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Additional benefits of federal air quality rules: model estimates of controllable biogenic secondary organic aerosol

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Abstract

Atmospheric models that accurately describe the fate and transport of trace species for the right reasons aid in development of effective air quality management strategies that safeguard human health, in particular to mitigate the impacts of fine particulate matter ($PM_{2.5}$). Controllable emissions from human activity facilitate formation of biogenic secondary organic aerosol (BSOA) to enhance the atmospheric $PM_{2.5}$ burden. Previous modeling with EPA's Community Multiscale Air Quality (CMAQ) model predicted that anthropogenic primary organic aerosol (POA) emissions had the greatest impact on BSOA. Those experiments included formation processes from semi-volatile partitioning, but not interactions with aerosol liquid water (ALW), a ubiquitous PM constituent that modulates BSOA. We conduct 17 CMAQ summertime simulations with updated chemistry and evaluate changes in predicted BSOA mass due to removal of individual pollutants and source sectors from model inputs for the continental U.S. Among individual sectors, CMAQ predicts that SO_2 emissions from electricity generating point sources and mobile source NO_x emissions have the largest impact on BSOA. Removal of anthropogenic NO_x, SO_2 and POA emissions during the simulated summertime period reduces nationally averaged BSOA by 23%, 14% and 8%, and $PM_{2.5}$ by 9.2%, 14% and 5.3% respectively. CMAQ-predicted ALW mass concentrations decrease by 10% and 35% in response to removal of NO_x and SO_2 emissions. This work contributes to the understanding of ancillary benefits of existing and planned Federal NO_x and SO_2 air quality rules through concurrent reductions in organic $PM_{2.5}$ mass.

INTRODUCTION

Enforcement of the Clean Air Act (CAA) and 1990 Amendments (CAAA) dramatically improves air quality across the United States. [1,2] EPA promulgates performance standards and regional emission trading programs for NO_x and SO_2 to assist States working to meet National Ambient Air Quality Standards (NAAQS) for ozone and $PM_{2.5}$. The Office of Management and Budget reports the largest monetized benefits to Americans from all

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Federal rules are derived from health benefits associated with the CAAA, namely reduced exposure to $PM_{2.5}$. [e.g., 3] Most $PM_{2.5}$ forms in the atmosphere, and effective strategies to reduce ambient concentrations consider gas-phase precursors (e.g., NO_x,[4] SO_2[5]). Ridley et al., suggest CAAA benefits are underestimated because reductions in the organic portion of $PM_{2.5}$ are unintended benefits of NAAQS attainment plans. [2]

The organic fraction of $PM_{2.5}$ is substantial, and non-fossil organic carbon, derived from the biosphere, is a major contributor.[e.g., 6,7,8] When biogenic volatile organic compounds (VOCs) react to form low volatility or high solubility species that condense and add to the atmospheric PM burden, the mass is called biogenic secondary organic aerosol (BSOA). Historically, regulators underestimate the ability of anthropogenic emission controls to reduce BSOA formation and largely consider it a natural part of background air. Field, modeling, and laboratory evidence indicate that chemicals emitted from human activity facilitate BSOA formation and influence chemical composition.[e.g., 9,10,11,12] In the Amazon, the highest BSOA mass concentrations are measured downwind of urban plumes, not in pristine air. [13,14] Despite higher biogenic VOC emissions in the Amazon, BSOA mass concentrations in the anthropogenically-influenced Southeast U.S. are consistently higher using multiple SOA indicators.[e.g., 8,13,14,15] Field measurements during the Southern Oxidant and Aerosol Study (SOAS)[16] suggest that BSOA surrogates (e.g., water-soluble organic carbon (WSOC) and mathematical factors present in aerosol mass spectra) are correlated with one or more indicators of anthropogenic pollution.[15] Further, throughout the U.S. organic carbon mass (OC) in $PM_{2.5}$ decreased over the last thirty years, despite no clear trend in biogenic VOC emissions and increasing non-fossil OC from fires. This OC concentration trend is partly due to reduced anthropogenic emissions and subsequent impacts on BSOA formation.[2] Thus, while biogenic VOCs are natural, some fraction of the subsequent $PM_{2.5}$ mass is not. Anthropogenic emissions facilitate ambient BSOA formation, and this fraction of $PM_{2.5}$ is controllable pollution.[9]

Previous CMAQ experiments using climatological averages and employing an SOA module that describes formation predominantly through semi-volatile partitioning[17] found that roughly half of BSOA mass in the eastern U.S. is a consequence of anthropogenic emissions.[9] Primary organic aerosol (POA) emissions were shown to facilitate BSOA formation to the largest extent, followed by NO_x, and then gas-phase reactive non-methane carbon (RNMC). Anthropogenic SO_2 impacts in those experiments were marginal. Recent evaluation of this SOA module underpredicted BSOA mass during Calnex in Pasadena and Bakersfield California even when precursor VOCs were overpredicted,[18] suggesting missing formation pathways. Water-related chemical pathways were not included in those simulations. Qualitative assessment with CMAQ suggests the chemical potential for BSOA formation in aerosol liquid water (ALW) is large in the Eastern U.S. and parts of California. [19] New understanding of gas-phase biogenic VOC oxidation, including isoprene chemistry, [20] further motivates revisiting the prior CMAQ study.

