Photochemical grid model implementation and application of VOC, NO_X, and O_3 source apportionment

R. H. F. Kwok[1], K. R. Baker[1], S.L. Napelenok[1]*, G. S. Tonnesen[2]

1 United States Environmental Protection Agency, 109 T.W. Alexander Drive, Research Triangle Park, NC 27711

2 United States Environmental Protection Agency, Region 8, 1595 Wynkoop Street, Denver, CO 80202-1129

*Corresponding author. Telephone: 1 (919) 541-1135, Fax: 1 (919) 541-1379, e-mail: Napelenok.Sergey@epa.gov.

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 track source 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. Where appropriate use depends on whether source attribution or source sensitivity is desired.

Key words: ozone, CMAQ, ISAM, source apportionment, sector contribution, photochemical model, NOX, VOC, deposition

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; U.S. 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, where compliance with the NAAQS is determined as the three-year average of the 4th highest daily maximum 8-hour 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, Section 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 (PO3) 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), and contribution from specific 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 $PM_{2.5}$ 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_3 source apportionment. This implementation is 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

71 factorization (PMF) receptor models provide information about source attribution to ozone precursors,
72 but not directly to ozone (Buzcu and Fraser, 2006; Chung et al., 1996; Kim et al., 2005; Scheff et al.,
73 1996; Tong et al., 2005). Statistical correlation analyses of the regional ozone pattern and time-lagged
74 correlation analyses have also been used to analyze transport effects (Guinnup and Collom, 1997; Husar
75 and Renard, 1997). These studies concluded that transport of O_3 and precursors could occur over the
76 distance of 300-600 km, but did not clearly differentiate the specific origins of transported ozone or the
77 confounding effects of meteorological factors (Guinnup and Collom, 1997).

78

79 Air quality model sensitivity simulations have been widely used to predict how O_3 responds to changes in
80 specific sources of emissions of VOC and NO_x (Russell and Dennis, 2000). Source sensitivity approaches
81 include photochemical model "brute force" simulations, in which a single emission source is reduced or
82 removed, and also model extensions that in a single simulation track multiple emissions sensitivities
83 forward (decoupled direct method, DDM) (Dunker et al., 2002) or backward (adjoint) (Mesbah et al.,
84 2012). Model sensitivity approaches have limitations when used for total source culpability, however,
85 because of the nonlinear dependence of O_3 on concentrations of VOC and NO_x. This is especially
86 problematic for evaluating contributions of NO_x because O_3 can have negative sensitivity to NO_x in
87 situations where the ratio of VOC to NO_x is low. Therefore, summing the O_3 change in response to
88 sensitivity simulations for multiple emissions sources can result in difficulty interpreting the cumulative
89 effect of those emissions on O_3.

90 In source apportionment approaches, the objective is to identify the amount of O_3 produced by
91 particular emissions sources rather than determining the sensitivity of O_3 to those sources. This
92 distinction is important in cases where O_3 has a non-linear sensitivity or negative sensitivity to changes
93 in emissions. Source apportionment methods also have the benefit of estimating contributions from

many different VOC and NO_x 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_3 formation. In the troposphere, O_3, nitrogen oxide (NO) and nitrogen dioxide (NO_2) react rapidly in a photo-stationary state (PSS) null cycle, shown in Reactions 1 to 3, which has no net effect on ambient O_3 concentrations:

$O_3 + NO \rightarrow NO_2 + O_2$	Reaction 1
$NO_2 + hv \rightarrow NO + O$	Reaction 2
$O + O_2 \rightarrow O_3$	Reaction 3

Photochemical formation of O_3 (PO3) in the troposphere occurs almost exclusively by the oxidation of VOC (Finlayson-Pitts and Pitts, 1986), as illustrated in Reactions 4 to 7 using methane (CH_4) reactions. While O_3 is not formed directly, Reactions 5 and 7 provide alternate pathways to convert NO to NO_2 without the loss of O_3 in Reaction 1, thereby allowing O_3 to accumulate as shown in Reaction 10:

$CH_4 + OH + O_2 \rightarrow CH_3OO + H_2O$	Reaction 4
$CH_3OO + NO \rightarrow CH_3O + NO_2$	Reaction 5
$CH_3O + O_2 \rightarrow HCHO + HO_2$	Reaction 6
$HO_2 + NO \rightarrow OH + NO_2$	Reaction7
$2\ NO_2 + hv \rightarrow 2\ NO + 2\ O$	Reaction 8
$2\ O + 2\ O_2 \rightarrow 2\ O_3$	Reaction 9

Net reaction:

$CH_4 + 4\ O_2 \rightarrow HCHO + H_2O + 2\ O_3$	Reaction 10

Because multiple families of precursors participate in the photochemical formation of O_3 (PO3), including NO_x, VOC and free radicals (HO_x=OH+HO_2+RO_2), the developer of a mass apportionment method for sources of PO3 must determine which precursor is of primary interest for source apportionment. For example, PO3 can be apportioned only on the basis of the NO_x emissions sources, or VOC emissions sources, or sources of HO_x that contribute to PO3 in Reactions 4 to 7. Alternatively, a hybrid approach can be used that combines attribution to multiple families of precursors, in which PO3 is attributed to either VOC or NO_x sources depending on whether PO3 occurs under VOC- or NO_x-sensitive conditions.

Ozone source apportionment approaches have been implemented in a number of 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).

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 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.*:

$$C_{bulk,O3}^{i,j,k} = \sum_{n=1}^{N} C_{O3_n}^{i,j,k} \qquad \text{Equation 1}$$

$$C_{bulk,VOC}^{i,j,k} = \sum_{n=1}^{N} C_{VOC_n}^{i,j,k} \qquad \text{Equation 2}$$

$$C_{bulk,NOx}^{i,j,k} = \sum_{n=1}^{N} C_{NOx_n}^{i,j,k} \quad \text{Equation 3}$$

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 O_3 and for the families of reactive NO_x and VOC species. The ratio of production of hydrogen peroxide to nitric acid ($PH_2O_2/PHNO_3$) is used to determine if PO3 occurs in either a NO_x- or VOC-sensitive chemical regime ($PH_2O_2/PHNO_3$ above or below 0.35, respectively; Sillman 1995). If PO3 occurs in a NO_x-sensitive regime, the NO_x tracers are used to attribute PO3 proportionally to the emissions sources that contributed to the NO_x concentration. Alternatively, if PO3 occurs in a VOC-sensitive regime, the VOC tracers are used to attribute PO3 to the emissions sources 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 PO3 is estimated based on its maximum incremental reactivity (MIR) (Carter,1994). The adjustment using MIR also accounts for increased PO3 from highly reactive VOC, such as aldehydes and 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 O3 = PO3 + DO3 Equation 4

where DO3 $\leq$ 0 indicates chemical destruction of O_3. In CAMx OSAT, PO3 is estimated as the net change in O_3 during the chemistry time step combined with amount of chemical destruction of O_3:

