^{\text{old}}], \quad (7)$$

where  $\text{VOC}_{j,\text{tag}}^{\text{new/old}}$  is the VOC species  $j$  for sector tag before (old) or after (new) the

Jacobian calculation;  $\mathbf{I}$  the identity matrix;  $\mathbf{J} = \mathbf{J} \left( \frac{[\text{C}_{\text{S,bulk}}^{\text{new}}] + [\text{C}_{\text{S,bulk}}^{\text{old}}]}{2} \right)$  the Jacobian matrix

calculated based on the average of bulk concentrations before and after any gas-phase solver for CB05 model species (e.g. Euler Backward Method, which is used here).

This system is solved by decomposing  $\left( \mathbf{I} - \frac{\Delta t}{2} \mathbf{J} \right)^{-1} \left( \mathbf{I} + \frac{\Delta t}{2} \mathbf{J} \right)$  into a product of lower and upper triangular matrices, which is known as LU decomposition. The solution is obtained only once for every model synchronization time step  $\Delta t$  instead of incremental chemical time steps to increase computational efficiency at little expense to accuracy.

### 3.2 Ozone regime indicators

The ratio of the instantaneous production rates of hydrogen peroxide to nitric acid ( $\text{PH}_2\text{O}_2/\text{PHNO}_3$ ) is used as an indicator to distinguish photochemical regimes, in which  $\text{PO}_3$  is primarily sensitive to either VOC or  $\text{NO}_x$ . Kleinman (1994) evaluated the dependence of  $\text{H}_2\text{O}_2$  on high and low  $\text{NO}_x$  photochemical regimes and Sillman (1995) proposed that a ratio of  $\text{H}_2\text{O}_2/\text{HNO}_3$  equal to 0.35 should distinguish  $\text{NO}_x$ -sensitive regimes ( $\text{H}_2\text{O}_2/\text{HNO}_3 > 0.35$ ) vs. VOC-sensitive regimes ( $\text{H}_2\text{O}_2/\text{HNO}_3 < 0.35$ ). Sillman (1995) evaluated the modelled daily maximum  $\text{O}_3$  sensitivity to VOC and  $\text{NO}_x$  as a function of the  $\text{H}_2\text{O}_2/\text{HNO}_3$  ratio and found that transition from VOC-sensitive to  $\text{NO}_x$ -sensitive regimes occurred at ratios in the range of 0.35 to 0.6, with the higher ratio occurring in aged air masses, in which concentrations of  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$  may have been affected by deposition. Tonnesen and Dennis (2000a, b) evaluated indicators of instantaneous production of  $\text{O}_x$  ( $\text{PO}_x$ ) and of daily maximum  $\text{O}_3$  concentration

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and found that indicator ratios had mixed performance for daily maximum O<sub>3</sub> concentration because of the effects of background concentrations and deposition. However, Tonnesen and Dennis (2000a) found that  $PH_2O_2/PHNO_3$  was an extremely robust indicator for instantaneous PO<sub>x</sub> sensitivity. Numerous other studies have evaluated the performance of several different indicator ratios for daily maximum O<sub>3</sub> sensitivity to VOC and NO<sub>x</sub> (Millford et al., 1994; Lu et al., 1998; Vogel et al., 1999; Sillman et al., 2000; Andreani-Aksoyoglu, 2002; Jimenez and Baldasano, 2004; Liang et al., 2006; Zhang et al., 2009; Peng et al., 2011; Torres-Jordan et al., 2012). While these studies have found variable and sometimes conflicting results for the usefulness of indicator ratios, each evaluated indicators of daily maximum O<sub>3</sub> concentration rather than PO<sub>3</sub>. Based on the most commonly used indicator ratio  $PH_2O_2/PHNO_3$ , ISAM attributes the instantaneous production term PO<sub>3</sub> to either VOC or NO<sub>x</sub> tracers.

Because O<sub>3</sub> production and loss processes occur simultaneously, the total PO<sub>3</sub> and DO<sub>3</sub> are calculated and used to update the O<sub>3</sub> tracers at each time step in the numerical chemistry solver used in the model, using the same approach as CAMx (ENVIRON, 2013). When PO<sub>3</sub> occurs in any grid cell,  $PH_2O_2/PHNO_3$  is used to determine if PO<sub>3</sub> is primarily NO<sub>x</sub>- or VOC-sensitive (above or below 0.35, respectively), and the O<sub>3</sub> tracers are updated with the production to intermediate O<sub>3</sub>N<sub>tag</sub><sup>middle</sup> and O<sub>3</sub>V<sub>tag</sub><sup>middle</sup> using:

$$\text{NO}_x\text{-sensitive O}_3\text{N}_{\text{tag}}^{\text{middle}} = \text{O}_3\text{N}_{\text{tag}}^{\text{old}} + \text{PO}_{3\text{bulk}} \times \frac{\text{NO}_{\text{tag}}^{\text{old}} + \text{NO}_{2\text{tag}}^{\text{old}}}{\sum_{\text{tag}} (\text{NO}_{\text{tag}}^{\text{old}} + \text{NO}_{2\text{tag}}^{\text{old}})} \quad (8)$$

$$\text{VOC-sensitive O}_3\text{V}_{\text{tag}}^{\text{middle}} = \text{O}_3\text{V}_{\text{tag}}^{\text{old}} + \text{PO}_{3\text{bulk}} \times \frac{\sum_s (\text{VOC}_{s,\text{tag}}^{\text{old}} \times \text{MIR}_s)}{\sum_{\text{tag}} \sum_s (\text{VOC}_{s,\text{tag}}^{\text{old}} \times \text{MIR}_s)} \quad (9)$$