ALW is a ubiquitous PM constituent [21,22] that modulates and often enhances formation of BSOA.[e.g., 23,24,25] Measurements in the Southeast U.S. indicate BSOA is predominantly water-soluble,[8,26] and ALW is abundant.[27,28] Certain BSOA species can only form in the presence of ALW,[29] and these species are observed in the Eastern U.S. [30,31] In continental

locations, ALW is predominantly anthropogenic, driven by inorganic particle constituents[32] including nitrate,[33] and in the eastern U.S., sulfate.[19,34,35] OC (biogenic) and ALW (anthropogenic) in the Southeast show similar, statistically-significant decadal decreases.[35] Incorporation of newly discovered formation pathways involving water into atmospheric model available for reactive uptake of organics changes BSOA predictions in response to perturbations of anthropogenic emissions,[31,36,37] and this alters interpretation of BSOA controllability. For example, NO_x inhibits BSOA formation from isoprene in lab experiments when semi-volatile partitioning in the absence of water dominates formation.[38,39] Yet process-level modeling experiments suggest NO_x enhances BSOA formation via cloud chemistry by increasing overall solubility of the gas-phase oxidation product distribution,[40] though that chemical mechanism did not include isoprene-epoxyiols (IEPOX). Measurements in the Amazon suggest that in the presence of ALW, anthropogenic NO_x reduces production of SOA from IEPOX, [41] however particle acidity enhances it, and the associated species are observed in ambient Southeast U.S. samples only in the presence of particulate sulfate. [42] Ambient observations find SOA mass derived from monoterpenes is positively correlated with NOz (sum of NO_3, HNO_2, HONO, alkyl nitrates, peroxynitrates and particle-phase organic nitrates), an index for the atmospheric processing of anthropogenic NO emissions. [43] Monoterpene SOA mass appears to dominate OC mass during SOAS.[43] Laboratory and field experiments provide direct evidence of biosphere-atmosphere interactions, and modeling provides a platform for quantification of the convoluted anthropogenic enhancement of BSOA.

In previous work, Pye et al. expanded the SOA formation mechanisms in CMAQ in ways that altered model dependence of BSOA on SO_x and NO_x emissions. [36,44,45] This includes addition of aqueous aerosol precursors such as IEPOX, glyoxal, methylglyoxal, and organic nitrates. SOA from IEPOX is modeled via acid-catalyzed reactive uptake in concert with nucleophilic addition in aqueous particles.[36] In this parameterization SOx emissions regulate IEPOX SOA formation through particle water and acidity,[31] and increase sensitivity of $PM_{2.5}$ and OC concentrations to SO_x emissions in regional U.S. air quality simulations. [36,46] In addition, monoterpene and isoprene nitrates form and partition to the particle-phase through vapor-pressure based-pathways and undergo a pseudo-hydrolysis reaction on short timescales. [44] These biogenically derived organic-nitrate SOA species involve direct interaction with NO_x, and alter overall sensitivity of CMAQ BSOA mass predictions (absolute and fractional amounts) to controllable NO_x. [44] Implementation of recent model developments regarding aqueous processes better reconcile field observations in the Southeast U.S., such as statistically robust positive associations among measured BSOA surrogates, with sulfate, and nitrate on decadal,[2] diurnal and seasonal scales.[15] For example, sulfate modulates ALW and subsequent uptake of organic species, provides protons for catalysis reactions, and facilitates further particle reactions through nucleophilic addition. Interactions among the presence of particle-phase nucleophiles, water and acidity are all typically driven by sulfate in the Southeast U.S. and untangling the controlling factors, including unexplored potential impacts on condensed phase oxidant species, in models to explain findings from field samples remains an active area of study.

We apply the current CMAQ model that incorporates recent BSOA formation pathways, including aqueous processes, to the continental U.S., and quantitatively investigate the extent

to which anthropogenic emissions influence BSOA formation. Controllable emissions of NO_x, SO_2, POA, and anthropogenic VOCs are removed by pollutant type and source sector. Some assumptions in the SOA framework employed in these simulations are debated and this qualifies the magnitude of reported absolute values. Specifically, kinetic limitations to thermodynamic equilibrium assumption for SOA formation via semi-volatile partitioning organic material are evolving [47,48,49] and may affect SOA predictions in the Western U.S. Liquid-like particles and equilibrium assumptions for SOA are valid for the Southeast U.S. [50] Phase separation in particles affects uptake of organic species, and consideration in CMAQ changes OC predictions in the Southeast U.S.,[45] but is not explicitly treated in this these simulations. Uncertainties regarding vapor pressure, solubility and the impacts on the reversibility of SOA formation are discussed below. Emission of VOCs of intermediate volatility (IVOCs) (e.g. long-chain alkanes and PAHS) are included in the CMAQ simulations,[51] but current inventories likely underestimate total IVOC emissions as a class. [52,53] Unspeciated IVOCs are not included in the simulations. These limitations introduce uncertainty, which is discussed below. In these experiments, we use CMAQ to simulate air quality for the summer of 2013 for the continental U.S. using day-specific model inputs. The simulations coincide with the SOAS campaign, [16] a time period that influenced CMAQ development and for which chemically specific BSOA tracers have been extensively evaluated in the Southeast U.S. [44,45,54]

METHODS

The Community Multiscale Air Quality (CMAQ) model version 5.1, [46] available via Github (https://github.com/USEPA/CMAQ; doi:10.5281/zenodo.1079909). is applied June 1 - August 15, 2013 to predict tropospheric chemical and physical processes including transport, chemistry, and wet and dry deposition. We present monthly average surface values for July 2013, which are typical of the entire simulation period, to facilitate concise discussion. A base case simulation (all emissions) serves as the benchmark for the 16 sensitivity simulations presented in Table 1, where controllable emissions of individual chemical species and source sectors for specific pollutants are removed from CMAQ inputs. All prognostic and emission models are applied to a domain covering the continental U.S. with 12 km × 12 km grid cells and 35 vertical layers from the surface to the tropopause. Vertical layer depth is prescribed by pressure and there is more resolution near the surface. Chemical boundary conditions are translated from a hemispheric GEOS-CHEM simulation, [55] and the potential effects on regional scale U.S. predictions of $PM_{2.5}$ mass and composition are discussed in detail by Henderson (2014) [55] and Baker (20 15). [56] Initial conditions are extracted from a longer CMAQv5.1 simulation initialized in December 2012.

