



# Causes and consequences of decreasing atmospheric organic aerosol in the United States

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Edited by Jos Lelieveld, Max Planck Institute for Chemistry, Mainz, Germany, and accepted by Editorial Board Member Hans J. Schellnhuber November 25, 2017 (received for review January 8, 2017)

**Exposure to atmospheric particulate matter (PM) exacerbates respiratory and cardiovascular conditions and is a leading source of premature mortality globally. Organic aerosol contributes a significant fraction of PM in the United States. Here, using surface observations between 1990 and 2012, we show that organic carbon has declined dramatically across the entire United States by 25–50%; accounting for more than 30% of the US-wide decline in PM. The decline is in contrast with the increasing organic aerosol due to wildfires and no clear trend in biogenic emissions. By developing a carbonaceous emissions database for the United States, we show that at least two-thirds of the decline in organic aerosol can be explained by changes in anthropogenic emissions, primarily from vehicle emissions and residential fuel burning. We estimate that the decrease in anthropogenic organic aerosol is responsible for averting 180,000 (117,000–389,000) premature deaths between 1990 and 2012. The unexpected decrease in organic aerosol, likely a consequence of the implementation of Clean Air Act Amendments, results in 84,000 (30,000–164,000) more lives saved than anticipated by the EPA between 2000 and 2010.**

carbonaceous aerosol | organic aerosol | PM mortality | anthropogenic emissions | long-term trends

Exposure to atmospheric particulate matter (PM) results in ~4.2 million premature deaths per year globally (1) and ~200,000 per year in the United States alone (2). There has been a significant decline in PM since 1990 in the United States, attributed primarily to the reduction in inorganic aerosol following implementation of the Clean Air Act Amendments (CAAA) (3). In 1990, the US Environmental Protection Agency (EPA) amended the Clean Air Act, placing controls on emissions of PM and PM precursor gases sulfur dioxide (SO<sub>2</sub>) and nitrogen dioxide (NO<sub>2</sub>). Marked declines in PM<sub>2.5</sub> (mass of particles smaller than 2.5 μm in diameter) were observed in the following decades (4, 5). A decline in black carbon (BC) has also been documented across the United States (6), primarily in the East, and attributed to emission controls on vehicular and other combustion sources (7). A decline in organic aerosol (OA) is implied by those studies, and measurements in the southeast United States indicate a decline in recent years (8, 9) that could be associated with anthropogenic emissions changes (10); however, no study has examined US-wide trends in organic aerosol since the 1990 amendments to the Clean Air Act.

Both BC and OA are produced from combustion of fossil fuel and other organic matter; for example, wildfires contribute up to 26% of the summertime OA in the West (11). Unlike BC, OA is also formed through oxidation of volatile organic carbon (VOC) emissions from both anthropogenic (12, 13) and biogenic sources (14, 15), the latter exhibiting strong seasonality (16). OA contributes 30–80% of total annually averaged PM<sub>2.5</sub> in the United States (6), with BC contributing less than 10% in most locations.

## Observed Decadal Trends in Speciated Aerosol Across the United States

We analyze surface concentration measurements from the Interagency Monitoring of Protected Visual Environments (IMPROVE)

network between 1990 and 2012 (*Materials and Methods*). We find ubiquitous declining trends in both OA and BC across the entire United States in winter and summer (Fig. 1). Annual OA and BC concentrations dropped substantially by 0.32 μg/m<sup>3</sup> per decade and 0.06 μg/m<sup>3</sup> per decade, respectively. This constitutes a 40% decline in OA and 55% decline in BC between 1990 and 2012 at these sites, representing 31% and 5% of the PM<sub>2.5</sub> reduction between 1990 and 2012, respectively. Although the OA loading is higher in the summer, we find that the fractional decline in OA is relatively consistent across both seasons and regions. The extent of the decline in OA is unexpected for three reasons: (i) natural sources of primary and secondary OA often make up a large fraction of the total OA (17); (ii) natural sources (i.e., wildfires and biogenic SOA precursors from vegetation) increase in a warming climate (18, 19); and (iii) modeling studies, including the 2011 EPA report to Congress on the benefits of the CAAA, do not predict a strong decline in OA (5, 20).

Remarkably similar normalized trends are observed in annual OA, BC, and inorganic aerosol (sulfate and nitrate) from IMPROVE measurements, and NO<sub>2</sub> and CO from the EPA chemical speciation network (Fig. 2*A* and *B*). Water associated with inorganic aerosol, calculated using IMPROVE measurements and the ISORROPIA thermodynamic model (21), shows a similar trend but the correlation is slightly lower relative to the other species (Fig. 2*A*;  $r = 0.76$ ). Surface sulfate, nitrate, NO<sub>2</sub>, CO, and BC (in the absence of fires) are predominantly anthropogenic in origin. Declines in concentration of these species are widely recognized to be a result of EPA regulations on emissions from power generation and vehicular sources (20).