Here,  $\text{VOC}_{s,\text{tag}}^{\text{old}}$  is the concentration of VOC species *s* for source sector tag. PO<sub>3bulk</sub> is the production of ozone in the grid cell. Table 1 lists the maximum incremental reactivity

(MIR) for each VOC species  $s$ , developed by Carter (1994) and tabulated by ENVIRON (2013), that are used to approximate the relative ozone forming potential of the VOC species. Carter (1994) also described alternative reactivity methods such as Maximum Ozone Incremental Reactivity (MOIR), and Equal Benefit Incremental Reactivity (EBIR). These alternate scales were also evaluated but did not provide significantly different results.

Following the production, subsequent apportionment of ozone destruction (where  $DO_3 \leq 0$ ) assumes only its depletion in both regimes for each sector:

$$O_3 X_{tag}^{new} = O_3 X_{tag}^{middle} + DO_{3bulk} \times \frac{O_3 X_{tag}^{middle}}{\sum_{tag} (O_3 N_{tag}^{middle} + O_3 V_{tag}^{middle})} \quad (10)$$

where  $X$  is either N or V.

## 4 Application and evaluation

A model simulation from 28 June to 5 July 2007 for the State of California (CA) using 12 km sized grid cells (79 columns and 106 rows) and 24 vertical layers was used to evaluate the CMAQ ozone ISAM. Anthropogenic emissions inputs were based on the 2008 National Emission Inventory (NEI) version 2 (US Environmental Protection Agency, 2013). Year specific emissions were included for electrical generating units. Meteorological inputs were generated using the Weather Research Forecasting (WRF) model (Skamarock et al., 2008). Biogenic VOC and  $NO_x$  emissions were estimated with the Biogenic Emissions Inventory System (BEIS) version 3.14 using temperature and solar radiation from the WRF model as inputs to BEIS (Carlton and Baker, 2011). Mexican emissions were projected from a 1999 inventory (US Environmental Protection Agency, 2011b). The 12 km model domain was nested in a 36 km continental domain, and boundary inflow to the 36 km domain were based on spatially and

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39 ppb in the central valley. The elevated point source emissions sectors of EGU, Non-EGU, MEX, and MARINE contribute relatively less to O<sub>3</sub> at the surface layer. Spatial correspondence is evident among O<sub>3</sub> (Fig. 1), NO<sub>x</sub>, and VOC concentrations (Supplement Figs. S1 and S2), as well as NO<sub>x</sub> and VOC emissions (Supplement Figs. S3 and S4) for most sectors suggesting that ISAM is predicting realistic source-signatures. For example, the wild fire in northern CA is reflected in O<sub>3</sub> (Fig. 1b), precursor concentrations (Supplement Figs. S1b and S2b) and emissions (Supplement Figs. S3b and S4b). O<sub>3</sub> produced from emission in the marine sector is distributed mostly along the coast (Fig. 1h), which is also seen in NO<sub>x</sub> and VOC concentrations (Supplement Figs. S1h and S2h). The corresponding marine emission plot tiles (Supplement Figs. S3h and S4h) indicate sources mostly near the San Francisco Bay area and the Port of Los Angeles. BCON contributions are highest at the lateral edges of the domain and in areas of elevated terrain as expected.

The ISAM contributions also realistically change in time similar to bulk modelled estimates and ambient measurements. This is demonstrated for two O<sub>3</sub> monitor sites, at Riverside in Fig. 2a and Sacramento in Fig. 2b, where monitor data are displayed with the model simulated ozone and ISAM-attributed data. Despite clear differences in the ozone formation behaviour at the two locations, including lower O<sub>3</sub> concentrations and greater nighttime titration of O<sub>3</sub> by NO<sub>x</sub> at the Sacramento monitor, the observed O<sub>3</sub> levels at the two sites are reproduced by CMAQ. Together with Supplement Fig. S5, Fig. 2 demonstrates the base model's ability to capture the temporal and regional variability in observed ozone.

## 4.2 ISAM/brute force comparisons

The brute force or zero out approach was used to provide an estimate of source contribution for comparison with the O<sub>3</sub> source apportionment algorithm. The brute force source sensitivity approach determines O<sub>3</sub> response to partial or total removal of an emission sector/region/species of interest, whereas ISAM is designed to account for the emission sector/region/species' contribution to O<sub>3</sub>. These approaches provide

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similar results in linear systems and less similar results in more non-linear systems. Therefore, given the nature of these approaches, source estimates will be similar but should never match given the inherent differences in methodology. Throughout this study, three types of brute force emission datasets were constructed for each sector.

5 The first type removes both NO<sub>x</sub> and VOC emissions from each tracked source, denoted by “Both-out”. The second one only removes NO<sub>x</sub>, denoted “N-out”. The third only removes VOC, denoted by “V-out”. Since the formation regime of boundary inflow O<sub>3</sub> is unknown, the “Both-out” includes zero out of BCON O<sub>3</sub>, NO, NO<sub>2</sub>, and the VOCs. The Both-out brute force simulations were used to compare ISAM O<sub>3</sub> collectively from both VOC- and NO<sub>x</sub>-sensitive regimes. The N-out was used to compare ISAM NO<sub>x</sub>-limited O<sub>3</sub> (O<sub>3</sub>N) as well as ISAM NO<sub>x</sub>, while the V-out assessed ISAM VOC-limited O<sub>3</sub> (O<sub>3</sub>V) as well as ISAM VOC. Bearing in mind that any zero-out run is subtracted from the base case run so that the resulting difference is compared with the corresponding ISAM sector, the remainder of this manuscript will refer to this difference simply as “Both-out”, “N-out” or “V-out”.