Surface measurements of speciated $PM_{2.5}$ are paired in space and time for comparison with CMAQ predictions at all sites operational in July 2013 within the Interagency Monitoring of Protected Visual Environments (http://vista.cira.colostate.edu/Improve) and Chemical Speciation Network (https://www3.epa.gov/ttnamti1/speciepg.html). ALW is calculated with ISORROPIA-II, as in CMAQ, for IMPROVE locations using observed aerosol composition, and temperature and relative humidity from the North American Regional Reanalysis (NARR) using a metastable state assumption.[35,57] Observational ALW estimates may be biased low because ammonium is not included in the calculations using ambient data for

consistency because it is not measured at all sites, and particle water volume is assumed to be additive. [58] Further, ALW in both observational estimates and CMAQ predictions may be biased low because ISORROPIA, as employed here, does not include contribution from organic compounds which is estimated to account for 35% of observed aerosol water in the Southeast US in summer. [59] Organic-ALW interactions depend on the intrinsic chemical properties of the individual organic compounds present. CMAQ predictions of particulate OC are sensitive to organic-ALW parameterizations to describe this chemistry, [45] and model development is ongoing. Secondary organic carbon (SOC) observational estimates are calculated at IMPROVE and CSN sites using an EC-tracer method that accounts for the semi-volatile nature of POA (See equations 28 and 29 of Reference [45])

Model Chemistry

We employ the gas phase chemical mechanism SAPRC-07 with additional isoprene-organic nitrate chemistry.[60] Inorganic aqueous chemistry includes sulfur oxidation reactions[61] and equilibrium gas-particle partitioning using ISORROPIA-II[32] in the forward mode for fine aerosol ALW content and particle pH. POA is treated as non-volatile although associated hydrogen and oxygen mass changes through heterogeneous hydroxyl radical reactions.[62] Some SOA formation pathways employ a yield-based approach including SOA from these precursors: toluene, xylenes, benzene, isoprene, monoterpenes, and sesquiterpenes. Other formation pathways exist and model development continues. Semi-volatile organic species become non-volatile through a zero order condensed phase oligimerization pathway with a half-life of 20 hours.[17] SOA also forms via oxidation of glyoxal and methylglyoxal in clouds[63] and uptake by particles.[44] BSOA formation pathways also include IEPOX and organic nitrates. [36,43] Chemically specific CMAQ model predictions traceable to individual BSOA markers for IEPOX, organic nitrates and monoterpenes have been extensively evaluated for the Southeast U.S. [36,43,44] in simulations that employ the same chemistry used in this work. We explore BSOA controllability overall, and for semi-volatile and aqueous-influenced pathways separately.

Emissions and meteorology

The Weather Research and Forecasting (WRF) model[64] v3.7 generates offline meteorology translated for CMAQ using the Meteorology-Chemistry Interface Processor.[65] Previous studies using this WRF configuration compare well against meteorological measurements.[66] Emissions are processed with the Sparse Matrix Operator Kernel Emissions (SMOKE) model v3.7. [67] Biogenic VOCs and soil NO emissions are developed from the Biogenic Emission Inventory System (BEIS) v3.61 with the Biogenic Emissions Landuse Database (BELD) v4,[68] with the same meteorology used for transport. The applied BEIS configuration reasonably replicates biogenic VOC mixing ratios in forested U.S. areas,[68] though underestimates of isoprene and overestimates of monoterpenes are noted for the SOAS site in Centreville, AL.[44,45] Anthropogenic emissions are based on the 2011 National Emission Inventory (NEI) v2.[69] Hourly Continuous Emissions Monitor data from 2013 are used for point sources when available. [(e.g., 70)] Mobile emissions are developed from the Motor Vehicle Emission Simulator (MOVES) model using MOVES2014a emission factors. [71] Emissions from wild fires are based on day-specific information and have been evaluated for the 2013 simulation period.[72]

RESULTS AND DISCUSSION

CMAQ-Predicted Biogenic SOA: Precursor Patterns and Contributions to Particle Mass

During the summertime period simulated, CMAQ predicts BSOA mass concentrations are substantial, as high as 7 μg m^{-3} in the base case simulation for the July 2013 surface mass average (Figure 1). CMAQ predicts BSOA contributes approximately half of total PM$_{2.5}$ mass in urban and rural areas of Georgia, Alabama and Louisiana (Figure S1). The organic carbon (OC) fraction of PM$_{2.5}$ is dominated by BSOA in the CMAQ simulations, which suggest more than 80% of particulate OC mass in the Southeast U.S., and more than 50% for most of the continental U.S. is BSOA (Figure S1). Mass concentrations of BSOA species derived from monoterpenes, sesquiterpenes, isoprene, and from condensed phase oligomerization and aqueous processes (see Table S1 for species classification) are all highest in the Southeast U.S. (Figure S2). Mixing ratios of all biogenic precursor VOCs are predicted to be highest in the Southeast (Figure S3), as are predicted mass concentrations of OC, a medium available for condensation of biogenic semi-volatile gas phase oxidation products (Figure 2). Concentrations of ALW, a species available for reactive uptake of water-soluble organic gases are also greatest in the Eastern U.S. (Figure 2). Summertime relative humidity is higher in the Eastern U.S., and sulfate-rich hygroscopic PM$_{2.5}$ typical of the region, which is influenced by SO$_2$ emissions from electricity generation, favors ALW and SOA formation.[19] The fraction of total BSOA mass formed via semi-volatile partitioning is highest in the Southeast U.S. and in some Northwest 'hotspot' locations. The largest amount of SOA formed through aqueous processes is predicted to be in the Southeast U.S., and the highest fraction is in the Western U.S. Model prediction in the desert and mountainous Western U.S. suggest very little to no SOA mass, while semi-empirical observational estimates suggest there are measureable amounts at nearly all locations (Figure 2c). The measurement-model discrepancy in this location is difficult to interpret due, in part, to a dearth of chemically specific BSOA measurements in the area.

Over the continental U.S., CMAQ ALW predictions are geospatially similar and close in magnitude to observational estimates at most of the rural IMPROVE sites for the simulation period, (Figure 2), suggesting the modeling system is able to capture areas where aqueous-influenced chemistry for BSOA formation is important. Differences among ALW measurement-model pairs can arise when there are differences in anion concentrations and/or meteorology. ALW similarity between CMAQ predictions and observational estimates is dependent of the range of RH at each individual site. For example, although nitrate is underpredicted at a few locations in Southern California (Figure S4), ALW predictions are consistent with observational estimates because RH is low and as a consequence total ALW mass is low in both. Detailed model evaluations of PM$_{2.5}$ mass, sulfate, nitrate, organic and elemental carbon are provided in the Supplemental Information (Figures S4, S5). We note that neither the monitoring site estimates nor CMAQ predictions incorporate the impacts of organic compounds on water uptake. Inclusion of such interactions affects predictions of ALW [35] and CMAQ predictions of particulate OC in the Southeast U.S.[45] Interactions of ALW, pH, organic partitioning and condensed phase chemistry with and without reactive nitrogen are uncertain and remain areas of ongoing research.