## Significance

**Ambient particulate matter (PM) was responsible for four million premature deaths globally in 2012. The deleterious health impacts of PM motivated the US Environmental Protection Agency (EPA) to curtail emission of PM and precursor gases. The 2011 EPA report to Congress on the efficacy of the Clean Air Act estimated a dramatic reduction in human mortality resulting from these emissions controls. Surface measurements from 1990 to 2012 indicate a significant US-wide decline in the organic portion of the PM, not accounted for in the EPA report. We show that the decline in organic aerosol is mediated primarily through changes in vehicle and residential fuel-burning emissions, indicating that the Clean Air Act is even more beneficial to US air quality than currently appreciated.**

Author contributions: D.A.R., C.L.H., and J.H.K. designed research; D.A.R. performed the research; K.J.R. contributed observational analysis; and D.A.R. and C.L.H. wrote the paper.

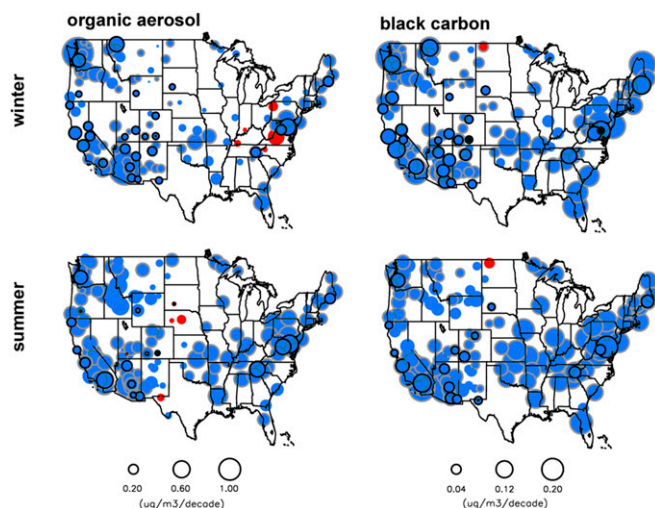
The authors declare no conflict of interest.

This article is a PNAS Direct Submission. J.L. is a guest editor invited by the Editorial Board.

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This article contains supporting information online at [www.pnas.org/lookup/suppl/doi:10.1073/pnas.1700387115/-DCSupplemental](http://www.pnas.org/lookup/suppl/doi:10.1073/pnas.1700387115/-DCSupplemental).



**Fig. 1.** Trends in observed BC and OA surface concentration. Trends ( $\mu\text{g}/\text{m}^3$  per decade) in OA, where OA is  $1.8 \times \text{OC}$  to account for noncarbon mass associated with the OA (Left) and BC (Right) between 1990 and 2012 (black outline) and between 2002 and 2012 (gray outline) are shown for all available IMPROVE data in winter (Upper) and summer (Lower). Circle size denotes the magnitude of the positive (red) or negative (blue) trend, and no border indicates an insignificant trend ( $P > 0.05$ ).

Controls on vehicle emissions have resulted in marked declines in  $\text{NO}_x$  and  $\text{PM}_{2.5}$ , so it is likely that OA from these sources will have also decreased, as has been shown for urban areas in California (22). The similarity between trends of primarily anthropogenic species and trends in OA strongly suggests that the decline in OA is driven, either directly or indirectly, by changes to anthropogenic emissions. We find consistent trends and correlations when parsing the sites by season or by population density (to separate rural and urban influence; *SI Appendix, Fig. S2*). The consistency between normalized trends in urban and rural locations is striking considering that in urban areas OA is declining two times faster and inorganic aerosol concentrations five times faster than in rural regions. This may indicate that the mechanisms behind the decline are similar in the two environments. We also find consistent results when focusing on the period 2002–2012, which increases the number of available sites from 33 to 159 (*SI Appendix, Fig. S3*).

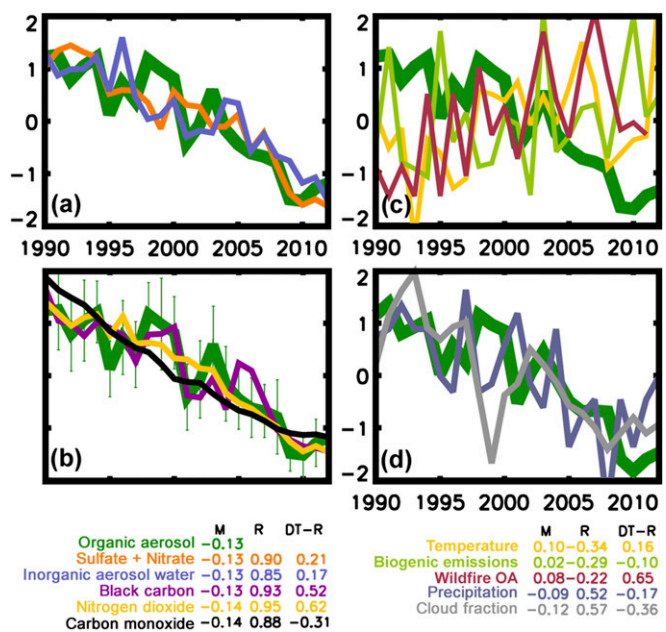
### Natural Influences on Organic Aerosol Trends