### Ozone

Figure 3 compares ISAM and Both-out results for O<sub>3</sub> from each tracked sector. Data points are daytime-averaged (6 a.m. to 6 p.m. Pacific Daylight Time) for each grid cell. In general, surface emissions such as BIOG, NNRD and ONRD (Table 2) give rise to higher surface O<sub>3</sub> concentrations attributed to these sectors. Negative O<sub>3</sub> brute force response in Non-EGU, ONRD, and MEX (Fig. 3c, e, and f) implies a disbenefit (i.e., O<sub>3</sub> increase) from removing both NO<sub>x</sub> and VOC emissions from these sectors. This is consistent with previous model sensitivity studies which show disbenefits for NO<sub>x</sub> emissions reductions, especially in urban areas that have typically low VOC/NO<sub>x</sub> ratios (Jimenez and Baldasano, 2004; Zhang et al., 2009). ISAM is designed to track sources that contribute to O<sub>3</sub> production, and Fig. 3e shows that even in cases where O<sub>3</sub> has a negative sensitivity to changes in ONRD emissions in certain grid cells, those emissions in an unperturbed environment contribute to O<sub>3</sub> production.

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The high BCON O<sub>3</sub> attribution by ISAM and Both-out shows notable inflow of O<sub>3</sub> from the boundaries. The global scale GEOS-Chem model is used to provide the O<sub>3</sub> BC, and therefore, source attribution of O<sub>3</sub> would also have to be used in GEOS-Chem to identify the sources that contribute to O<sub>3</sub> inflow at the boundary. However, ISAM predicts systematically more BCON O<sub>3</sub> than the Both-out case. By comparing domain-averaged daily total O<sub>3</sub> of all sectors (including unspecified emissions OTHR) among ISAM, Both-out and CMAQ bulk concentrations (Fig. 4), it is evident that the sum of ISAM contributions closely matches the bulk O<sub>3</sub>, but the sum of zero-out contributions is significantly lower than the bulk ozone concentration (15 % lower on average). While ISAM appears to conserve bulk mass as designed, the zero-out case shifts the chemical system into another part of the non-linear, often negative, O<sub>3</sub> response to source change. Similar qualitative features are also exhibited in total O<sub>3</sub> deposition (Supplement Figs. S6 and S7).

Perhaps one of the most substantial ISAM/Both-out comparison contrasts lies in the BIOG sector, in which ISAM sometimes attributes approximately half as much O<sub>3</sub> as Both-out. Previous studies have also found strong nonlinearity in the model response to biogenic emissions (Chameides et al., 1988). Biogenic VOC emissions are generally large in rural areas with low NO<sub>x</sub> emissions where O<sub>3</sub> is less sensitive to changes in VOC emissions in these areas. Yet the dominance of biogenic VOC alone cannot adequately explain the ISAM/Both-out discrepancy.

Another CMAQ diagnostic tool called decoupled direct method in three dimensions with high order terms (HDDM-3D) (Napelenok et al., 2008) was also used to calculate the biogenic O<sub>3</sub> contribution. The output of CMAQ-HDDM provides both first and second order O<sub>3</sub> sensitivity to a perturbation in the biogenic sector, which is then scaled to 100 % emissions rates. With all-hour samples averaged, Fig. 5 shows that the first order DDM approximation explains only 67 % of the brute force response, while the second order DDM approximation explains 88 % of the zero-out response. This results suggests a highly nonlinear system in which a zero out difference is the least likely to compare well with the source apportionment results.

## NO<sub>x</sub>

In addition to estimating O<sub>3</sub> contribution from precursors, ISAM also allows for tracking precursor NO<sub>x</sub> to model estimated nitrogen containing species concentration and deposition. Figure 6 shows ISAM/N-out NO<sub>x</sub> scatter plots for individual sectors. For the modelled region, the most dominant sector is ONRD, followed by NNRD and MARINE, as shown more clearly in stacked bar plots in Fig. 7. As expected, the order in maximum NO<sub>x</sub> concentrations in those sectors is similar to that in the domain-total NO<sub>x</sub> emissions (Table 2), in which ONRD and NNRD NO<sub>x</sub> emissions dominate. It is interesting to note that the high NO<sub>x</sub> concentrations in ONRD, NNRD and MARINE sectors are where VOC/NO<sub>x</sub> emissions ratios are low. Conversely, the low NO<sub>x</sub> concentration in BIOG sector is where a very large VOC/NO<sub>x</sub> emissions ratio occurs.

All sectors have correlation coefficients of above 0.90 for the NO<sub>x</sub> comparison (Fig. 6). Qualitative features in total NO<sub>x</sub> deposition (Supplement Figs. S8 and S9) are also similar to those of the corresponding ambient concentrations (Figs. 6 and 7).