PO3 = Delta O3 -DO3 Equation 5

PO3 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 DO3. 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 1 to 3 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 acts 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 PO3 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 1 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 1, the O_3 that is subsequently formed in Reactions 2 and 3 is considered anthropogenic. Because the PSS null cycle does not result in any net PO3, 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 5 and 7 to represent PO3, 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 PO3. Therefore, this approach may underestimate the contribution of high reactivity VOC and overestimate the contribution of low reactivity to PO3. 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 based on monitoring data. Previous $PM_{2.5}$ source apportionment implementations have been evaluated by comparing source contributions to changes in $PM_{2.5}$ 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_3 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_3 has a strong non-linear dependence on precursors, such as the sensitivity to NO_x 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_3 source apportionment method to 20% perturbations in precursor NO_x emissions. Dunker et al. (2002) compared CAMx O_3 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_3 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_3, with the exception of urban areas in which O_3 had negative sensitivity to NO_x. In each of the studies described above, small emissions reductions or first-order DDM sensitivities do not account for non-linearity in the O_3 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_3 attainment strategies and recommended that large emissions changes should be used to assess model sensitivity. Therefore, similar to previous studies, ISAM O_3 contributions

231 are compared here with model sensitivity simulations to determine if ISAM provides generally
232 consistent results. However, instead of using small emissions changes, we use brute force zero-out
233 scenarios of emissions sectors to account more reliably for non-linearity in the O_3 response to changes in
234 precursors. While we expect that there will be some differences in the sensitivity and source
235 apportionment results, especially for strongly non-linear NO_x sensitivity in urban areas, we believe this
236 approach to be useful for evaluating the accuracy of ISAM O_3 source attributions for conditions that do
237 not have strongly non-linear sensitivities.

238

239

240 **3 METHOD**

241 *3.1 Implementation Overview*

242 The ISAM for O_3 has been implemented in the CMAQ version 5.0.2 model, which was developed by the
243 United States Environmental Protection Agency (EPA) and is used by EPA, other regulatory agencies, and
244 academic institutions to characterize local to continental scale ozone formation and transport (Byun and
245 Schere, 2006; Foley et al., 2010). The ISAM O_3 source apportionment implementation is designed to
246 track the contribution from user selected categories of NO_x and VOC emissions to model estimated NO_X,
247 VOC, and ozone concentration and deposition. In addition to precursor emissions, the model tracks O_3,
248 NO_x, and VOC from the lateral boundary conditions, and initial conditions. Precursor emissions tracers
249 can be defined geographically using an additional model input file that assigns the fractional area of
250 each model grid cell to specified sub-regions (typically a State or Province). Precursor emissions tracers
251 can also be defined by source sector (typically, major point sources, mobile sources, biogenic sources,
252 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 $PM_{2.5}$ 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 nitrogen and VOC species, whereas CAMx uses two tracers to represent the families of NO_x and VOC. Ozone production is attributed to either VOC or NO_x emissions sources based on the ozone chemical formation regime that is estimated using the $PH_2O_2/PHNO_3$ indicator ratio, similar to the implementation in CAMx. As described above, the bulk concentration of each VOC and NO_x species is equal to the sum of the tracers used to identify the sources of VOC and NO_x. The bulk O_3 concentration in each model grid cell is equal to the sum of O_3 tracers that were produced in either VOC- or NO_x-sensitive conditions:

$$O3_{bulk} = \sum_{tag} O3V_{tag} + \sum_{tag} O3N_{tag} \qquad \text{Equation 6}$$

where $O3V_{tag}$ and $O3N_{tag}$ are the VOC-sensitive and NO_x-sensitive 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 14 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 nine nitrogen compounds in CB05 that participate in the O_3 formation chemistry include NO, NO_2, nitrogen trioxide (NO_3), dinitrogen pentoxide (N_2O_5), nitrous acid (HONO), peroxyacyl nitrates (PAN), higher peroxyacyl nitrates (PANX), peroxynitric acid (PNA), and organic nitrates (NTR).

ISAM apportions CMAQ-calculated wet and dry deposition of O_3, NO_x, and all VOC species into individual sources as done in the previous $PM_{2.5}$ ISAM code. Both of these processes follow simple linear algorithms where the mass removed is a function of existing mass and a removal coefficient and thus did not require additional consideration for the ozone implementation.

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 entered into the same algorithm in a matrix solution:

$$\left[VOC_{s,tag}^{new}\right] = \left(\mathbf{I} - \tfrac{\Delta t}{2}\mathbf{J}\right)^{-1}\left(\mathbf{I} + \tfrac{\Delta t}{2}\mathbf{J}\right)\left[VOC_{s,tag}^{old}\right] \qquad \text{Equation 7}$$

, where $VOC_{s,tag}^{new/old}$ is the VOC species *j* for sector *tag* before (*old*) or after (*new*) the Jacobian calculation; $\mathbf{I}$ the identity matrix; $\mathbf{J}$ the Jacobian matrix calculated based on the average of bulk concentrations before and after any gas-phase solver for CB05 model species $\left(\frac{[C_{S,bulk}^{new}]+[C_{S,bulk}^{old}]}{2}\right)$ (e.g. Euler Backward Method, which is used here). This system is solved by decomposing $\left(\mathbf{I} - \tfrac{\Delta t}{2}\mathbf{J}\right)^{-1}\left(\mathbf{I} + \tfrac{\Delta t}{2}\mathbf{J}\right)$ 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 Δt instead of incremental chemical time steps to increase computational efficiency at little expense to accuracy as was previously shown in the original implementation of the CMAQ decoupled direct method (DDM) (Hakami, 2004) .

296

297 *3.2 Ozone Regime Indicators*

298 The ratio of the instantaneous production rates of hydrogen peroxide to nitric acid ($PH_2O_2/PHNO_3$) is
299 used as an indicator to distinguish photochemical regimes, in which PO3 is primarily sensitive to either
300 VOC or NO_x. Kleinman (1994) evaluated the dependence of H_2O_2 on high and low NO_x photochemical
301 regimes and Sillman (1995) proposed that a ratio of H_2O_2/HNO_3 equal to 0.35 should distinguish NO_x-
302 sensitive regimes (H_2O_2/HNO_3 >0.35) versus VOC-sensitive regimes (H_2O_2/HNO_3 <0.35). Sillman (1995)
303 evaluated the modelled daily maximum O_3 sensitivity to VOC and NO_x as a function of the H_2O_2/HNO_3
304 ratio and found that transition from VOC-sensitive to NO_x-sensitive regimes occurred at ratios in the
305 range of 0.35 to 0.6, with the higher ratio occurring in aged air masses, in which concentrations of H_2O_2
306 and HNO_3 may have been affected by deposition. Tonnesen and Dennis (2000a,b) evaluated indicators
307 of instantaneous production of O_x (POx) and of daily maximum O_3 concentration and found that
308 indicator ratios had mixed performance for daily maximum O_3 concentration because of the effects of
309 background concentrations and deposition. However, Tonnesen and Dennis (2000a) found that
310 $PH_2O_2/PHNO_3$ was an extremely robust indicator for instantaneous POx sensitivity. Numerous other
311 studies have evaluated the performance of several different indicator ratios for daily maximum O_3
312 sensitivity to VOC and NO_x (Milford et al., 1994; Lu et al., 1998; Vogel et al., 1999; Sillman et al., 2000;
313 Andreani-Aksoyoglu, 2002; Jimenez and Baldasano, 2004; Liang et al., 2006; Zhang et al., 2009; Peng et
314 al., 2011; Torres-Jordan et al., 2012). While these studies have found variable and sometimes conflicting
315 results for the usefulness of indicator ratios, each evaluated indicators of daily maximum O_3
316 concentration rather than PO3. Based on the most commonly used indicator ratio $PH_2O_2/PHNO_3$, ISAM
317 attributes the instantaneous production term PO3 to either VOC or NO_x tracers.