Comparison of SOC Predictions and Observational Estimates

CMAQ predicts SOC and total OC mass concentrations greater than values derived from reported measurements at many monitor locations in the Southeast. (Figures 2, S5) Measurement-model discrepancies can arise from a variety of sources including incomplete chemistry, emission and meteorology errors. A contributor to the positive CMAQ bias for OC in the Southeast U.S. may be the non-volatile POA assumption employed in this simulation. Inclusion of semi-volatile POA improves bias in CMAQ-measurement comparisons to Calnex and SOAS data, and in particular reduces the amount of predicted OC in the Southeast U.S.[52] Overestimates of IMPROVE measured OC do not necessarily suggest the CMAQ modeling system misrepresents BSOA formation. Reported OC measurements and the derived SOC estimates may be biased low compared to actual ambient values. Semi-volatile OC is lost due to field latency of filters and uncontrolled conditions during handling and shipping of samples for the IMPROVE network.[73] A fraction of BSOA mass formed through aqueous processes forms reversibly and evaporates with water during summertime sampling in the Southeast U.S.[74] On average 15–30%, of OC is lost when miscible organic compounds are removed from filters during equilibration and conditioning at 35% RH,[74,75] and during OC analysis when water is removed to prevent interference with the near infrared (NDIR) laser detection. Comparison of side-by-side WSOC derived from Federal Reference Method (FRM) $PM_{2.5}$ filters and real-time, direct measurements from a Particle-Into-Liquid Sampler (PILS) demonstrate up to 30% lower WSOC from FRM filters compared to the PILS,[76] consistent with the SOA reversibility findings of El-Sayed (2016). This is suggestive that in the Southeast U.S., an area characterized by higher isoprene and lower NO_x, [77] where BSOA and ALW mass concentrations are high, and ambient RH is above 35%, OC losses at routine monitoring sites are greatest. Measurement-CMAQ discrepancies for reported OC values and SOC observational estimates in the Southeast U.S. may arise, in part, because observations are biased low relative to the actual values during ambient conditions in this region of the U.S.

In contrast to the Southeast U.S., CMAQ OC predictions are less than the reported measurement values at many IMPROVE monitoring locations in the mountainous and desert Western U.S. where SOC mass concentrations and SOC-to-TOC ratios are underpredicted at nearly all sites (Figure 2). The causes of model-measurement discrepancies in this region are difficult to diagnose due to a lack of chemically speciated OC measurements for most of the region. In terms of BSOA formation, CMAQ predicts that aqueous processes contribute at least half of the total BSOA mass in the Western U.S. The extent to which this is accurate remains to be tested in field measurements. BSOA in this region is predicted to exist predominantly is a glassy solid phase state, which may challenge the instantaneous equilibrium assumption for which semi-volatile SOA model parameterizations have been traditionally developed. [78] Partitioning of polar, biogenically derived organic compounds to ALW and their complexation with inorganic ions varies with anion identity as a function of aerosol molality, [79, 80] which is highest in the Western U.S. where ALW mass concentrations are low. [81] The controlling electrochemical factors are unknown. For example, glyoxal and methylglyoxal differ by a single methyl group, yet exhibit the opposite partitioning behavior as a function of atmospherically-relevant salt-induced molality. [79, 80] The implications of organic compounds partitioning to non-ideal, high ionic strength, glassy particles and the

subsequent impacts regarding potential kinetic limitations to semi-volatile partitioning, reactive uptake, multiphase chemistry and the controlling factors of BSOA formation in this region of the Western U.S. are poorly understood. While CMAQ predictions and SOC observational estimates exhibit bias relative to each other in terms of absolute values, they both suggest BSOA mass concentrations are highest in the eastern U.S. and comparisons imply the model reasonably represents overall formation regimes as they occur in the atmosphere over the U.S. For example, the highest absolute amount of BSOA mass from aqueous-influenced pathways is in areas where ALW mass is highest, and lowest where ALW observations are low (Figures 1, 2a). Predicted particulate OC from fires is highest in Idaho (Figure 2b), where fire activity was the most prevalent during the simulation period. [72]

Model Response to Removal of Anthropogenic Emissions: Pollutants and Source Sectors

Increased chemical complexity in CMAQ representation of BSOA formation changes the nature and extent to which controllable emissions modulate predicted BSOA and $PM_{2.5}$ relative to the 2010 estimates (Table 1; Figure 1). Total BSOA mass decreases most in response to complete removal of anthropogenic emissions of NO_x, followed by SO_2 and then POA (Figures 1 and 3). This model response sharply contrasts the earlier BSOA controllability estimates, [9] which predicted SOA was highly sensitive to POA, somewhat sensitive to NO_x, and largely insensitive to SO_2. Removal of controllable NO_x and SO_2 reduces predicted amounts of ALW in the Midwest and Eastern U.S., (Figure 4), where ALW mass concentrations are predicted to be highest (Figure 2a).

The largest regional scale NO_x impacts occur in the Southeast U.S., and arise from the mobile sector according to CMAQ. Mobile emissions of on-road gasoline and diesel vehicles (Figure 5) facilitate BSOA to the greatest degree as a NO_x source class. Point source NO_x emissions also enhance BSOA, most notably in eastern TX from the oil & gas sector. NO_x impacts, though substantial, may yet be underestimated because the CMAQ modeling system underpredicts formation of organic nitrate compounds during the daytime when compared to near real-time observations of this BSOA fraction during SOAS, [44] and these species contribute significantly to the SOA mass budget in the Southeast U.S. [43] Systematic testing of anthropogenic NO_x perturbations at percent change levels of −100, −75, −50, −25 and +25 demonstrate a near linear response, and consistent spatial patterns in the total amount of BSOA mass change when averaged over the contiguous U.S. (Figures 3, S6). This adds support to the findings from complete NO_x removal, which is a large perturbation to the model oxidative chemical regime. It is interesting to note that while CMAQ predicts a nearly linear response in BSOA to NO_x reductions, the spatial patterns in the benefits of controllable NO_x from individual source sectors to reduce BSOA mass concentrations closely mirror the spatial distribution of BVOC emissions and BSOA mass concentrations, rather than NO_x emissions. Some areas with high controllable NO_x emissions (e.g., Southern California and the I-95 corridor in the Northeast) show little BSOA benefit, whereas major BSOA reductions are predicted in rural areas in the Southeast that have relatively higher absolute BSOA mass and lower NO_x emissions.

