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CHEMICAL REVIEWS

Review

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Chemistry and the Linkages between Air Quality and Climate Change

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1. INTRODUCTION

Climate change and air pollution are critical environmental issues both in the here and now and for the coming decades. A recent OECD report found that unless action is taken, air pollution will be the largest environmental cause of premature death worldwide by 2050.[1] Already, air pollution levels in Asia are far above acceptable levels for human health, and even in Europe, the vast majority of the urban population was exposed to air pollution concentrations exceeding the EU daily limit values, and especially the stricter WHO air quality guidelines in the past decade.[1−3] The most recent synthesis of climate change research as presented in the fifth IPCC Assessment Report (AR5) states that the warming of the climate system is unequivocal, recognizing the dominant cause as human influence, and providing evidence for a 43% higher total (from 1750 to the present) anthropogenic radiative forcing (RF) than was reported in 2005 from the previous assessment report.[4]

In many areas of science and policy, these two environmental challenges are viewed as separate issues, while in fact they are highly connected. There are a number of ways in which air pollution and climate change are linked, including (1) emissions, (2) atmospheric properties, processes, and chemistry, and (3) mitigation options. It is clear that many of

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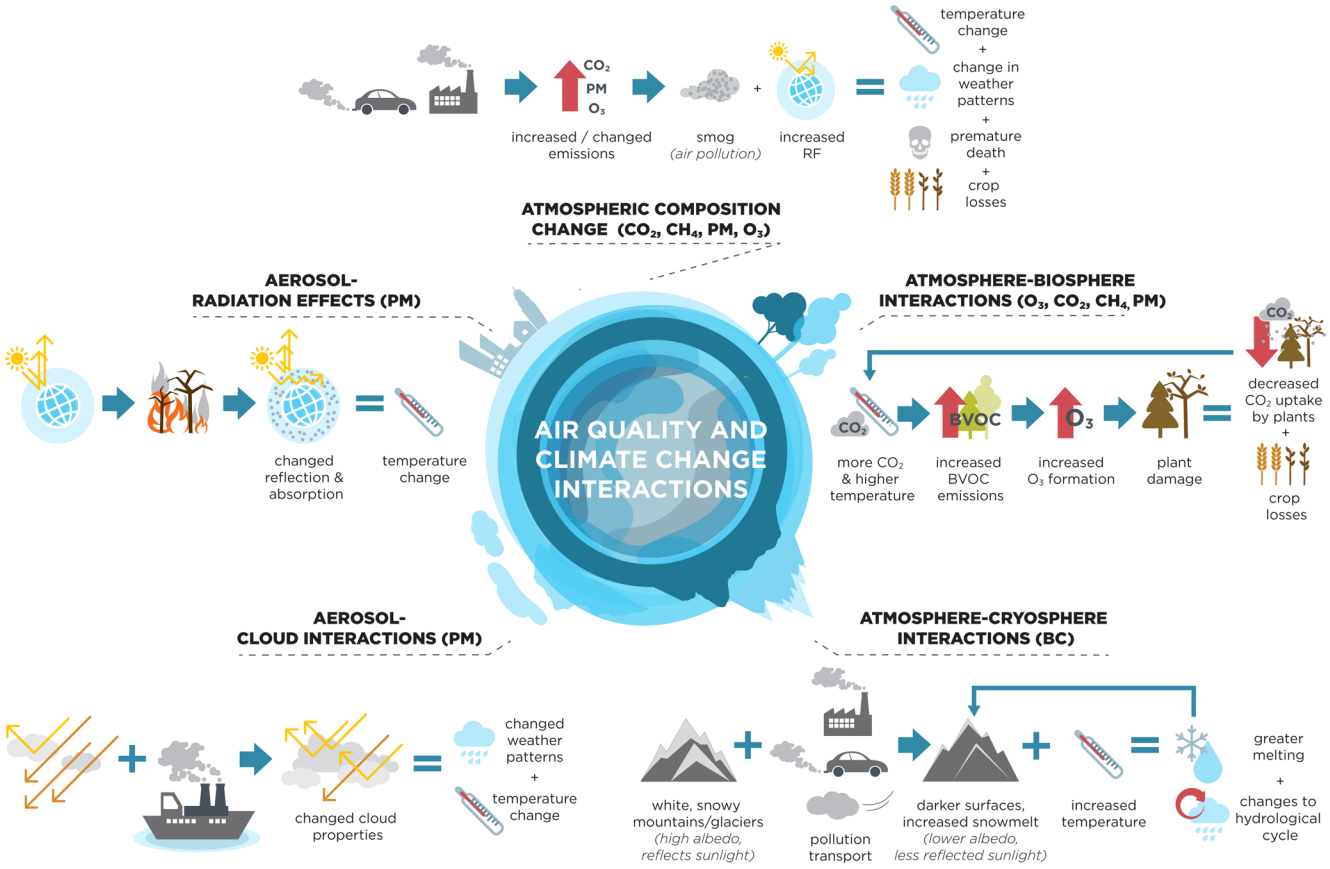