## VOC

Figure 8 shows ISAM/V-out scatter plots of carbon-weighted VOC for individual sectors, which is calculated from ISAM-output VOC species:

$$V_{\text{tag}} = \sum_s \text{VOC}_{s,\text{tag}} \times \text{NCARB}_s, \quad (11)$$

where  $V_{\text{tag}}$  is the aggregated VOC for each tag;  $s$  is the ISAM-output CB05 species for each tag; and NCARB is the number of carbon atoms in species  $s$  (see Table 1 for the complete list).

Correlations are high in most sectors except for EGU and MARINE (Fig. 8g and h), but magnitudes are also small for these two sectors. While BIOG is the most dominant VOC sector, the high maximum VOC concentrations from FIRE do not necessarily lead to a bigger share in the domain-averaged VOC concentration (Fig. 9). In fact,

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domain-wide major VOC sectors are BIOG, BCON and ONRD (Fig. 9). Similar features are evident in the total VOC deposition (Supplement Figs. S10 and S11).

To more closely examine the evolution of individual VOC species in BIOG, BCON and ONRD sectors, daytime domain-averaged ambient concentrations and daily total deposition of individual VOC species are displayed (Supplement Figs. S12a, c and S14a, c). Further, we explore the influence of gas-phase degradation of those VOCs by calculating ISAM and V-out contributions from the three sectors while turning off the gas and aerosol chemistry. The corresponding VOC breakdowns are also displayed in Supplement Figs. S12b, d and S14b, d. Prior to gas-phase chemistry, VOC portions are very similar between ISAM and V-out in all three sectors. Although evolution characteristics of the VOC species with photochemistry are different across these sectors, secondary formation of acetaldehyde ALD2, higher aldehydes ALDX, and formaldehyde FORM is evident in BIOG and ONRD emissions sectors where primary emissions of the aldehydes are low. These results are consistent with the modelled VOCs' degeneration into formaldehyde (or higher aldehydes) as illustrated in Reactions (R4) through (R6). On the other hand, the evolution of BCON's aldehydes is more complicated, since both imported and secondarily formed aldehydes can be equally important, none of which were explicitly distinguished by ISAM.

## 5 Summary and discussion

General similarities between ISAM and zero-out cases establish credibility of the ISAM results, while specific differences, whether in magnitude or in relative portions, demonstrate different functionalities of the two approaches, depending on whether source sectors/regions of interest are either to be accounted for pollutant levels in a given scenario, or to be perturbed for the outcome of alternate scenarios. Implementation of O<sub>3</sub> tracking capability in CMAQ-ISAM adopts the two-regime approach, with nitrogen and VOC species explicitly tracked through all chemical transport model science processes to facilitate analysis of their chemical and physical transformations. Brute force

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zero-out CMAQ model simulations serve as a reference to compare the ISAM results applied for a California application in the summer of 2007. In general, correlations between ISAM/zero-out estimates are high for both ambient concentration and deposition of O<sub>3</sub> for the major emissions sectors; higher ISAM estimates than nitrogen-out for NO<sub>x</sub> in most sectors except boundary condition; and similar ISAM estimates compared to VOC-out in VOC in most sectors except EGU and MARINE. Differences between ISAM and zero out were found in the tracking of O<sub>3</sub> from biogenic emissions, where the model sometimes predicts half of the contribution indicated by zero out. In the condition of extremely low NO emissions in this sector, high nonlinearity in the gas phase chemistry, supported by the pronounced difference between DDM-based apportionment using 1st order sensitivity coefficients and using 1st and 2nd order coefficients, was found to be responsible for this discrepancy. Explicit VOC tracking, available in ISAM, also provides new opportunities to analyze species-specific ozone formation mechanisms (see Supplement Figs. S12, S13, and S14). This approach not only compliments results derived from receptor-based models such as CMB and PMF, but also offers a diagnostic tool to track the chemical evolution of the VOC species that cannot be otherwise adequately explained by receptor-based models alone. In addition to providing VOC contribution information similar to a receptor based source apportionment model, this source based approach also estimates contribution for nitrogen species, O<sub>3</sub>, and deposition of each.

The source apportionment technique is recommended when an assessment of contributing sources is desired for model predicted species. Where the change in air quality resulting from perturbing contributing sources is desired then a source sensitivity approach such as brute-force or DDM may be more appropriate. Further, source apportionment should generally be applied for sources or source groups that are well characterized since limitations in the emissions inventory will manifest in photochemical model and source contribution estimates.

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**Table 1.** Maximum Incremental Reactivity in CB05 VOC species on ozone production.

CB05 VOC name	CMAQ acronym	Number of carbon atoms	MIR
Acetaldehyde	ALD2	2	4.45
Higher aldehydes	ALDX	2	6.81
Ethene	ETH	2	4.37
Ethane	ETHA	2	0.11
Ethanol	ETOH	2	1.04
Formaldehyde	FORM	1	4.50
Internal olefin	IOLE	4	13.11
Isoprene	ISOP	5	11.56
Methanol	MEOH	1	0.36
Olefin	OLE	2	8.24
Paraffin	PAR	1	0.32
Monoterpenes	TERP	10	8.82
Toluene	TOL	7	2.94
Xylene	XYL	8	14.79

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**Table 2.** All-hour domain averaged NO<sub>x</sub> and VOC emissions rates for Californian 12 km domain during 28 June–5 July 2007.