The impacts of NO_x emissions on BSOA are chemically complex. Nearly all BSOA species decrease in response to anthropogenic NO_x removal, with the exception of SOA species

produced from IEPOX (AIETET, AIEOS, ADIM) (Figure S7). [36] Removal of NO_x alters the preceding gas phase chemistry by changing the NO3 radical budget, which directly forms SOA and alters mixing ratios of other oxidants such as OH, O^3P, and O_3 (as shown in Figure S8) that are important and define gas phase oxidation of the parent biogenic VOCs and subsequent formation of condensable organic species. Some biogenic semi-volatile species, such as monoterpene and isoprene organic nitrates AMTNO3 and AISOPNN, only form in the presence of NO_x [44] and their concentrations decrease nearly 100% domain-wide (lightning and biomass burning NO_x are not removed in the sensitivity simulations). Species AMTHYD forms in the condensed phase from these species, and its mass concentration is also substantially reduced.

Removal of controllable NO_x emissions limits CMAQ production of particle-phase nitrate and sulfate (Figure S9), hygroscopic species that have a controlling influence on the amount of ALW.[19,33] Most notably in these simulations ALW mass concentrations are reduced in an area of the Midwest, and in Southern California (Figure 4a). Because particulate nitrate is biased low relative to measurements is areas of California and Chicago (Figure S4), NO_x-ALW-BSOA impacts may be underestimated. However, due to its volatility particulate nitrate concentrations are often lowest in the summer, the season simulated in this work. SOA species that form through aqueous processes such as reactive uptake like AGLY decrease, in part, due to reduced presence of ALW as a result of its influence on particle surface area (Figures 4, S7, S10). AGLY decreases by approximately half in the Eastern U.S. (Figure S11), where ALW and the gas phase precursor, glyoxal, are most abundant in the base case simulation (Figure 4). In response to removal of anthropogenic SO_2 emissions, model species derived from IEPOX or MPAN (AIETET, AIEOS, ADIM, AIMGA and AIMOS) (Table S1) decrease 100% because sulfur is directly involved in their formation through both physical and chemical mechanisms. [31,36]

Limited impacts of anthropogenic VOC emission reductions are observed predominantly along the mid-Atlantic coast of the Eastern U.S. and near Los Angeles for aqueous SOA (Figure S12). Unlike removal of anthropogenic NO_x and SO_2, removing VOCs slightly increases ALW mass concentrations in the Midwest (Figure 4c). Removal of VOCs reduces gas phase competition for the hydroxyl radical and facilitates oxidation of SO_2 and NO_x to sulfate and nitrate, hygroscopic particle species that promote ALW. Semi-volatile biogenic species (e.g., ATRP, ASQT) decrease in concentration in response to removing anthropogenic POA emissions (Figure S13), consistent with the earlier CMAQ experiments investigating BSOA controllability. Though not produced directly from semi-volatile partitioning, model species AMTHYD exhibits similar sensitivity to POA because its production and the overall mass amount formed is a function of MTNO3, a semi-volatile species that partitions to pre-existing organic aerosol [44] such as POA should it be present.

Atmospheric Implications and Successful Environmental Rules

Inclusion of chemically detailed gas- and condensed- phase oxidation chemistry changes how atmospheric modeling informs air quality management strategies for $PM_{2.5}$. Emission reductions of SO_2 and NO_x impact the sulfate, nitrate and organic fractions of the atmospheric $PM_{2.5}$. This work is supportive of recent findings by Ridley et al. (2018) and