318

Because O_3 production and loss processes occur simultaneously, the total PO3 and DO3 terms are calculated and used to update the O_3 tracers at each time step in the numerical chemistry solver used in the model, using the same approach as CAMx (ENVIRON, 2013). When PO3 occurs in any grid cell, $PH_2O_2/PHNO_3$ is used to determine if PO3 is primarily NO_x- or VOC-sensitive (above or below 0.35, respectively), and the O_3 tracers are updated with the production to intermediate $O3N_{tag}^{middle}$ and $O3V_{tag}^{middle}$ using:

NOx-sensitive $$O3N_{tag}^{middle} = O3N_{tag}^{old} + PO3_{bulk} \times \frac{NO_{tag}^{old} + NO2_{tag}^{old}}{\sum_{tag}\left(NO_{tag}^{old} + NO2_{tag}^{old}\right)}$$ Equation 8

VOC-sensitive $$O3V_{tag}^{middle} = O3V_{tag}^{old} + PO3_{bulk} \times \frac{\sum_{s}\left(VOC_{s,tag}^{old} \times MIR_s\right)}{\sum_{tag}\sum_{s}\left(VOC_{s,tag}^{old} \times MIR_s\right)}$$ Equation 9

Here, $VOC_{s,tag}^{old}$ is the concentration of VOC species *s* for source sector *tag*. $PO3_{bulk}$ 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 ozone production apportionment, subsequent apportionment of ozone destruction (where DO3 <= 0) assumes only its depletion in both regimes for each sector:

$$O3X_{tag}^{new} = O3X_{tag}^{middle} + DO3_{bulk} \times \frac{O3X_{tag}^{middle}}{\sum_{tag}\left(O3N_{tag}^{middle} + O3V_{tag}^{middle}\right)}$$ Equation 10

where X is either *N* or *V*.

4 APPLICATION AND EVALUATION

A model simulation from June 28 to July 5, 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 (U.S. 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 (U.S. 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 temporally variant concentration data from a 2007 year-specific annual GEOS-Chem version 8-03-02 simulation (Harvard University, 2012).

To demonstrate the functionality of ISAM, eight emission sectors were chosen as tracked contributors to ozone formation. The five point source sectors represented electricity generating units (EGU), non-electricity generating units (Non-EGU), wild fires (FIRE), commercial marine (MARINE), and point sources in Mexico (MEX). The three area sources were on-road mobile (ONRD), non-road mobile (NNRD), and biogenic (BIOG). Tracers were also used for O_3, VOC and NO_x from the lateral boundary conditions (BCON) and initial conditions (ICON). Finally, a single additional tracer (OTHR) was used for all remaining emissions categories that were not explicitly tracked. Table 2 displays emission rates of NO_x and aggregated VOC in those sectors. Percentages of the total emissions contributed by each sector are also

362 listed for reference. For the modelled region, the leading NO_x emissions sectors by mass were ONRD
363 (49.1%), NNRD (13.7%) and BIOG (9.1%), though the untracked emissions accounted for 15.8%. VOC
364 emissions were dominated mostly by BIOG (88.9%). ISAM also has the capability to track regional
365 sources with a user-provided map file in IOAPI/netCDF format and specific flagged point sources.
366 Further details of the brute force setup are described in Section 4.2.

367

368 *4.1 Sector contributions*

369 Figure 1 displays spatial plots of individual contributing sectors to ambient O_3 in CA at 16:00 local time
370 on July 5th, 2007. On this day meteorological conditions were generally stagnant, sunny with light
371 northerly to northwesterly winds. The CMAQ model performed well this day with an O_3 bias of 4.7ppb
372 and average error of 9ppb across the domain during daytime hours. Nighttime hours were excluded
373 from ozone analysis, because ISAM was not designed to predict titration events that often occur at night
374 in areas of large NO_x emissions. For this application, the BCON contribution (Figure 1-j) is largest with
375 contribution from 20 to 40 ppb in coastal CA and contributions of 40 to 60 ppb in eastern CA.
376 Contributions from surface emissions sectors including ONRD and NNRD are also notable with
377 contributions to O_3 as much as 64 ppb near urban areas. BIOG emissions were also an important
378 contributor to O_3 with a maximum of 39 ppb in the central valley. The elevated point source emissions
379 sectors of EGU, Non-EGU, MEX, and MARINE contribute relatively less to O_3 at the surface layer. Spatial
380 correspondence is evident among O_3 (Figure 1), NO_x, and VOC concentrations (Supp Figures 1 and 2), as
381 well as NO_x and VOC emissions (Supp Figures 3 and 4) for most sectors suggesting that ISAM is
382 predicting realistic source-signatures. For example, the wild fire in northern CA is reflected in O_3 (Figure
383 1-b), precursor concentrations (Supp Figures 1-b and 2-b) and emissions (Supp Figures 3-b and 4-b). O_3
384 produced from emission in the marine sector is distributed mostly along the coast (Figure 1-h), which is

385 also seen in NOx and VOC concentrations (Supp Figures 1-h and 2-h). The corresponding marine
386 emission plot tiles (Supp Figures 3-h and 4-h) indicate sources mostly near the San Francisco Bay area
387 and the Port of Los Angeles. BCON contributions are highest at the lateral edges of the domain and in
388 areas of elevated terrain as expected.

389 The ISAM contributions also realistically change in time similar to bulk modelled estimates and ambient
390 measurements. This is demonstrated for two O_3 monitor locations, at Riverside in Figure 2-a and
391 Sacramento in Figure 2-b, where monitor data are displayed with the model simulated ozone and ISAM-
392 attributed data. Each location had data availability at six separate monitoring sites and Figure 2 shows
393 the average measured and modeled quantities. Individual monitor results are shown in Supp Fig 5.
394 Despite clear differences in the ozone formation behaviour at the two locations, including lower O_3
395 concentrations and greater nighttime titration of O_3 by NO_x at the Sacramento monitor, the observed O_3
396 levels at the two sites are reproduced by CMAQ. Results presented in Supplement Fig 5 and Figure 2
397 demonstrate the base model's ability to capture the temporal and regional variability in observed ozone.

398

399 *4.2 ISAM/brute force comparisons*

400 The brute force or zero-out approach was used to provide an estimate of source contribution for
401 comparison with source contribution estimated with the O_3 source apportionment algorithm. The brute
402 force source sensitivity approach determines O_3 response to partial or total removal of an emission
403 sector/region/species of interest, whereas ISAM was used to provide an alternate estimate of source
404 sector/region/species' contribution to O_3. These approaches provide similar results in linear systems
405 and less similar results in more non-linear systems. Therefore, given the nature of these approaches,
406 source estimates will be similar but should never match given the inherent differences in methodology.
407 Throughout this study, three types of brute force emission datasets were constructed for each sector.

The first type removes both NO_x and VOC emissions from each tracked source, denoted by "Both-out". The second one only removes NO_x, denoted "N-out". The third only removes VOC, denoted by "V-out". Since the formation regime of boundary inflow O_3 is unknown, the "Both-out" includes zero-out of BCON O_3 , NO, NO_2, and the VOCs. The Both-out brute force simulations were used to compare ISAM O_3 collectively from both VOC- and NO_x-sensitive regimes. The N-out was used to compare ISAM NO_x-limited O_3 (O3N) as well as ISAM NO_x, while the V-out assessed ISAM VOC-limited O_3 (O3V) 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_3 from each tracked sector. Data points are daytime-averaged (6 am to 6 pm 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_3 concentrations attributed to these sectors. Negative O_3 brute force response in Non-EGU, ONRD, and MEX (Figures 3-c, e, and f) implies a disbenefit (i.e., O_3 increase) from removing both NO_x and VOC emissions from these sectors. This is consistent with previous model sensitivity studies which show disbenefits for NO_x emissions reductions, especially in urban areas that have typically low VOC/NO_x ratios (Jimenez and Baldasano 2004; Zhang et al 2009). ISAM is designed to track sources that contribute to O_3 production, and Figure 3-e shows that even in cases where O_3 has a negative sensitivity to changes in ONRD emissions in certain grid cells, those emissions in an unperturbed environment contribute to O_3 production.