To examine the potential role of meteorology (temperature, precipitation, and cloud cover), biogenic VOC emissions (isoprene and monoterpene), and biomass burning in the observed decline in OA, we use assimilated meteorology from the NASA Modern-Era Retrospective analysis for Research and Applications (MERRA) and emissions estimated using the GEOS-Chem chemical transport model (*Materials and Methods*). Observed OA concentrations correlate weakly and negatively with both temperature and biogenic VOC emissions (Fig. 2B;  $r = -0.23$  and  $-0.35$ ), because neither decrease over time. Biomass burning OA, derived from emissions databases (*Materials and Methods*), increases significantly ( $P > 0.05$ ) and shows poor correlation with observed OA ( $r = -0.25$ ). However, a positive correlation ( $r = 0.65$ ) between detrended observed OA and detrended modeled fire OA indicates that the interannual variability in observed OA is influenced by biomass burning, despite the diverging long term trends. Precipitation exhibits a significant ( $P > 0.05$ ) decreasing trend (*SI Appendix, Fig. S4A*), and thus increased wet deposition cannot explain the decreasing OA trends. Cloud cover also decreases significantly (*SI Appendix, Fig. S4B*); although the resulting increase in insolation and thus VOC oxidation is counter to

the observed trend in OA, aqueous-phase production of OA (23) may have decreased. However, the 3–4% change in cloud cover over the United States results in a  $<5\%$  change in the simulated surface concentration of sulfate, which is predominantly formed by oxidation in the aqueous phase. Thus, even if all OA was produced in the aqueous phase, this change in cloud cover is unable to explain the observed decline in OA. The trends in the meteorological variables, biogenic emissions, and biomass burning OA strongly suggest that the OA surface concentration is declining despite these factors, rather than because of them.

### Simulating Anthropogenic Carbonaceous Aerosol Trends

To identify a causal link between the observed trend in surface concentration in the United States and changes in anthropogenic BC and OC emissions, we construct a temporally varying emissions database for BC and OA, using countywide  $\text{PM}_{2.5}$  reports and BC and OC emissions ratios for 1990 through 2012 (*Materials and Methods*). The OC classified as primary organic aerosol (POA) in the emissions is likely to contain low-volatility emissions as well as POA that evaporates and recondenses, material that may be considered secondary organic aerosol (SOA) under other circumstances (10). The US emissions of both BC and OC decrease by 55% and 52%, respectively, over the 23-y period (Fig. 3). These reductions are largely driven by changes in vehicle emissions for BC (80% of the decline) and both vehicle emissions and residential fuel burning for OC (38% and 40% of the decline, respectively). We use the GEOS-Chem model to simulate the



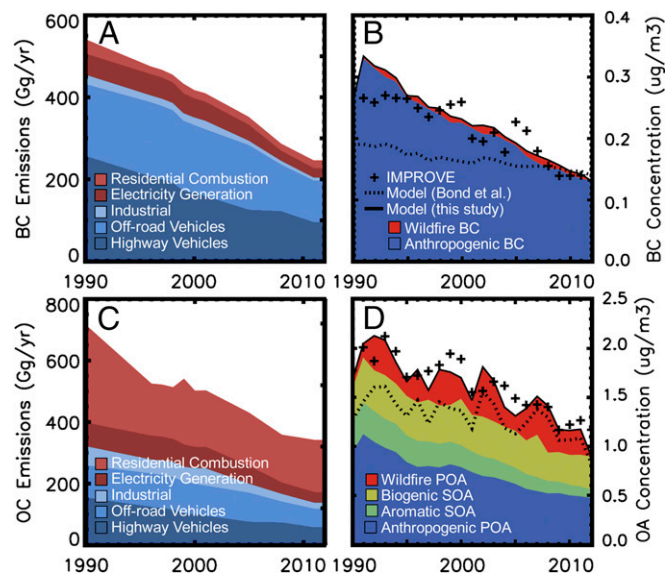
**Fig. 2.** Relationship between observed organic aerosol and anthropogenic, meteorological, and biogenic variables. (A) Normalized (SDs from the 1990–2012 mean) annual observed median concentrations of OA (dark green),  $\text{SO}_4^{2-} + \text{NO}_3^-$  (orange), and inorganic aerosol water (blue) between 1990 and 2012 for all available IMPROVE data. (B) Same as A, including BC from IMPROVE (purple),  $\text{NO}_2$  (yellow), and CO (black) from colocated EPA CSN network sites. The uncertainty (25–75 percentile range of individual sites) of the normalized OA is displayed as bars (dark green; shown only on B, but the same for A, C, and D). (C) Same as A, including 2-m temperature from MERRA reanalysis (yellow), biogenic emissions from MEGAN (light green), and modeled biomass burning OA from GFED and RETRO (red) all sampled to IMPROVE sites across the United States. (D) Same as A for precipitation frequency (dark gray) and cloud cover (light gray) from MERRA reanalysis. The slope (M), correlation coefficient (R) with OA, and the correlation with linearly detrended OA (DT-R), to isolate interannual variability, are listed for each variable. The data are broken into four panels for clarity.