Figure 1. An overview of the main categories of air quality and climate change interactions including a depiction of an example interaction or feedback for each category. Depicted emission sources are examples of possible sources but do not encompass all emission sources relevant to the depicted interaction. The most relevant components are listed in the brackets following the category. PM (particulate matter) indicates all aerosol sources, including OA (organic aerosol), BC (black carbon), and SO_2; O_3 (ozone) includes O_3 and its precursor compounds, NO_x, NMVOCs, and CO.

the same sources emit both greenhouse gases and air pollutants. For example, emissions from vehicles include particulate matter, nitrogen oxides, carbon monoxide, and carbon dioxide (CO_2). Once in the atmosphere, the emitted species have a variety of atmospheric properties that determine whether or not they have a direct or indirect influence on radiative forcing (climate change), their lifetime in the atmosphere, the atmospheric chemistry processes they are involved in, and their influence on human health and ecosystems. For example, particulate matter has a direct influence on radiative forcing by scattering or absorbing incoming radiation, depending on the composition, as well as an adverse effect on human health,[5−7] in addition to an indirect effect where particles can act as cloud condensation nuclei and thereby affect radiative forcing, as well as weather patterns. Figure 1 provides an overview of the groups of processes relevant to air quality and climate change interactions with examples depicted for each process type.

Finally, many mitigation options offer the possibility to both improve air quality and mitigate climate change, such as improvements in energy efficiency, or a switch to wind or solar power, all of which reduce emissions across the board.[8] There are, however, also mitigation options that may provide benefits to one sector, while worsening the situation in another. One example is increasing the use of wood (biomass) burning for residential heating: While the overall amount of CO_2 emissions is reduced (such initiatives are often promoted as "carbon-neutral"), without proper emission controls this type of heating contributes significantly to particulate matter emissions and thereby degrades air quality.[9] Such options that are not win−win, but rather win−lose, are referred to as trade-offs. There are possible benefits of coordinated action that takes these linkages into account, and these have been gaining more attention as high profile political initiatives, such as the Climate and Clean Air Coalition (CCAC) (www.ccacoalition.org), aim to spur action in this area of overlap to make faster and more efficient progress toward protecting human health and ecosystems while mitigating (near-term) climate change. A variety of studies have shown that acting without delay to mitigate both air pollutants and greenhouse gases substantially reduces the risk of crossing the 2 °C threshold, as illustrated in Figure 2.[10,11]

While the focus of this Review will not be on the mitigation options, it is important to recognize that the sources and physical and chemical processes that link air quality and climate have impacts and implications beyond atmospheric chemistry in the broader context of decision-making and science−policy. That said, the focus of this Review will be the atmospheric properties, processes, and chemistry, including information on the emission sources that lead to the linkages between air pollution and climate change and the associated feedback effects. Both the role of the pollutants for climate, such as their effect on radiative forcing, as well as their