Emissions Sectors	NO <sub>x</sub> emis mole s <sup>-1</sup>	% of total NO <sub>x</sub> emis	VOC emis mole C s <sup>-1</sup>	% of total VOC emis	VOC/NO <sub>x</sub> mole C mole <sup>-1</sup>
BEIS (BIOG)	76.3	9.1	20 939.2	88.9	274.4
Marine (MARINE)	28.7	3.4	7.5	0.0	0.3
Fire (FIRE)	10.7	1.3	312.7	1.3	29.2
Nonroad (NNRD)	115.4	13.7	469.7	2.0	4.1
Onroad (ONRD)	413.7	49.1	535.7	2.3	1.3
Mexican point sources (MEX)	6.6	0.8	6.6	0.0	1.0
Elec. Gen. Units (EGU)	21	2.5	2.1	0.0	0.1
Non Elec. Gen. Units (Non-EGU)	36.9	4.4	25.5	0.1	0.7
Untraced emissions (OTHR)	133.1	15.8	1264.9	5.4	9.5
Emissions Totals	842.4		23 563.9		28.0

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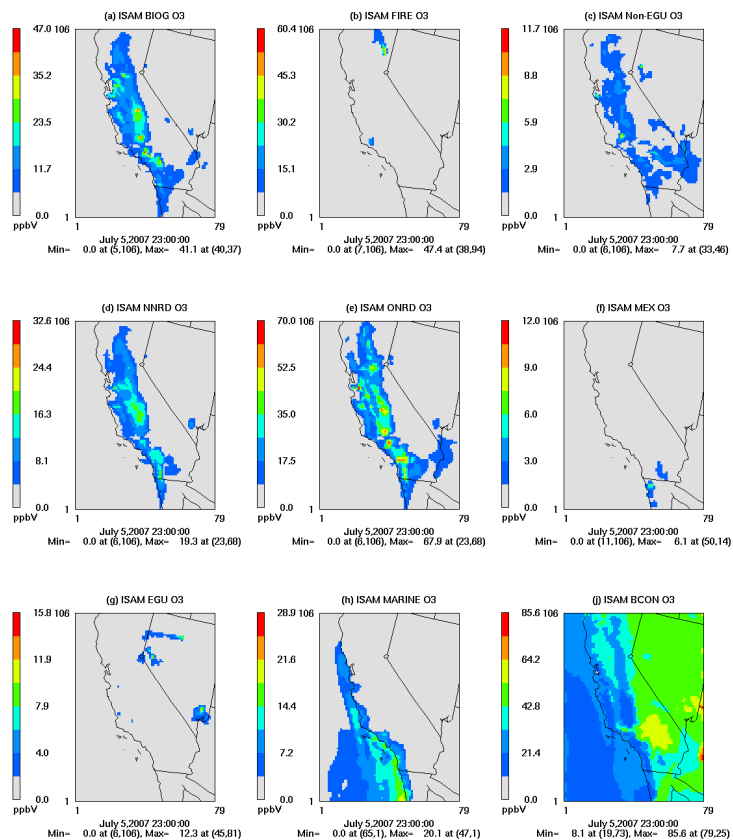
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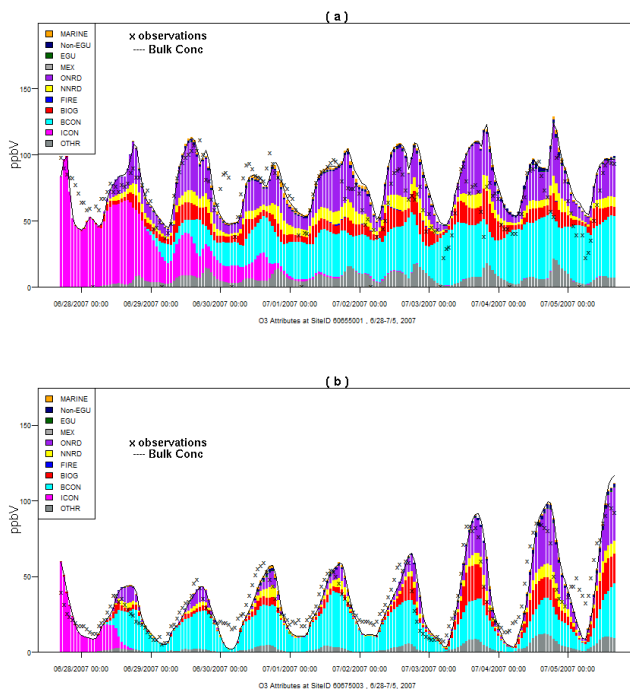
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**Figure 1.** Spatial tiles of 9 source sectors contributing to ambient O<sub>3</sub>, at 23:00 UTC (16 PDT) 5 July 2007. **(a)** Biogenic BIOG, **(b)** wild fires FIRE, **(c)** non-electricity generation units Non-EGU, **(d)** non-road mobile NNRD, **(e)** on-road mobile ONRD, **(f)** Mexican point sources MEX, **(g)** electricity generation units EGU, **(h)** marine MARINE, and **(i)** boundary conditions BCON. Note different scales across the tiles.