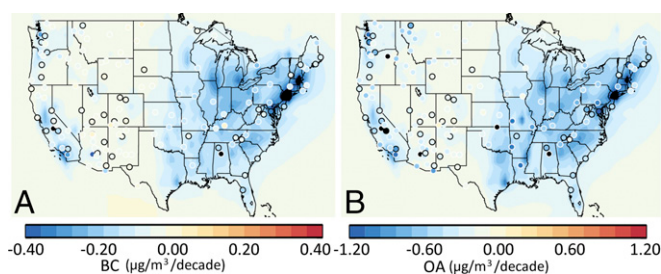
impact of these declining emissions. Nonvolatile and low-volatility anthropogenic emissions of organics are not modeled independently, but lumped together to account for the fact that vapors (including evaporated POA) are likely to oxidize and form OA with high yields (24). The model also simulates POA from wildfires and SOA formation from aromatics (25), isoprene (14), and other biogenic species (26). Simulated SOA formation depends on the existing concentration of OA, but not the concentration of inorganic aerosol (27). Given the complexity and poor understanding of the dominant sources of SOA in the atmosphere, the simulation of SOA formation, and its contribution to the OA trend, is highly uncertain. However, as we discuss below, our analysis suggests that the vast majority of the observed decline in OA can be explained by decreases in anthropogenic emissions of POA.

Given the uncertainties surrounding SOA, we first examine the model skill in describing the trend in BC as a test of our new emissions. The model captures the observed trend in BC concentration averaged over all sites (Fig. 3B), with a relatively small overestimate of the trend magnitude ( $-0.087 \mu\text{g}/\text{m}^3$  per decade versus the observed trend of  $-0.067 \mu\text{g}/\text{m}^3$  per decade) that is consistent between winter and summer (SI Appendix, Figs. S6–S10). The bias in the model trend primarily stems from high BC concentrations in the eastern United States before 1995. Use of an alternate global inventory (28) in the model yields comparable BC concentrations in present day but captures less than a third of the observed decline in BC (Fig. 3A and SI Appendix, Fig. S5), as seen in previous studies (5). However, our emissions estimates remain within the large uncertainty of this global inventory (29). Good agreement between model and measurements, especially in winter when anthropogenic BC accounts for almost all of the measured BC concentration, strongly suggests that our emissions inventory adequately represents the change in anthropogenic carbon emissions.

The modeled trend in OA at IMPROVE sites ( $-0.40 \pm 0.05 \mu\text{g}/\text{m}^3$  per decade) matches the observed trend ( $-0.37 \pm$



**Fig. 3.** Anthropogenic emissions changes in BC and OA. (A) Trends in anthropogenic primary emissions of BC derived from EPA emission inventory are displayed for 1990–2012 as colored areas. (B) Modeled BC surface concentration averaged across IMPROVE sites using our new EPA-derived emissions inventory (purple), using the Bond et al. (28) emissions (dashed thin black line) and IMPROVE measurements (thick black line). (C) Same as A, but for anthropogenic primary OC emissions from the EPA emissions inventory. (D) Same as B, but for observed OA concentrations and modeled anthropogenic OA concentrations. The contribution to modeled OA from POA (purple), aromatic SOA (green), and biogenic SOA (olive) are shown.



**Fig. 4.** Observed and anthropogenic modeled trends in BC and OA. (A) Trends ( $\mu\text{g}/\text{m}^3$  per decade) in median annual surface BC concentration simulated in GEOS-Chem (contours) and at IMPROVE sites with at least 18 y of data (black circles) and at least 10 y of data (white circles) between 1990 and 2012. Model trends are for anthropogenic BC emissions only, derived from the EPA emission inventory. (B) Same as A, but for OA. Model trends are for anthropogenic OA emissions only.

$0.04 \mu\text{g}/\text{m}^3$  per decade) within the trend uncertainty estimate and with high correlation over time ( $r = 0.92$ ). We also find that the spatial distribution of the modeled trends largely matches the observations (Fig. 4). Anthropogenic emissions of condensable OC account for the majority of the modeled trend (66%) with an additional decrease from aromatic SOA (28%) and biogenic SOA (13%), indicating that changes in anthropogenic emissions of condensable OC can explain much of the observed trend in OA. Wildfire emissions vary strongly from year to year but result in a small positive trend in OA that is similar in magnitude, but opposite in sign, to the decline in biogenic SOA. The decline in aromatic SOA is primarily driven by the fivefold decline in aromatics since 1990 (SI Appendix, Fig. S11) and is partially offset by the enhanced aromatic SOA yield as  $\text{NO}_x$  concentrations decrease by  $\sim 20\%$  in the model (25). The decline in biogenic SOA in the model, despite no clear trend in biogenic emissions (Fig. 2B), is largely confined to the Southeast (SI Appendix, Fig. S12) and is driven by the reduction in anthropogenic OA and the associated reduction in SOA condensation.