The high BCON O_3 attribution by ISAM and Both-out shows notable inflow of O_3 from the boundaries as shown more clearly in the stacked bar charts in Figure 4. The global scale GEOS-Chem model is used to provide the O_3 BC, and therefore, source attribution of O_3 would also have to be used in GEOS-Chem to identify the sources that contribute to O_3 inflow at the boundary. However, ISAM predicts systematically more BCON O_3 than the Both-out case. By comparing domain-averaged daily total O_3 of all sectors (including unspecified emissions OTHR) among ISAM, Both-out and CMAQ bulk concentrations (Figure 4), it is evident that the sum of ISAM contributions closely matches the bulk O_3, 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_3 response to source change. Similar qualitative features are also exhibited in total O_3 deposition (Supp Figures 6 and 7).

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_3 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_x emissions where O_3 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_3 contribution. The output of CMAQ-HDDM provides both first and second order O_3 sensitivity to a perturbation in the biogenic sector, which is then scaled to 100% emissions rates. With all-hour samples averaged, Figure 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.

NOx

In addition to estimating O_3 contribution from precursors, ISAM also allows for tracking precursor NO_X to model estimated nitrogen containing species concentration and deposition. Figure 6 shows ISAM/N-out NO_x 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 Figure 7. Expectedly, the order in maximum NO_x concentrations in those sectors is similar to that in the domain-total NO_x emissions (Table 2), in which ONRD and NNRD NO_x emissions dominate. It is interesting to note that the high NO_x concentrations in ONRD, NNRD and MARINE sectors are where VOC/NO_x emissions ratios are low. Conversely, the low NO_x concentration in BIOG sector is where a very large VOC/NO_x emissions ratio occurs.

All sectors have correlation coefficients of above 0.90 for the NO_x comparison (Figure 6). Qualitative features in total NO_x deposition (Supp Figures 8 and 9) are also similar to those of the corresponding ambient concentrations (Figures 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:

$$V_{tag} = \sum_{s} VOC_{s,tag} \times NCARB_{s} \quad \text{Equation 11}$$

, where V_{tag} is the aggregated VOC for each *tag*; $VOC_{s,tag}$ ISAM-output CB05 species *s* for each *tag*; and $NCARB_{s}$ 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 (Figure 8-g and 8-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 (Figure 9). In fact, domain-wide major VOC sectors are BIOG, BCON and ONRD (Figure 9). Similar features are evident in the total VOC deposition (Supplement Figures 10 and 11).

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 Figures 12-a, 12-c, 13-a, 13-c, 14-a and 14-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 were also displayed in Supplement Figures 12-b, 12-d, 13-b, 13-d, 14-b and 14-d. Prior to gas-phase chemistry, VOC portions are very similar between ISAM and V-out in all the three sectors. Although evolution characteristics of the VOC species with photochemistry are different across these sectors, secondary formation of acetaldehyde ALD2, high aldehydes ALDX, and formaldehydes 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 4 through 6. 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 & 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. The choice of appropriate methodology depends on whether source sector/region attribution or sensitivity is of interest Implementation of O_3 tracking capability in CMAQ-ISAM for the CB05 gas-phase chemical mechanism 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 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_3 for the major emissions sectors. ISAM estimates of NO_x are higher than nitrogen-out in most sectors except boundary condition. And ISAM VOC estimates are similar when compared to VOC-out in most sectors except EGU and MARINE. Differences between ISAM and zero-out were found in the tracking of O_3 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 1^{st} order sensitivity coefficients and using 1^{st} and 2^{nd} 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 Supp Figs). This approach not only complements 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_3, 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.

5 CODE AVAILABILITY

The implementation of the ISAM source apportionment technique for O_3 and its precursors in the CMAQ photochemical grid model presented here is freely available online at https://www.cmascenter.org. This includes code, documentation, and a small test case for benchmarking and illustrating ISAM setup and capability.

Disclaimer

Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

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712

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

Table 2. All-hour domain averaged NOx and VOC emissions rates for Californian 12-km domain during Jun 28-Jul 5, 2007.

Emissions Sectors	NOx emis mole/s	% of total NOx emis	VOC emis moleC/s	% of total VOC emis	VOC/NOx moleC/mole
BEIS *(BIOG)*	76.3	9.1	20939.2	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		23563.9		28.0