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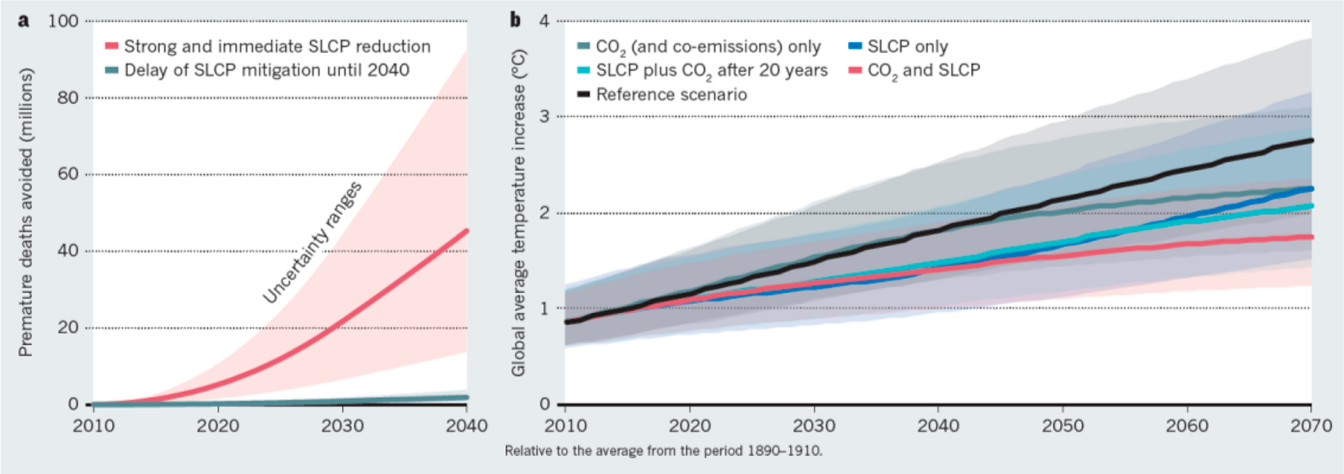

Figure 2. More than 40 million deaths from respiratory and cardiovascular diseases could be prevented by 2030 by halving the concentration of short-lived climate-forcing air pollutants (SLCPs) in the atmosphere immediately (a). Mitigating climate-forcing air pollutants and carbon dioxide simultaneously is more effective than doing just either one or both, but with a delay (b). Reprinted with permission from ref 10. Copyright 2014 Nature Publishing Group.

importance for air quality, their impact on human health and ecosystems, will be addressed.

2. AIR POLLUTANTS AND THEIR EFFECT ON CLIMATE AND HEALTH

2.1. Gaseous Pollutants

2.1.1. Tropospheric Ozone. Ozone (O_3) is a secondary air pollutant that is formed in the atmosphere from a combination of nitrogen oxides ($NO_x = NO_2 + NO$), volatile organic compounds (VOCs), carbon monoxide (CO), and methane (CH_4) in the presence of sunlight. The well-established ozone formation chemistry occurs via the following reactions:[12,13]

$$\mathrm{VOC} + \mathrm{OH} \xrightarrow{O_2} \mathrm{RO_2} + \mathrm{H_2O} \tag{1}$$

$$\mathrm{CO} + \mathrm{OH} \xrightarrow{O_2} \mathrm{HO_2} + \mathrm{CO_2} \tag{2}$$

$$\mathrm{RO_2} + \mathrm{NO} \xrightarrow{O_2} \text{secondary VOC} + \mathrm{HO_2} + \mathrm{NO_2} \tag{3}$$

$$\mathrm{HO_2} + \mathrm{NO} \rightarrow \mathrm{OH} + \mathrm{NO_2} \tag{4}$$

$$\mathrm{NO_2} + h\nu \rightarrow \mathrm{NO} + \mathrm{O} \tag{5}$$

$$\mathrm{O} + \mathrm{O_2} + \mathrm{M} \rightarrow \mathrm{O_3} + \mathrm{M} \tag{6}$$

In the presence of nitrogen oxides, VOC emissions contribute to the formation of tropospheric (surface) ozone. Oxidation of VOCs by the hydroxyl radical (OH), O_3, or nitrate radical (NO_3) produces peroxy radicals; these replace ozone in the oxidizing reaction of NO to NO_2, thus causing ozone accumulation in the atmosphere.[14] The reaction chain recycles the oxidizing agent, the OH radical, and enables further propagation of the VOC oxidation. Because ozone is dependent on photochemical reactions, the highest concentrations of ozone tend to be observed during the spring (and summer) periods, with minimum concentrations generally observed in autumn.[15,16] Different chemical regimes exist in which ozone is formed, typically referred to as NO_x-sensitive or VOC-sensitive. The regimes are affected by VOC/NO_x ratios, VOC reactivity, biogenic emissions, photochemical aging, and meteorological conditions. In addition, the type of regime is closely associated with sources (produced by photolysis of O_3, HCHO, and other intermediate organics) and sinks of the odd hydrogen radicals, as shown in reactions 7−11.[12]