If anthropogenic inorganic species (e.g.,  $\text{NO}_x$ ,  $\text{SO}_2$ ) promote SOA formation from biogenic precursors (30–33), decreases in the emissions of such species could potentially contribute to the observed trends in OA; however, such anthropogenic–biogenic interactions are unlikely to explain the trends observed. For example, although SOA formation mechanisms included in the model do not account for  $\text{NO}_x$  dependence of the biogenic SOA yield, the  $\text{NO}_x$  dependence of monoterpene and isoprene SOA implies higher yields with lower  $\text{NO}_x$  (30), counter to the observed trends. Changes in inorganic aerosol water volume and acidity, via decreasing  $\text{SO}_2$  emissions, have been suggested as a mechanism for reduction of OA formation in the Southeast (32–35) where sulfate and aerosol water concentrations have decreased dramatically (SI Appendix, Fig. S1). However, the consistent fractional decrease in OA between regions with limited inorganic aerosol water (western United States) and abundant inorganic aerosol water (southeast United States) indicate that aerosol water is unlikely to be a dominant controlling factor across all regions. Similarly, a significant decline in OA in the northeast United States is observed during winter when sulfate-mediated isoprene SOA formation is unlikely to occur. Therefore, although mechanisms elucidated by recent measurements in the Southeast (32, 34) are likely to play important roles regionally, few appear to explain the observed US-wide year-round trend. Only the response of sesquiterpene SOA to  $\text{NO}_x$  changes follows the observed relationship (31). Nighttime formation of biogenic OA precursor gases via the  $\text{NO}_3^\bullet$  radical, a mechanism proposed for the southeast United States (32), which may be underestimated by the model, could contribute to the OA reduction in regions where monoterpenes are present. If we

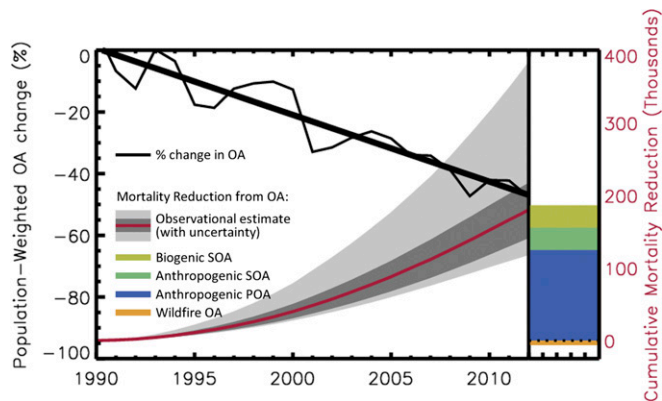
consider the limiting case in which the observed decline in summertime OA in the southeast United States is entirely the result of a decrease in biogenic SOA and we assume a commensurate fractional decline in all other regions and seasons, only half of the OA trend across all IMPROVE sites is captured on average (*SI Appendix*). Moreover, even this likely overestimates the importance of decreases in biogenic SOA, given that it requires the unrealistic assumption that POA emissions have not changed.

Field measurements of the contemporary carbon fraction put an observational limit on how much of the decline can be explained by anthropogenic fossil fuel emissions, and indicate that the modeled fossil fraction (fossil fuel POA and aromatic SOA) is consistent with observations. The anthropogenic emissions produce fossil carbon fractions similar to the observed fossil carbon fractions of 50% in urban locations and 5–15% in rural locations (36) (*SI Appendix, Fig. S13*). Because all of the fossil carbon is accounted for by these sources, the contribution of anthropogenic emissions to the OA is unlikely to be greater than estimated here; the remaining OA mass must result from biogenic emissions or anthropogenic modulation of biogenic SOA formation.

We expect that improvements in our understanding of SOA formation from both anthropogenic and biogenic sources, beyond the capabilities of current global chemical transport models, will substantially reduce the regional biases in the simulated OA concentrations and refine the comparison of trends with observations. Despite this, the above analysis demonstrates that primary anthropogenic emissions alone can explain, on average, two-thirds of the observed decline in OA over the past two decades. The combined effect of changes in aromatic SOA, anthropogenic-modulation of biogenic SOA formation, biogenic emissions, wildfires, and meteorology are likely to explain the remaining third.