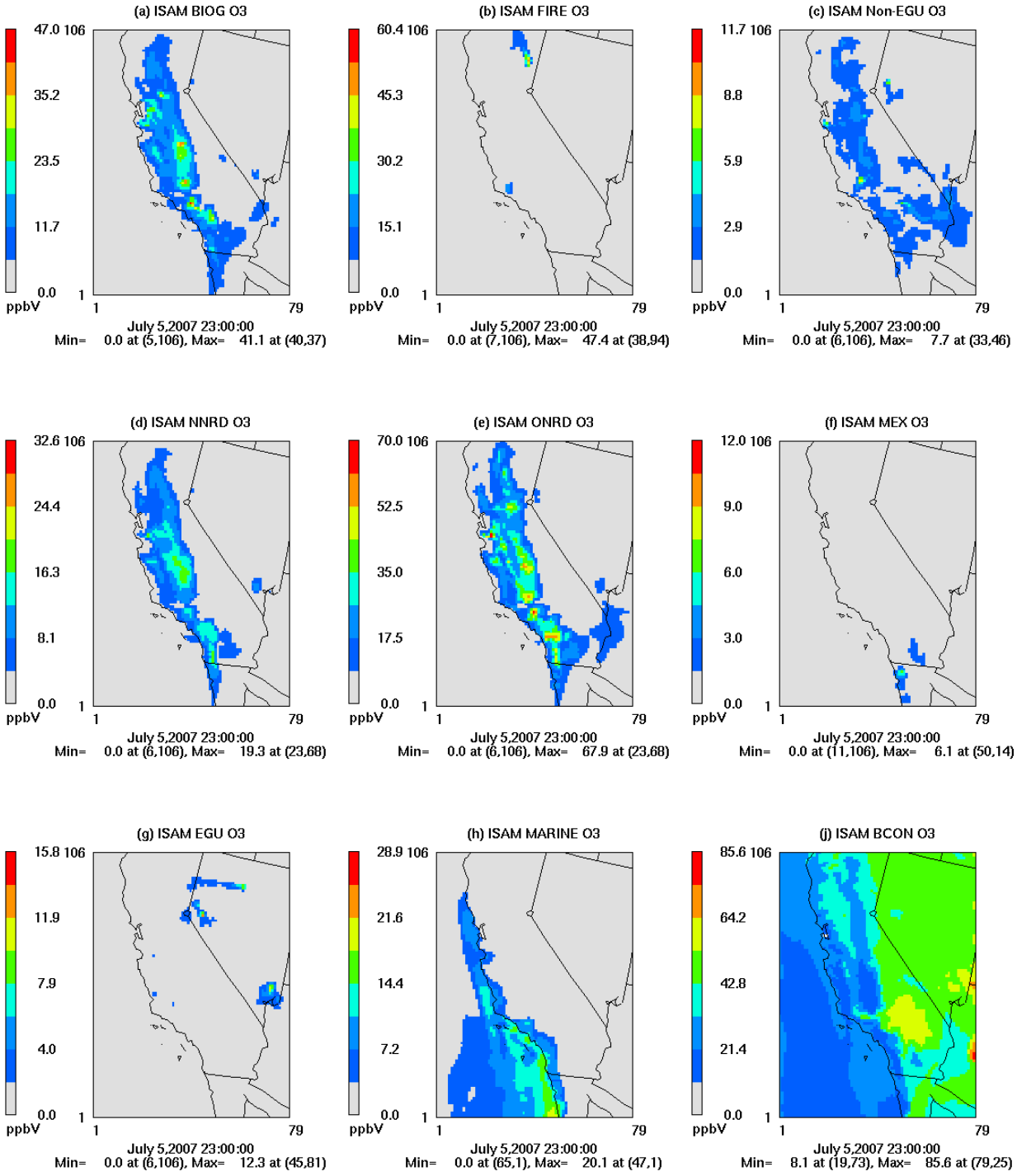

Figure 1. Spatial tiles of 9 source sectors contributing to ambient O3, at 23UTC (16 PDT) July 5, 2007. (a) biogenic BIOG, (b) wild fires FIRE, (c) non-electricity generation units Non-EGU, (d) non-road mobile NNRD, (e) on-road mobile ONRD, (f) Mexican point sources MEX, (g) electricity generation units EGU, (h) marine MARINE, and (j) boundary conditions BCON. Note different scales across the tiles.

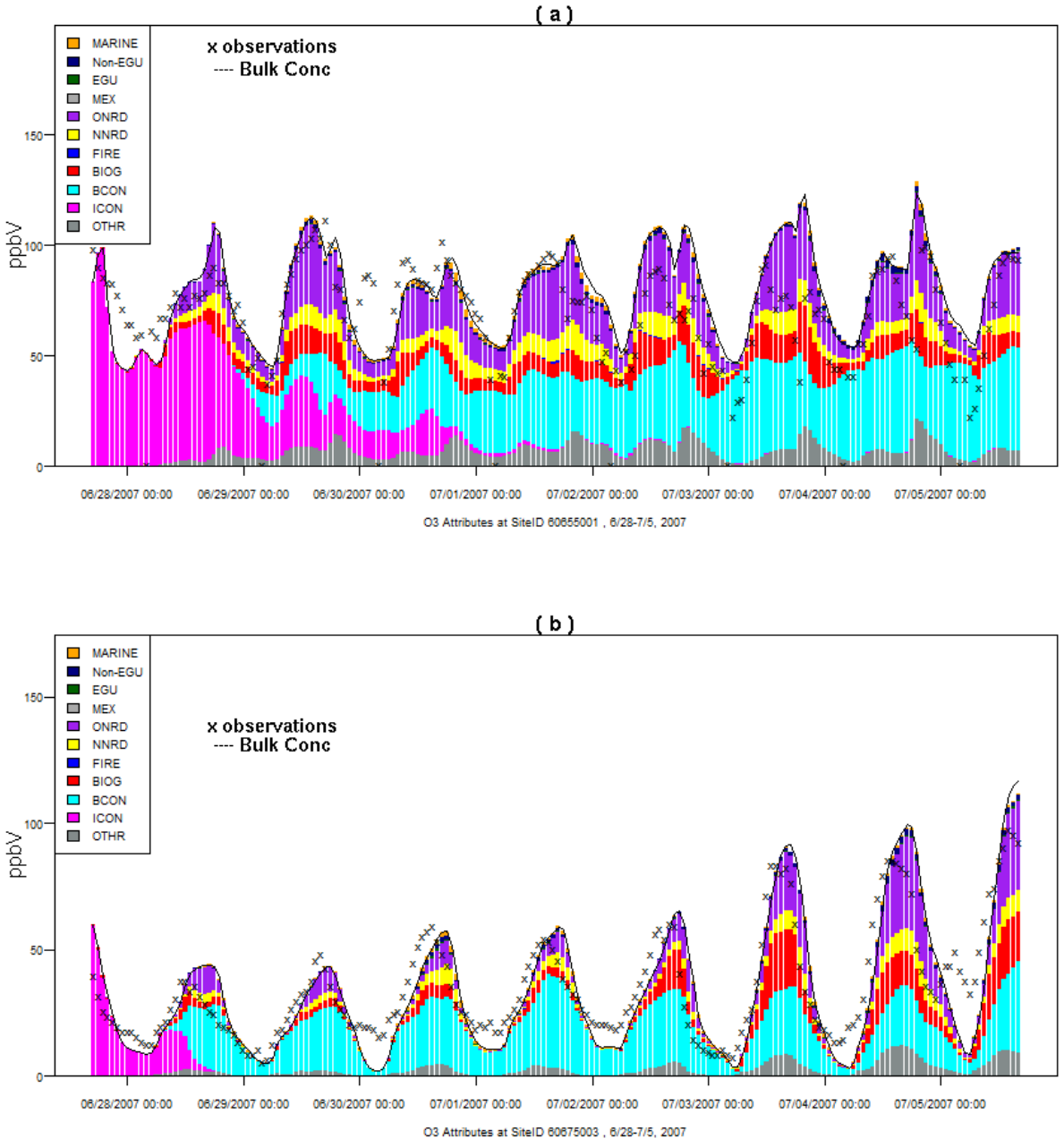

Figure 2. Hourly time series of O3 observations (crosses) at sites of California Air Resources Board monitoring network; and the corresponding CMAQ-ISAM sector breakdowns (stacking colored bars). Locations are (a) Riverside and (b) Sacramento. The colors represent sector sources: marine (MARINE orange), 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 O3 concentration.