provides detailed chemical explanations for reduced organic $PM_{2.5}$ mass as a consequence of existing and planned Federal rules that regulate NO_x and SO_2 to meet ozone and $PM_{2.5}$ NAAQS. Epidemiological studies indicate a strong link between $PM_{2.5}$ mass and numerous human health effects. Mounting evidence indicates that specific PM constituents differ in toxicity. Recent studies characterize BSOA toxicity, including compounds formed specifically through interactions with anthropogenic emissions, [82,83] providing plausible toxicological explanations for observed associations in epidemiological studies between fine particle mass and health endpoints which are elusive for other particle phase constituents such as sulfate and nitrate.[84] Therefore, it is possible that the controllable BSOA fraction identified in this study makes a disproportionate contribution to health. Atmospheric modeling that includes state-of-the-art chemical mechanisms facilitates quantification of BSOA controllability by pollutant type and source sector as provided in this work. Expansion and evaluation of chemical complexity in CMAQ suggests description of OC and $PM_{2.5}$ formation in CMAQ is more complete. Continued model development that capitalizes on new laboratory and field observations and resolves present uncertainties ensures future source attribution for $PM_{2.5}$ will be improved and aid in development of effective air quality strategies that protect human health.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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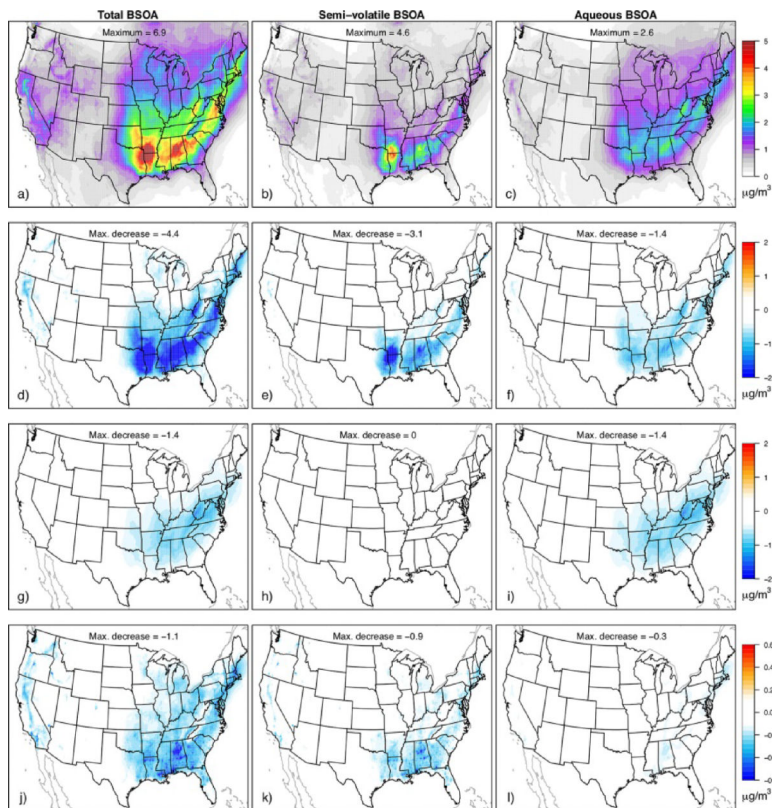
Figure 1.