### Estimating the Premature Mortality Reduction Owing to Organic Aerosol

The change in OA constitutes a significant decline in  $PM_{2.5}$  and has therefore reduced premature mortality through improvements in air quality. The resulting countrywide decline in premature mortality cannot be estimated based on heterogeneously distributed surface sites alone. We use the IMPROVE observations to scale the model  $PM_{2.5}$  (and OA concentration, as previously discussed) to provide US-wide population-weighted concentrations at the county scale (*Materials and Methods* and *SI Appendix*). Following Burnett et al. (37), we estimate that the observed decline in population-weighted organic aerosol of  $1.86$  ( $1.43$ – $2.31$ )  $\mu\text{g}/\text{m}^3$  since 1990 translates into 180,000 (117,000–389,000) fewer lives lost, cumulatively, between 1990 and 2012 (Fig. 5), with 14,000 (9,000–32,000) in 2010 alone. The envelope on Fig. 5 indicates the total uncertainty resulting from both the PM–mortality relationship and the derivation of the US-wide observational estimate of OA concentration and trend. The contribution of each modeled OA component to the change in premature mortality is shown in Fig. 5. Our analysis suggests that 83% of the decline in population-weighted OA, and therefore the reduction in premature mortality, results directly from the decline in anthropogenic SOA and POA. Changes in vehicular and residential wood-burning emissions of POA and SOA precursors are responsible for the majority of the decline, based on the underlying emissions. The concurrent decline in other anthropogenic emissions, such as  $\text{SO}_2$  and  $\text{NO}_x$ , likely influence formation of biogenic SOA; hence, attributing 83% of the premature mortality reduction to anthropogenic factors is considered a lower limit. Each of these changes can be traced to emissions regulations implemented via the 1970 Clean Air Act and subsequent amendments. Further regulations on residential and commercial wood-burning emissions (Clean Air Act Section 111), and the requirements of the CAAA Title II, continue to force changes in fuel composition, engine design, and exhaust



**Fig. 5.** Premature mortality associated with OA. The decline in population-weighted OA concentration averaged across the United States (thin black line) and the trend (thick black line) based on a combination of model and IMPROVE observations. The cumulative reduction in premature mortality (in 1,000) resulting from the declining trend in OA (red line) is displayed with the mortality uncertainty resulting from the  $1\text{-}\sigma$  uncertainty in population-weighted  $PM_{2.5}$  and OA estimates (dark gray) and the  $1\text{-}\sigma$  uncertainty when combined with the relative risk uncertainty, determined by Burnett et al. (37) for diseases linked to PM exposure (light gray; *SI Appendix*). The premature mortality for modeled biogenic SOA (olive), anthropogenic SOA (green), primary OA (blue), and wildfire OA (orange) are shown relative to the estimate based on the combination of model and IMPROVE observations.

technologies to reduce vehicular emissions beyond those set in the Clean Air Act (38).

The decline in anthropogenic OA from 2000 to 2010 was underestimated by a factor of five in the model-based assessment of the efficacy of the CAAA provided in the 2011 US EPA Report to Congress [ $-0.14$   $\mu\text{g}/\text{m}^3$  versus the anthropogenic fraction (83%) of  $-0.85$   $\mu\text{g}/\text{m}^3$  shown here]. We find that the decline in anthropogenic OA between 2000 and 2010 was responsible for averting 84,000 (30,000–164,000) more premature deaths than estimated based on previous modeling studies (*SI Appendix*), and may be even higher if some of the decline in biogenic SOA can be attributed to anthropogenic modulation. This represents a substantial overlooked benefit of the Clean Air Act. As anthropogenic sources of OA continue to decline and future changes in climate, likely cause biogenic and wildfire sources of OA, continue to increase, natural sources will become progressively more dominant. A better understanding of both anthropogenic and natural emissions of organic aerosol and relevant precursors, especially from vehicles (39), and the influence of anthropogenically controlled SOA formation is required to further resolve the sources of the observed trend, and to predict the future health benefits of reducing anthropogenic emissions.

### Materials and Methods

**Surface Concentration Measurements.** Two networks are used to provide speciated PM concentration measurements: the IMPROVE network (40) situated primarily in National Parks, and the EPA’s Speciation Trends Network (STN) measurement sites, situated in more urban locations (41). Both networks make 24-h integrated measurements of  $PM_{2.5}$ , along with crustal, inorganic, and organic components every third day. Filters are equilibrated to  $\sim 35\%$  relative humidity, so volatile, water-soluble organic species are not collected. The carbonaceous material in the sample is volatilized, pyrolyzed, and combusted to give BC and OC concentrations (42). We assume a conversion factor of 1.8 from OC to the OA mass. This will likely vary between locations (43) and may change over time, but the uncertainty in the specific organic compounds necessitates a simplified conversion (the same is applied to the model). There are differences in the filter and extraction processes between networks, leading to differences in measured BC and OC as well as the sensitivity to adsorption and volatilization artifacts (44). Because of these differences, we focus on the IMPROVE network throughout the OA temporal trend analysis and only use both the STN and IMPROVE data when estimating concentrations for  $PM_{2.5}$  exposure.