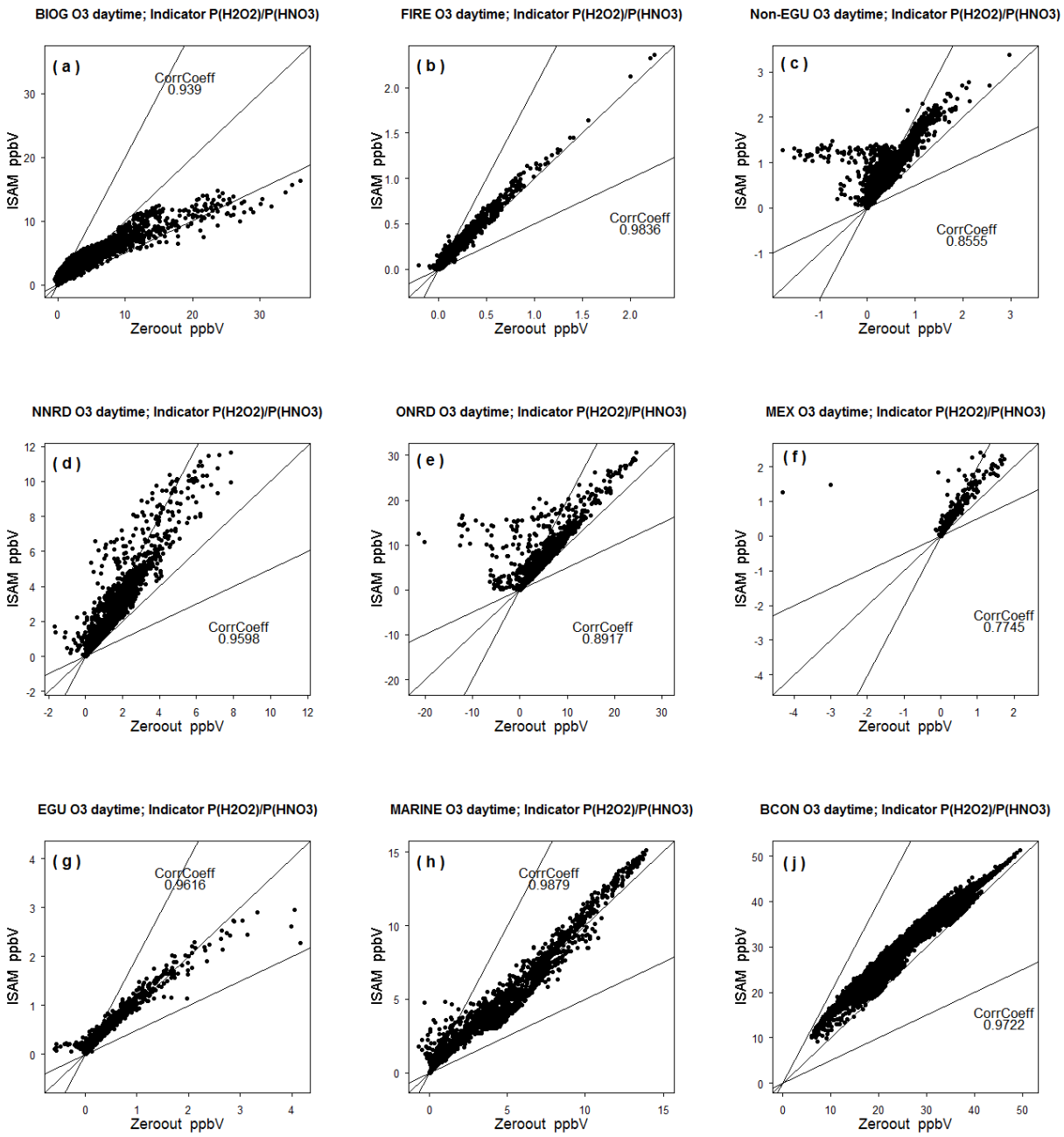

Figure 3. ISAM/both-out O3 comparison for each sector during daytime hours. The sectors are: (a) biogenic BIOG, (b) wild fires FIRE, (c) non-electricity generation units Non-EGU, (d) non-road mobile NNRD, (e) on-road mobile ONRD, (f) other point sources MEX, (g) electricity generation units EGU, (h) marine MARINE, and (j) boundary conditions BCON. Note different scales across the panels.

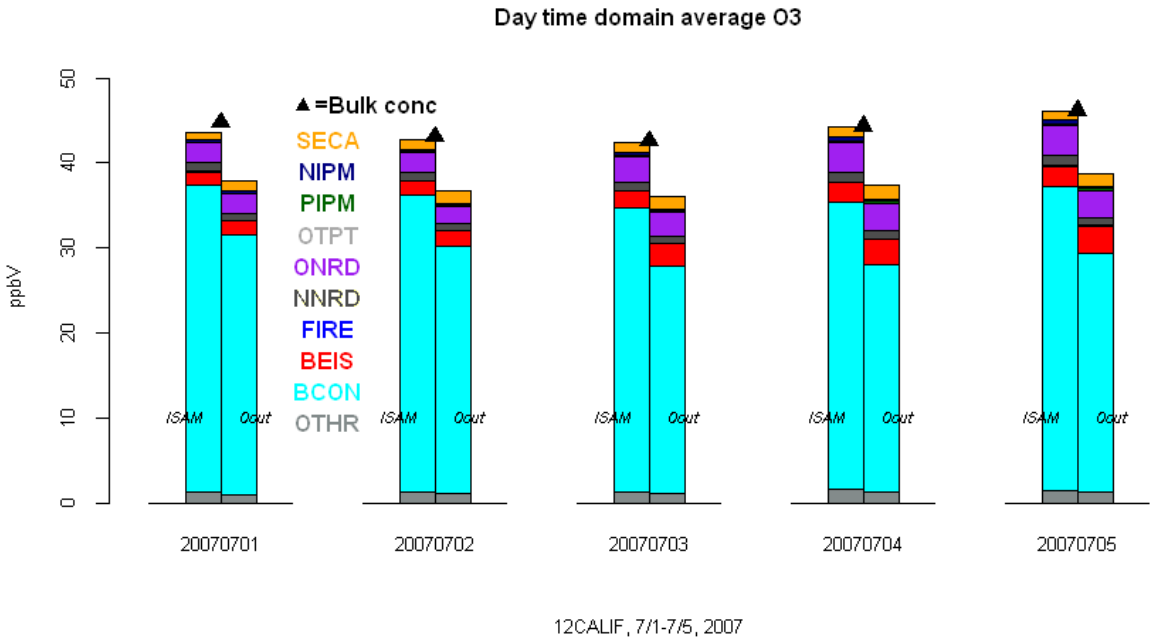

Figure 4. Daytime domain-averaged ambient O3, July 1-5, 2007 (June 28-30 excluded due to large initial conditions influence). In the bar plot, each day consists of two stacked columns (ISAM on the left; Both-out total on the right) and above them a black triangle designating bulk ambient concentration 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), biogenic (BIOG red), boundary conditions (BCON cyan), and remaining unspecified emissions (OTHR grey).

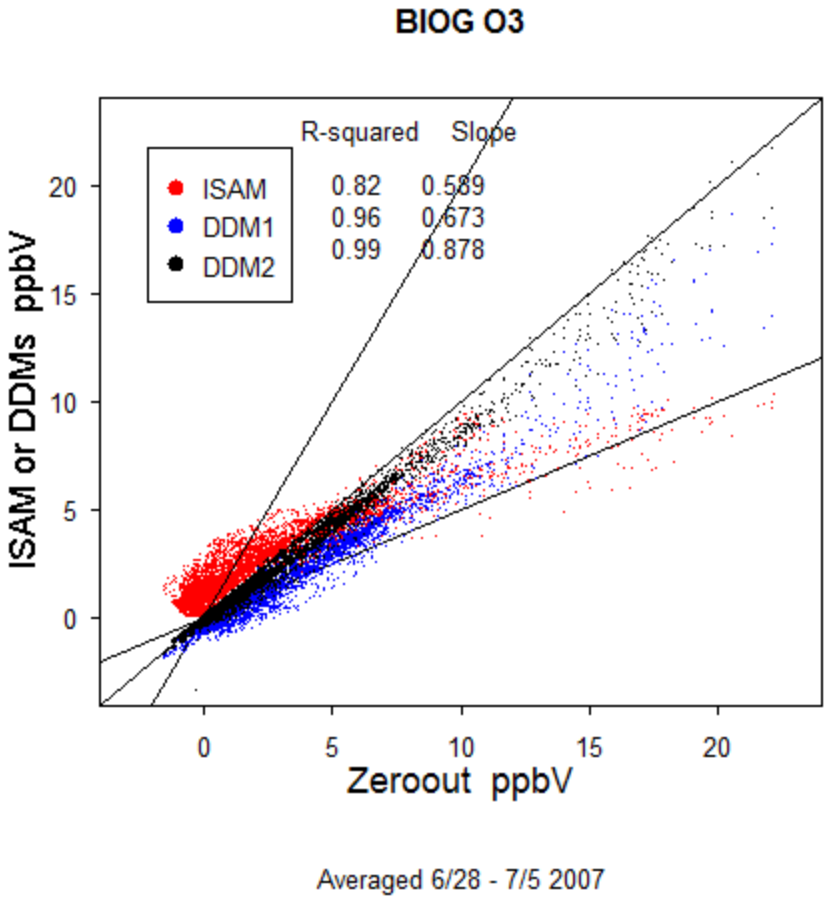

Figure 5. Scatter plots of biogenic O3 with respect to the zero-out brute force, sampled on all-hour-averaged data. Red: ISAM, blue: first order decoupled direct method (DDM1), black: second order decoupled direct method (DDM2). The corresponding R-squared values and regression slopes are also displayed.