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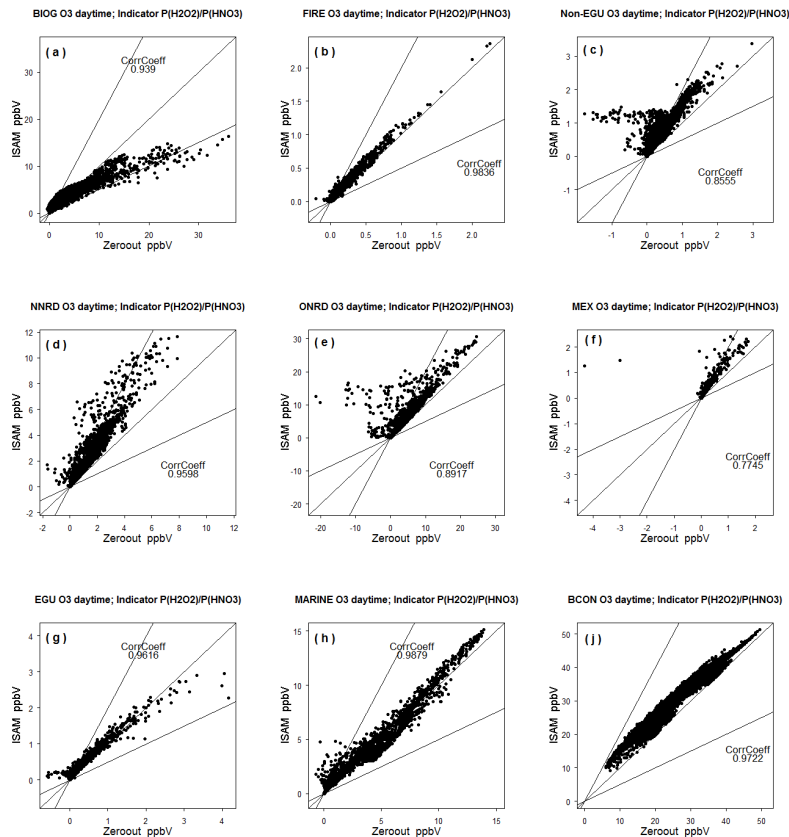


**Figure 2.** Hourly time series of O<sub>3</sub> observations (crosses) at sites of California Air Resources Board monitoring network; and the corresponding CMAQ-ISAM sector breakdowns (stacking colored bars). Locations are **(a)** Riverside and **(b)** Sacramento. The colors represent sector sources: marine (MARINE orange), non-electricity generation units (Non-EGU deep blue), electricity generation units (EGU green), other point sources (MEX light grey), on-road mobile (ONRD purple), non-road mobile (NNRD yellow), wild fires (FIRE blue), biogenic (BIOG red), boundary conditions (BCON cyan), initial conditions (ICON magenta), and remaining unspecified emissions (OTHR grey). The solid black trace on top of the bars denotes the modeled bulk O<sub>3</sub> concentration.



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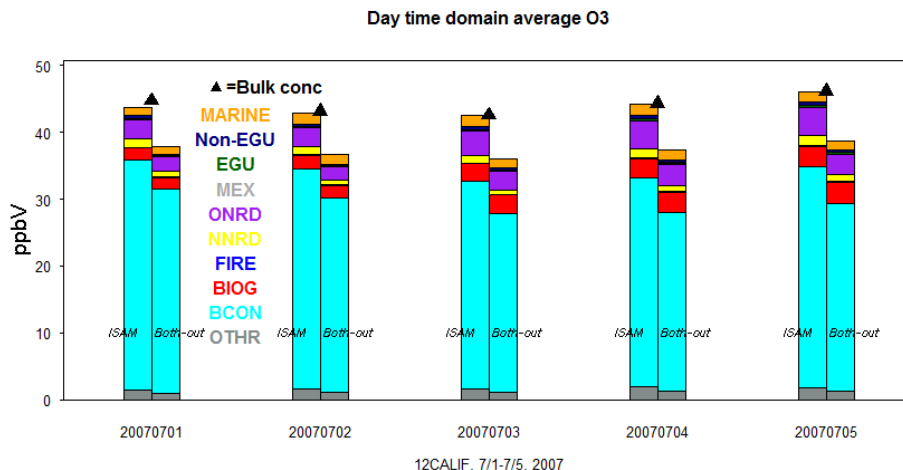
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**Figure 3.** ISAM/both-out O<sub>3</sub> scatter plots for each sector, averaged on daytime samples. The sectors are: **(a)** biogenic BIOG, **(b)** wild fires FIRE, **(c)** non-electricity generation units Non-EGU, **(d)** non-road mobile NNRD, **(e)** on-road mobile ONRD, **(f)** other point sources MEX, **(g)** electricity generation units EGU, **(h)** marine MARINE, and **(i)** boundary conditions BCON. Note different scales across the panels.

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**Figure 4.** Daytime domain-averaged ambient O<sub>3</sub>, 1–5 July 2007. In the bar plot, each day consists of two stacked columns (ISAM on the left; Both-out total on the right) and above them a black triangle designating either bulk ambient concentration or bulk total deposition calculated from regular CMAQ. The colors represent sector sources: marine (MARINE orange), non-electricity generation units (Non-EGU deep blue), electricity generation units (EGU green), other point sources (MEX light grey), on-road mobile (ONRD purple), non-road mobile (NNRD yellow), wild fires (FIRE blue), BIOG3 vegetations (BIOG red), boundary conditions (BCON cyan), and remaining unspecified emissions (OTHR grey).