The daily and third-daily measurements are aggregated by season (October–March and April–September). The median concentration is used, rather than the mean, to reduce biasing toward exceptionally high values (e.g., from local wildfire events). When comparing normalized species concentrations, we subtract the climatological mean from the annual concentration and divide by the SD (i.e., the z-score). To detrend the data (when calculating the detrended correlation), the slope and the intercept of the variable is subtracted from the time series before calculating the correlation coefficient.

**EPA Emissions Database.** The National Emissions Inventory provides comprehensive US-wide emissions for a range of gas phase and particle species. However, the change in data processing between years makes trend analysis difficult with such a dataset. For this study, we create a US countywide emissions inventory for BC and OC, varying on a yearly basis between 1990 and 2012. The emissions of BC and OC are derived from the EPA countywide criteria pollutant emissions summaries gathered for years 1990, 1996–2002, 2005, 2008, and 2011. These contain estimates of PM<sub>2.5</sub> emissions for a range of point, area, and mobile sources in mega source categories: open biomass burning, residential, energy/power, industrial, transport, and other (<https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data>). The fraction of PM<sub>2.5</sub> that is BC and OC is derived from BC:PM<sub>2.5</sub> and OC:BC generated by the SPECIATE database, which compiles source emission profiles from numerous studies (see tables 4-1 and 4-2 in ref. 45).

Before 1999, condensable materials (in the gas phase during passage through the exhaust/stack but condensing rapidly to the particle phase and contribution to the PM<sub>2.5</sub> mass in ambient conditions) were not included in the emissions. This leads to a clear increase in the reported PM<sub>2.5</sub> for energy-related categories between 1999 and 2002, depending on when the condensable material is incorporated into the emission reports. We assume that the noncondensable PM<sub>2.5</sub> emissions are equal in the year that condensable materials are included, and in the year before inclusion. The difference in emission between these 2 y is considered to be the condensable material concentration. An offset is then applied to all years before addition of the condensable materials to account for their emission. Relative to 1999 emissions, the offset is 68% for electricity generation, 12% for residential fuel combustion, and 9% for industrial emissions. EPA modeling of vehicle emissions uses MOVES after 2002; before that, emissions were generated using MOBILE. This yields a considerable increase in PM<sub>2.5</sub> between 2001 and 2002, especially for highway vehicles (a factor of 2); we apply the same scaling methodology as for the condensable material to account for the change in emissions model and estimate the vehicular emissions before 2002 (an offset of 52% and 14% of the 2002 emissions for highway vehicles and off-road vehicles, respectively). In general, the PM<sub>2.5</sub> emissions are declining during this period; therefore, assuming equal emissions for the year prior is likely to underestimate the extra PM<sub>2.5</sub> in previous years. This method also assumes that the ratio of particulate to condensable emissions remains constant. Our emissions indicate a 26% and 27% decline in PM<sub>2.5</sub> emissions for highway and off-road vehicles between 1996 and 2006. This is higher than the 17% and 22% assessed from fuel consumption and emission factors in the study by Dallman and Harley (46). Therefore, the simple scaling used in our study to link the MOBILE and MOVES vehicle emissions may overestimate the decline in OA from vehicles by ~7%. See *SI Appendix* for comparison with other emissions databases (28, 47).

**Meteorological Fields.** MERRA assimilated meteorology is provided by the Global Modeling and Assimilation Office at NASA. The meteorological fields (e.g., winds, precipitation, cloud cover, temperature) are available on 1-hourly and 3-hourly temporal resolution and available throughout the 1990–2012 period of this study. We use the number of days in which precipitation occurs for the grid box in which a surface site is located as a metric for precipitation. This precipitation frequency is less likely to be biased by extreme rain events that will not have a proportional impact on wet deposition of the aerosol. We consider column cloud fraction as the metric for cloud, but also explored cloud liquid water path as a metric, which showed no significant trend and poor correlation with OA.

**Fire Emissions.** We use a combination of Global Fire Emissions Database version 3 (48) from 1997 to 2012 and RETRO (49) from 1990 to 1996 to estimate emissions of BC and OC from fires on a monthly basis. The RETRO emissions are scaled to give the same total emissions as the GFED emissions over North America for the period in which the datasets overlap (1997–2000). We find no evidence of a decline in OA emissions from US or Canadian fires between 1990 and 2012, consistent with previous evidence that wildfires in the western United States have been increasing and will continue to increase under a warming climate (11, 19).

**Inorganic Aerosol Water.** We estimate the inorganic aerosol water content using the thermodynamic equilibrium model ISORROPIA. The model determines aerosol

water from the mass concentration of SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, temperature, and relative humidity. The mass concentrations of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> are taken from the IMPROVE and STN network and the temperature and relative humidity come from the North American Regional Reanalysis. We assume a constant NH<sub>4</sub><sup>+</sup> concentration across the United States because of a lack of observational constraints. Studies show a general increase in NH<sub>4</sub><sup>+</sup> over the period of interest across the United States, although observations from the Southeastern Aerosol Research and Characterization study suggest a reduction in NH<sub>4</sub><sup>+</sup> of 0.6 μg/m<sup>3</sup> between 1999 and 2010. Although this is a source of uncertainty, applying a positive or negative trend of 50% from an initial 1.0 μg/m<sup>3</sup> constant concentration in 1990 does not substantially impact the long-term regional trends in aerosol water.