July 2013 average CMAQ-predicted surface level a) total BSOA, b) BSOA formed via semi-volatile partitioning, and c) BSOA formed via ALW-related chemistry. The change in BSOA relative to the benchmark is calculated as [BSOA]sensitivity-[BSOA]base in each grid cell for anthropogenic NO_x (d-f), SO_2 (g-i), primary OA (j-l). Cool colors indicate decreases in BSOA mass concentrations due to precursor reductions and warm colors would indicate increases (disbenefits). CMAQ species definition for SOA categories is described in Table S1. Scales differ by row.
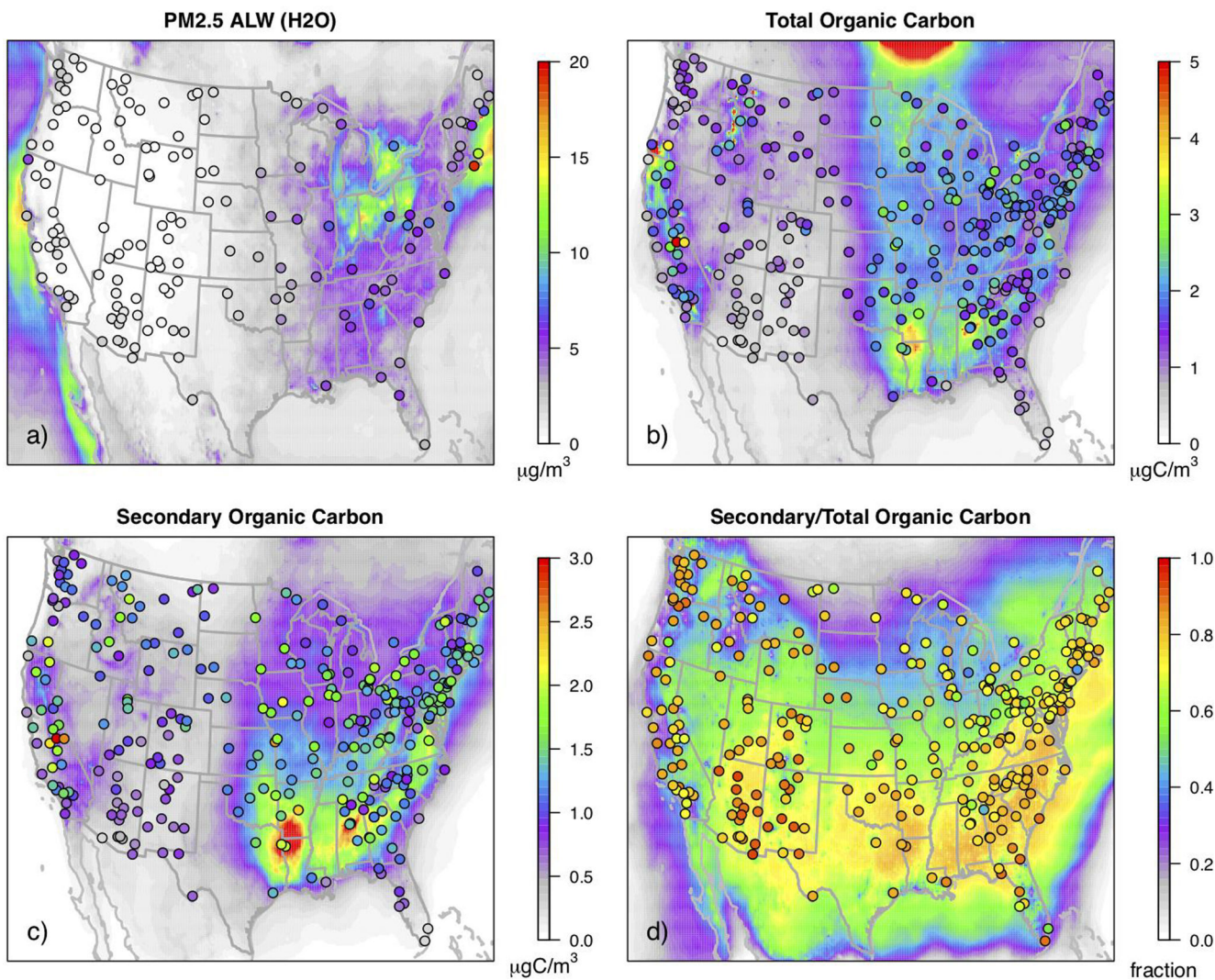
Figure 2.
CMAQ-predicted a) ALW, b) OC, c) secondary organic carbon (SOC), and d) ratio of secondary to total OC. CMAQ predictions are shown as contours. Observations shown as circles with the same color scale. ALW observational estimates calculated with ISORROPIA (as in CMAQ) using observed sulfate, nitrate, NARR-derived temperature and relative humidity (RH). SOC is estimated according to Equations 28 and 29 in Reference [44].
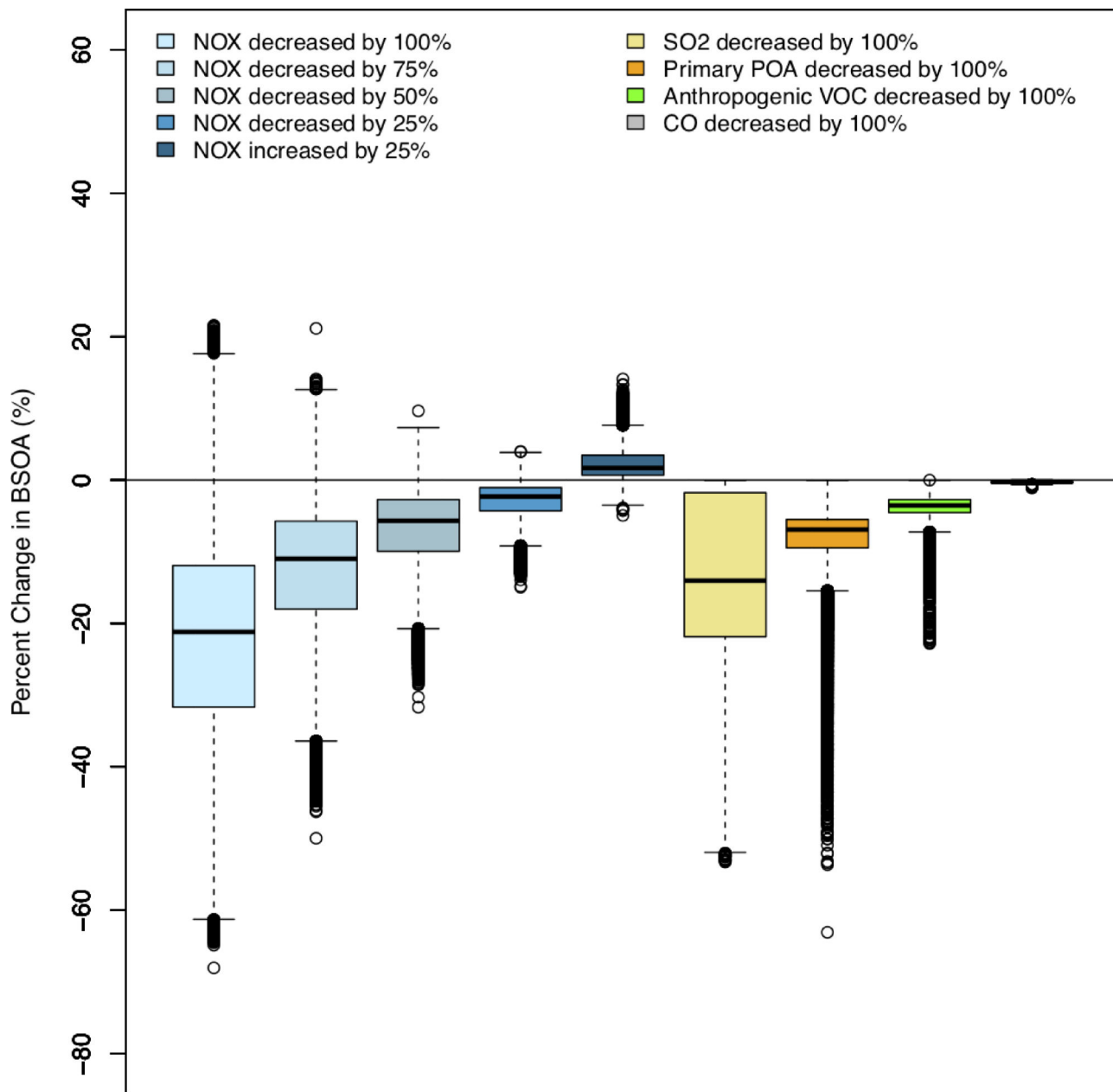
Figure 3.
Percent change in biogenic SOA surface mass for July 2013 for the sensitivity simulations relative to base case (all emissions). The distribution is shown as median (black line), 25th and 75th percentiles (bottom and top of box), and 10th and 90th percentiles (bottom and top whiskers). The distribution is calculated from all hourly values in grid cells where baseline predicted BSOA is greater than 0.05 μg m^{-3} (N=62,994).
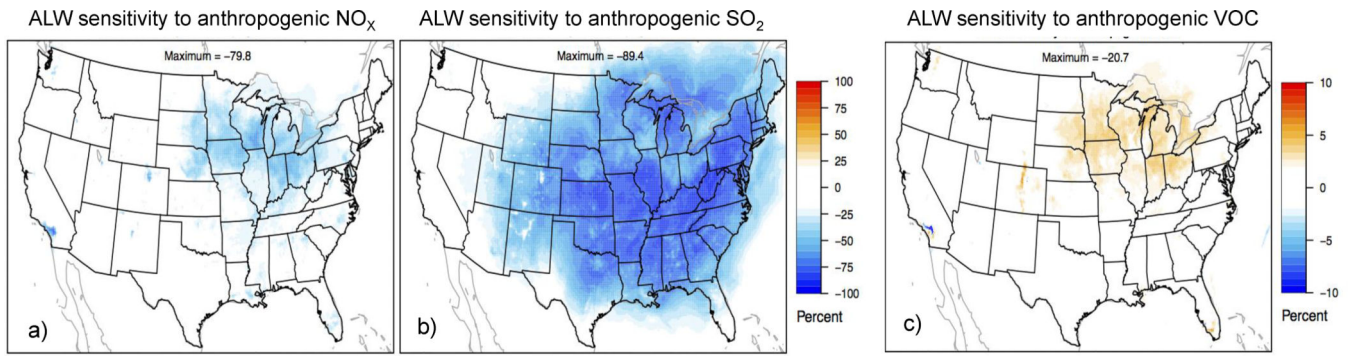
Figure 4.
PM$_{2.5}$ ALW (AH2OIJ) monthly average change in response to total removal of anthropogenic precursor emissions a) NO$_x$, b) SO$_2$ and c) VOC.
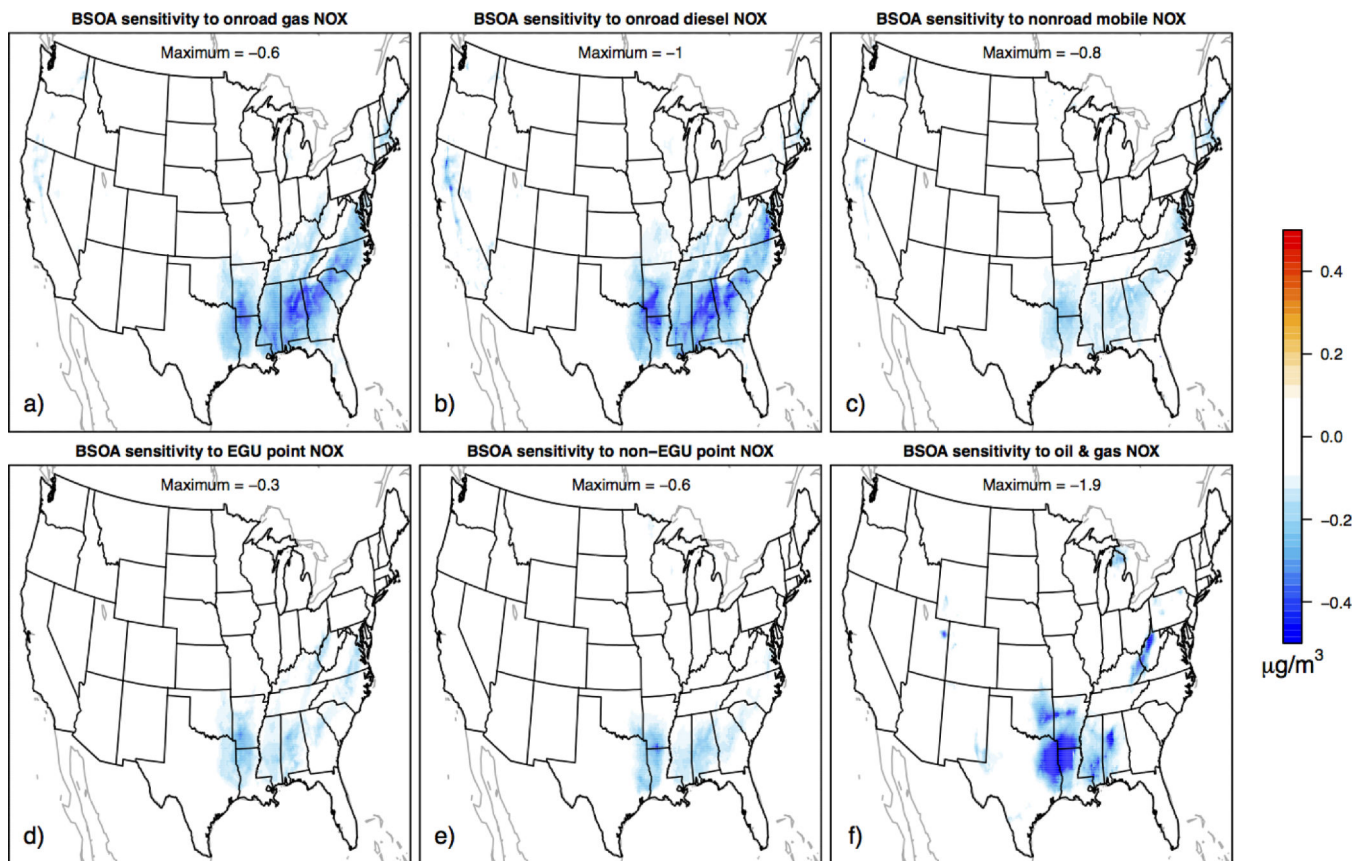
Figure 5.
July 2013 average CMAQ-predicted surface level sensitivity of BSOA to 'zeroed-out' anthropogenic NO_x from specific sectors including a) onroad gasoline vehicles, b) onroad diesel vehicles, c) nonroad mobile, d) EGU point, e) non-EGU point, and f) oil & gas exploration.