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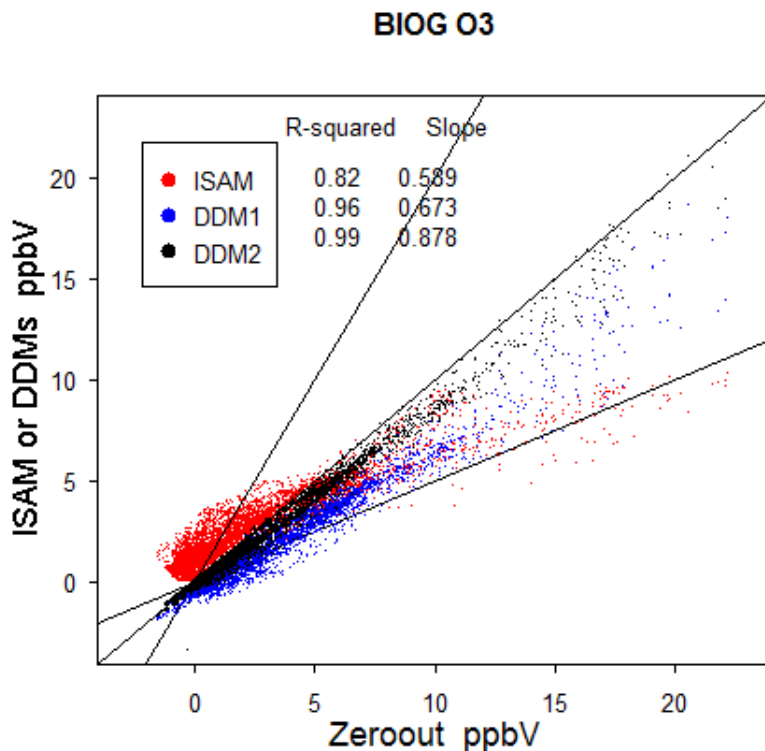
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**Figure 5.** Scatter plots of BIOG biogenic O<sub>3</sub> with respect to the zero-out brute force, sampled on all-hour-averaged data. Red: ISAM, blue: first order decoupled direct method (DDM1), black: second order decoupled direct method (DDM2). The corresponding R-squared values and regression slopes are also displayed.

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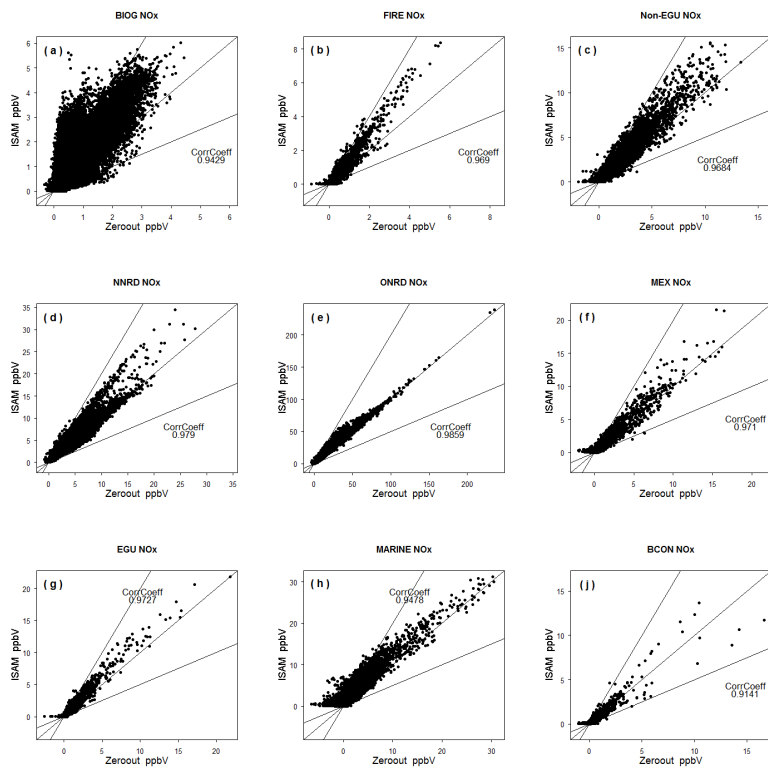
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**Figure 6.** ISAM/N-out  $\text{NO}_x$  scatter plots for each sector, with all hours samples used. The sectors are: **(a)** biogenic BIOG, **(b)** wild fires FIRE, **(c)** non-electricity generation units Non-EGU, **(d)** non-road mobile NNRD, **(e)** on-road mobile ONRD, **(f)** other point sources MEX, **(g)** electricity generation units EGU, **(h)** marine MARINE, and **(j)** boundary conditions BCON. Note different scales across the panels.

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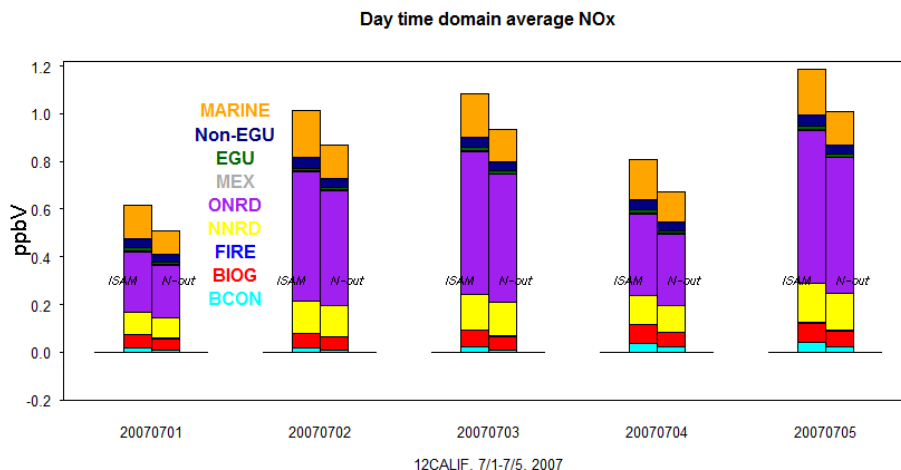
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**Figure 7.** Daytime domain-averaged ambient NO<sub>x</sub>, 1–5 July 2007. As in Fig. 4, for each day left column designates ISAM total, and right one the zero-out. The colors represent sector sources: marine (MARINE orange), non-electricity generation units (Non-EGU deep blue), electricity generation units (EGU green), other point sources (MEX light grey), on-road mobile (ONRD purple), non-road mobile (NNRD yellow), wild fires (FIRE blue), BEIS3 vegetations (BIOG red), and boundary conditions (BCON cyan).