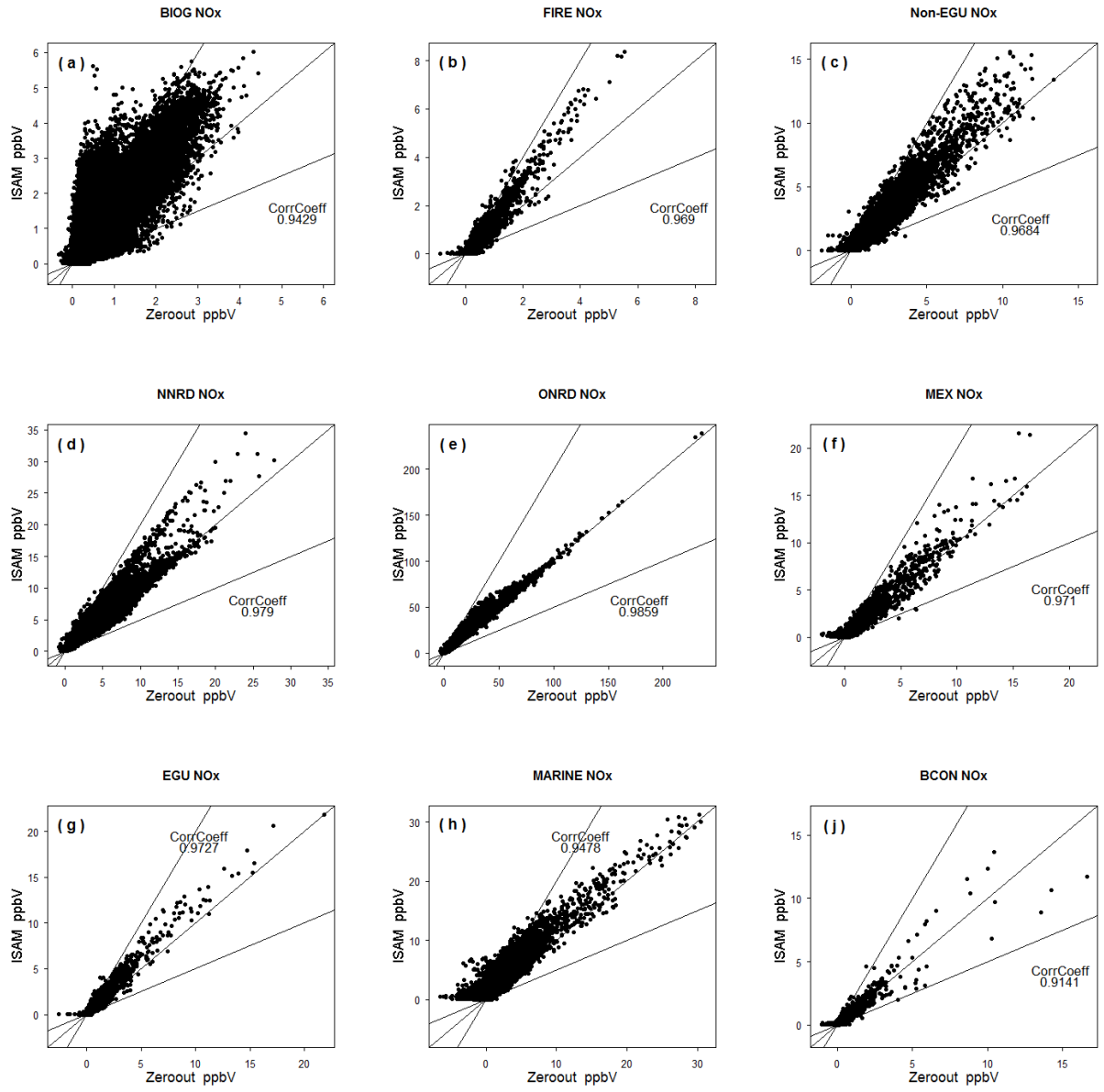

Figure 6. ISAM/N-out NOx ($NO+NO_2$) comparison for each sector and all simulated hours. The sectors are: (a) biogenic BIOG, (b) wild fires FIRE, (c) non-electricity generation units Non-EGU, (d) non-road mobile NNRD, (e) on-road mobile ONRD, (f) other point sources MEX, (g) electricity generation units EGU, (h) marine MARINE, and (j) boundary conditions BCON. Note different scales across the panels.

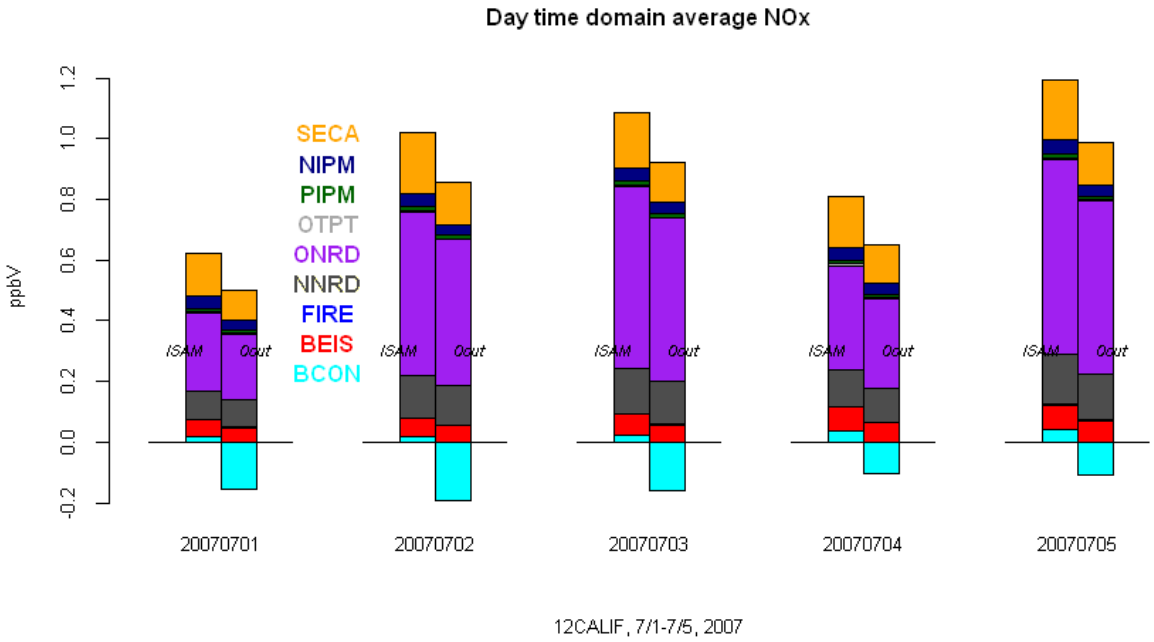

Figure 7. Daytime domain-averaged ambient NOx ($NO+NO_2$), July 1-5, 2007 (June 28-30 excluded due to large initial conditions influence). As in Fig. 4, for each day left column designates ISAM total, and right one the zero-out. . The colors represent sector sources: marine (MARINE orange), non-electricity 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), biogenic (BIOG red), and boundary conditions (BCON cyan).