Sources:

$$\mathrm{O_3} + h\nu \xrightarrow{H_2O} 2\mathrm{OH} \tag{7}$$

$$\mathrm{HCHO} + h\nu \xrightarrow{O_2} \mathrm{HO_2} + \mathrm{CO} \tag{8}$$

Sinks:

$$\mathrm{HO_2} + \mathrm{HO_2} \rightarrow \mathrm{H_2O_2} + \mathrm{O_2} \tag{9}$$

$$\mathrm{RO_2} + \mathrm{HO_2} \rightarrow \mathrm{ROOH} + \mathrm{O_2} \tag{10}$$

$$\mathrm{OH} + \mathrm{NO_2} \rightarrow \mathrm{HNO_3} \tag{11}$$

Many urban areas tend to be NO_x-saturated or VOC-sensitive. While the main cause of reduced ozone in urban areas is removal of HO_x radicals via reaction 11, ozone levels can also be depressed through a phenomenon dubbed "NOx titration", whereby in regions of significant sources of NO emissions, O_3 is removed through reaction with NO.

$$\mathrm{NO} + \mathrm{O_3} \rightarrow \mathrm{NO_2} + \mathrm{O_2} \tag{12}$$

The atmospheric chemistry of ozone is an important context to understand the linkages between air quality and climate change, because many indirect effects are linked to this chemistry. However, a comprehensive overview of ozone chemistry is not the aim of this Review. For this we recommend work by Sillman,[12] the recent Monks et al. review,[13] or atmospheric chemistry textbooks, such as *Atmospheric Chemistry and Physics* by Seinfeld and Pandis.[17]

An important role of ozone in atmospheric chemistry is the oxidation of biogenic VOCs. When ozone attacks the double bond in VOC carbon chain, a Criegee intermediate (carbonyl oxide with two free radical centers, e.g., CH_2OO) is formed.[18−20] Part of the Criegee intermediates go through unimolecular decomposition, but the stabilized Criegee intermediates form hydroxyl radicals (OH), which are important oxidizers of sulfur dioxide (SO_2) and VOCs in

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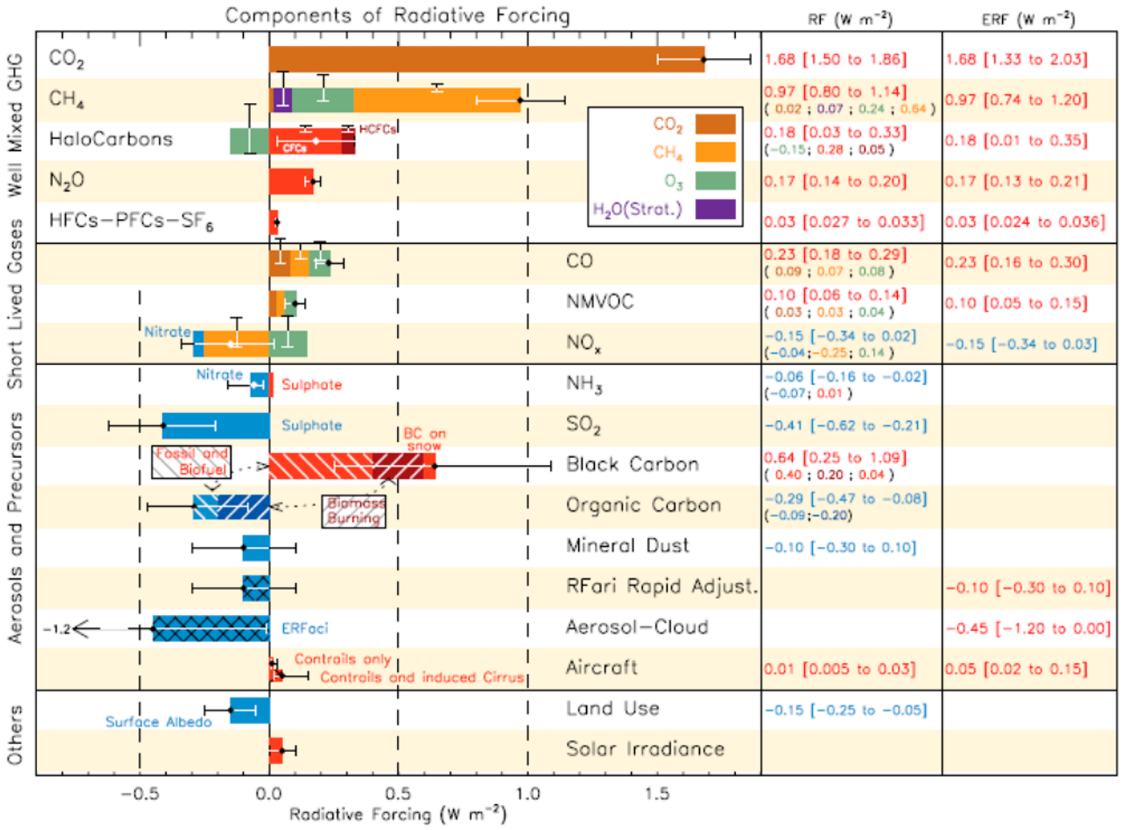