**Chemical Transport Model.** We use the GEOS-Chem chemical transport model (v9-01-03; [www.geos-chem.org](http://www.geos-chem.org)) driven by MERRA meteorology (see above). The model incorporates a global 3D simulation of coupled oxidant–aerosol chemistry at a resolution of 2.5° by 2.0° over 47 vertical levels and simulates sulfate–nitrate–ammonium aerosols (50), carbonaceous aerosols [primary emissions and SOA from aromatics (25) and from biogenic VOCs (14, 26) in this study; see ref. 51 for more information] (14, 25, 26, 52, 53), mineral dust (54), and sea salt (55). We linearly interpolate model concentrations to the location of STN and IMPROVE sites between 1990 and 2012 for comparison with observations. SO<sub>2</sub> and NO<sub>x</sub> emissions are following Leibensperger et al. (5) with EDGAR Hyde 1.3 (56) for 1990 interpolated to EDGAR 3.2FT (57) for 2000 and growth factors following the IPCC A1B scenario forward from 2000. Emissions of aromatic VOCs are taken from EDGAR 3.2FT and scaled from the 2000 base year using the total fossil fuel emission (58, 59). Other nonmethane VOCs are provided by the National Emissions Inventory 2005 EPA database. Emissions in the baseline run are provided by the database presented in Bond et al. (28) and implemented in GEOS-Chem by Leibensperger et al. (5). Following Leibensperger et al. (5), the emissions beyond 2000 are calculated based on biofuel and fossil fuel growth factors derived from the Integrated Model to Assess the Greenhouse Effect (60) as in the IPCC A1B scenario (61). Updated anthropogenic BC and OC emissions in the United States are from the database developed in this study based on EPA source inventory (see above). These countywide emissions are area-weighted to the model grid resolution. The model is run with and without biomass burning emissions (see below) to estimate fire OA concentrations. We also use the model to estimate biogenic VOC concentrations based on emissions from the Model of Emissions of Gases and Aerosols from Nature (MEGAN) module (62). We also run the nested North American 0.5 × 0.67° resolution version of GEOS-Chem for 2011 to provide scaling factors for the PM<sub>2.5</sub> and OA when calculating trends and countywide premature mortality.

**Premature Mortality Estimates.** The annual adult (>25 y) premature mortality owing to PM<sub>2.5</sub> exposure is assessed using the following relationship:

$$\Delta M_{i,a,d} = m_d \frac{(RR_{a,d} - 1)}{RR_{a,d}} P_{i,a}$$

where  $m$  is the population mortality rate (per 100,000) for disease,  $d$ , from the Institute for Health Metrics and Evaluation (63). Following Burnett et al. (37),  $RR$  is the relative risk from PM<sub>2.5</sub> exposure for each age demographic,  $a$ , associated with disease,  $d$ , and  $P$  is the population (in 100,000 s) at location,  $i$ . The relative risk considers the change in mortality as a function of PM<sub>2.5</sub> for four diseases,  $d$ : ischemic heart disease, cerebrovascular disease (stroke), chronic obstructive pulmonary disease, and lung cancer (37). The relative risk is assessed for different age demographics,  $a$ , in 5-y intervals from 25 to 80 y and over (only stroke and ischemic heart disease metrics vary as a function of age) and is taken from the Global Burden of Disease (GBD) 2010 study, as in Burnett et al. (37). We use county population data from the 2010 US Census and assume a linear decrease in population back to 1990 US totals. The annual OA and PM<sub>2.5</sub> in each county is produced by interpolating the model OA and PM<sub>2.5</sub> concentration after an annual bias correction is applied, based on the regression between model and surface network PM<sub>2.5</sub> measurements (*SI Appendix*). To isolate the change in mortality attributed to the change in OA,  $\Delta M$  is calculated for each year between 1990 and 2012 and subtracted from the  $\Delta M$  estimated when holding OA at the 1990 levels. We follow the methodology of the GBD MAPS Working Group (63) to correctly partition the mortality attributable to OA, i.e.,  $RR_{a,d} = 1 + (RR_{a,d} - 1) \times f_{OA}$ , where  $f_{OA}$  is the fraction of the PM<sub>2.5</sub> comprised of OA. This is repeated for the upper and lower 95% confidence limits of  $RR$  and the concentration of OA and PM<sub>2.5</sub> to provide an estimate of uncertainty (Fig. 5).

**ACKNOWLEDGMENTS.** This work was supported by the NSF (Grant AGS-1238109), NASA (Grant NNX14AP38G), and the National Oceanic and Atmospheric Administration (Grant NA13OAR4310072). K.J.R. was supported by a NSF Graduate Research Fellowship.

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