Table 1.

Domain-wide percent change in average July 2013 surface-level CMAQ-predicted BSOA, OC, and ALW mass concentrations resulting from changes in anthropogenic emissions. Percentages are calculated relative to the base case simulation [100*(sensitivity - baseline)/baseline] for grid cells where the baseline simulation predicted BSOA concentration greater than 0.05 μg/m^3.

Pollutant	Sector	% Emissions Change	% [BSOA] mean Change	% [OC] mean Change	% [ALW] mean change	% [PM$_{2.5}$] mean change
NO$_X$	All anthropogenic	−100	−22.5	−12.2	−9.7	−9.2
NO$_X$	All anthropogenic	−75	−12.7	−7.1	−6.3	−5.4
NO$_X$	All anthropogenic	−50	−6.9	−3.9	−3.9	−3.1
NO$_X$	All anthropogenic	−25	−3.0	−1.7	−1.8	−1.4
NO$_X$	All anthropogenic	+25	+2.4	+1.4	+1.7	+1.1
NO$_X$	Electric Generating Unit (EGU) point	−100	−1.0	−0.6	−1.6	−0.9
NO$_X$	non-EGU point	−100	−1.2	−0.7	−0.7	−0.5
NO$_X$	Onroad gasoline	−100	−2.4	−1.4	−1.3	−1.1
NO$_X$	Onroad diesel	−100	−2.5	−1.5	−1.2	−1.1
NO$_X$	Nonroad	−100	−1.9	−0.9	−1.3	−0.9
NO$_X$	Oil & gas exploration	−100	−1.6	−1.0	−0.6	−0.6
POA	All anthropogenic	−100	−8.0	−13.5	−0.1	−5.3
SO2	All anthropogenic	−100	−13.7	−5.8	−34.6	−13.9
SO$_2$	EGU point	−100	−11.4	−4.8	−26.5	−10.8
VOC	All anthropogenic	−100	−3.8	−2.6	+0.8	−0.8
CO	All anthropogenic	−100	−0.3	−0.1	+0.1	+2.1