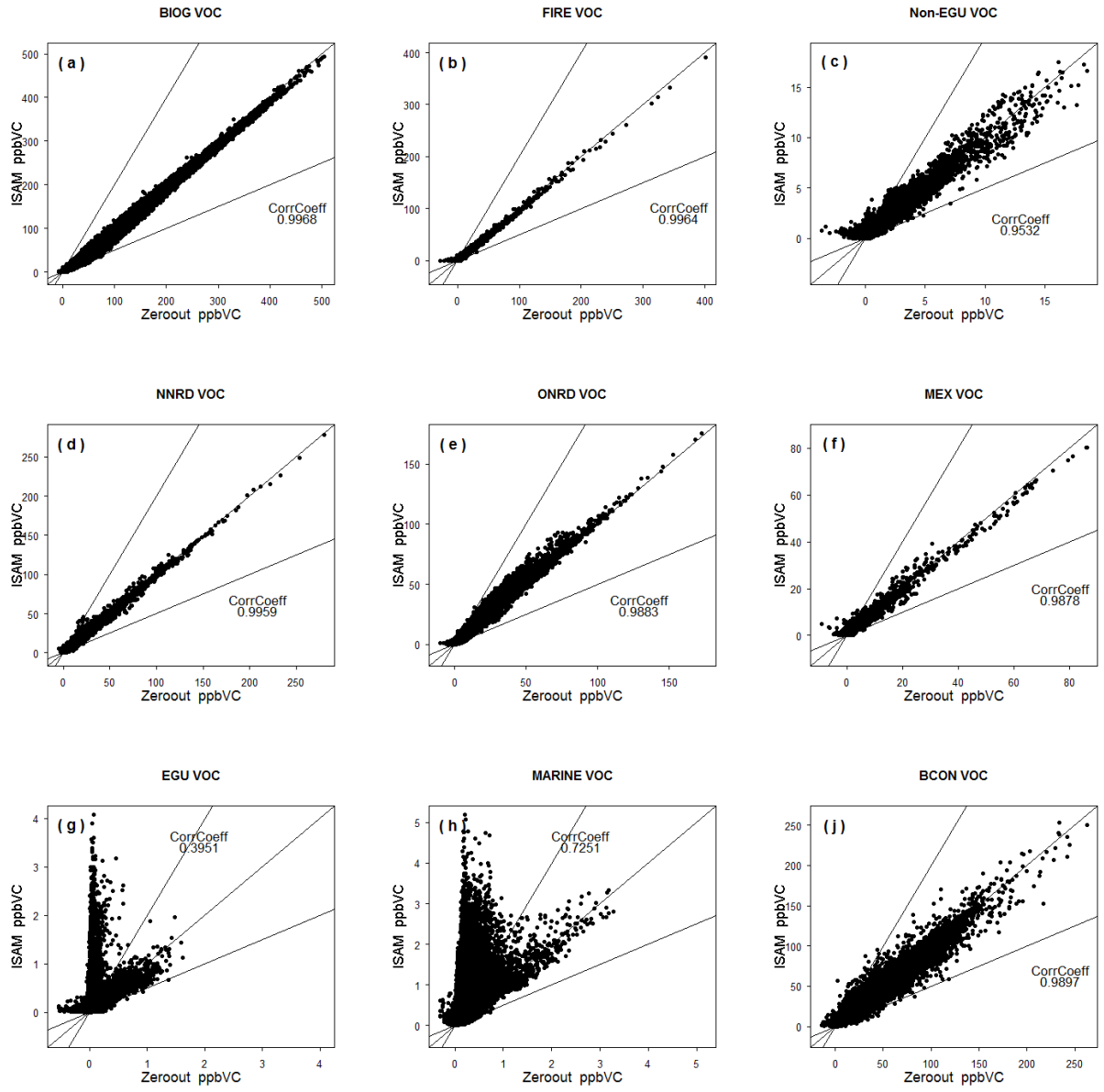

Figure 8. ISAM/V-out VOC comparison for each sector and all simulated hours. The sectors are: (a) biogenic BIOG, (b) wild fires FIRE, (c) non-electricity generation units Non-EGU, (d) non-road mobile NNRD, (e) on-road mobile ONRD, (f) other point sources MEX, (g) electricity generation units EGU, (h)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

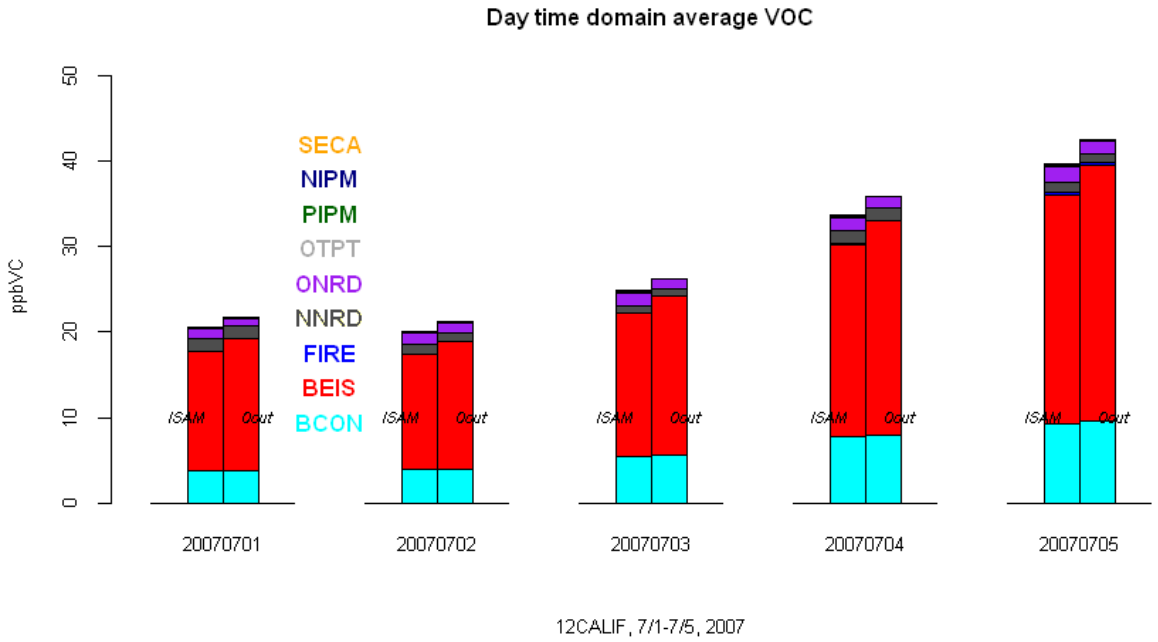

Figure 9. Daytime domain-averaged ambient VOC, July 1-5, 2007 (June 28-30 excluded due to large initial conditions influence). As in Fig. 4, for each day left column designates ISAM total, and right one the zero-out. The colors represent sector sources: marine (MARINE orange), non-electricity generation 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), biogenic (BIOG red), and boundary conditions (BCON cyan).