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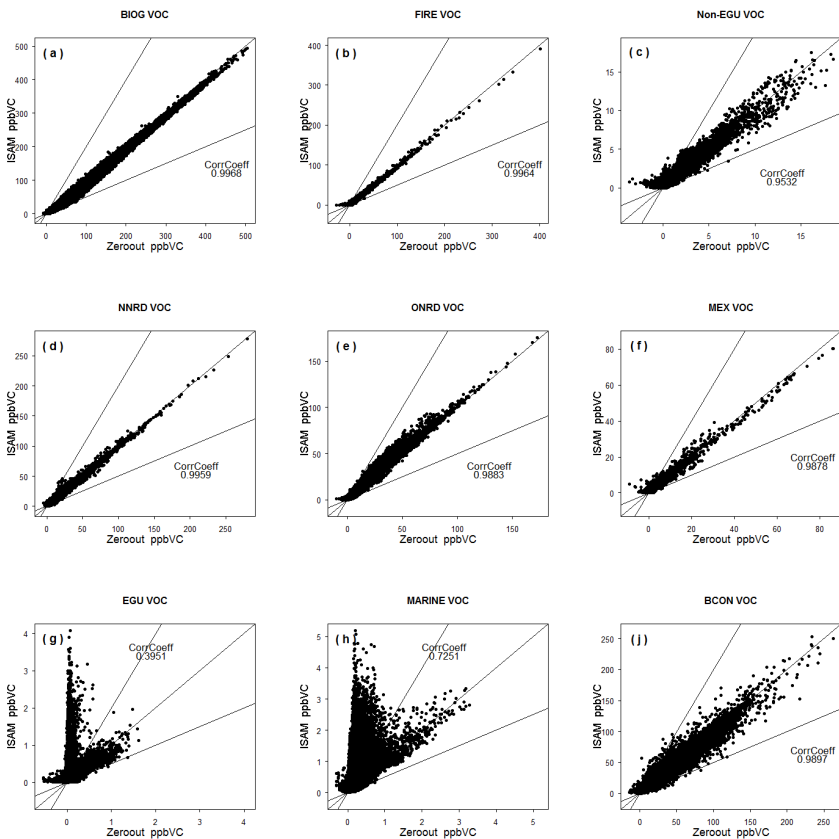
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**Figure 8.** ISAM/V-out VOC scatter plots for each sector, with all hours' samples used. The sectors are: (a) biogenic BIOG, (b) wild fires FIRE, (c) non-electricity generation units Non-EGU, (d) non-road mobile NNRD, (e) on-road mobile ONRD, (f) other point sources MEX, (g) electricity generation units EGU, (h) marine MARINE, and (i) boundary conditions BCON. Note different scales across the panels.

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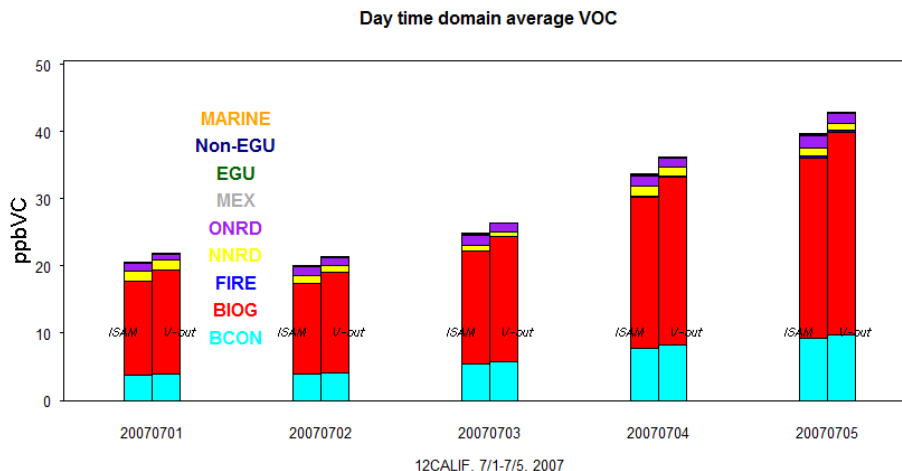


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**Figure 9.** Daytime domain-averaged ambient VOC, 1–5 July 2007. As in Fig. 4, for each day left column designates ISAM total, and right one the zero-out. The colors represent sector sources: marine (MARINE orange), non-electricity generation units (Non-EGU deep blue), electricity generation units (EGU green), other point sources (MEX light grey), on-road mobile (ONRD purple), non-road mobile (NNRD yellow), wild fires (FIRE blue), BEIS3 vegetations (BIOG red), and boundary conditions (BCON cyan).

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