Figure 3. Radiative forcing of climate change shown by emitted components from 1750 to 2011. The horizontal bars indicate the overall uncertainty, while the vertical bars are for the individual components (bertical bar lengths proportional to the relative uncertainty, with a total length equal to the bar width for a ±50% uncertainty). Best estimates for the totals and individual components (from left to right) of the response are given in the right column. Values are RF except for the effective radiative forcing (ERF) due to aerosol−cloud interactions (ERFaci) and rapid adjustment associated with the RF due to aerosol−radiation interaction (RFari Rapid Adjust). (For further details, see source: IPCC AR5 Technical Summary.[33])

the atmosphere. The resulting oxidized SO_2 forms sulfuric acid, and this process thereby contributes significantly to the total sulfuric acid formation at least in rural environments.[18,21] Additionally, the same ozone oxidation reaction of biogenic VOCs can be followed by rapidly repeated auto-oxidation reactions, in which the oxidized VOC oxidizes further by reacting with oxygen molecules. This auto-oxidation pathway leads with high molar yield (6−8%) to formation of heavily oxidized extremely low volatility organic compounds (ELVOC), which can condense on atmospheric particles even in the nanometer size scale.[22,23] The effect of this condensation of biogenic VOCs is discussed in more detail in section 2.2.4.

As an air pollutant, ozone has a variety of adverse effects on human health, including decreased pulmonary function, aggravation of pre-existing diseases such as asthma, increases in hospital admissions, especially respiratory ailments, and premature mortality.[24] The current WHO recommended limit value for ozone is 100 μg m^{-3} (8 h mean), although considerable variation in individual responses to ozone exists, with adverse effects likely also occurring below the threshold.[25] Ozone concentrations range from 26 to 62 μg m^{-3} in the relatively pristine southern hemisphere marine boundary layer[16] to concentrations in excess of 240 μg m^{-3} in polluted urban regions of China (e.g., Han et al.[26]). Long-term exposure to ozone may have also chronic effects. Recent studies have attributed 0.2 million (0.1−0.3 million) or 0.47 million (95% confidence interval, 0.14−0.9 million) premature (respiratory) deaths globally and annually to present (year 2000) ozone air pollution.[27,28] In addition, ozone is phytotoxic with adverse effects on vegetation/ecosystems.[24,29,30] It can penetrate the leaves of plants through the stomata to oxidize plant tissue, impair photosynthesis, and affect the metabolic activity, among other effects.[31,32] Because of this, ozone can be detrimental to crop yields. A recent study estimated that for soybean, wheat, and maize, global crop losses due to ozone damage ranged from 2% to 15% depending on crop and metric used for the year 2000, for a worth of $11−18 billion U.S. The global ozone burden has been estimated using satellite retrievals at 314 Tg, with 52% of that amount being found in the northern hemisphere and 48% in the southern hemisphere.[16] Comparisons with ground-based measurements indicate good capture of seasonal cycle and spatial distribution, although at high latitudes the satellite retrievals were found to have a high bias up to 25% relative to some measurement stations.[16]

Ozone is not only an air pollutant, but also a radiatively active greenhouse gas. The model derived change in radiative forcing from 1750 to 2011 attributed to ozone is +0.35 [+0.15 to +0.55] W m^{-2}, of which +0.40 [+0.20 to +0.60] W m^{-2} is attributed to tropospheric ozone and −0.05 [−0.15 to +0.05] W m^{-2} to stratospheric ozone.[33] While the focus in this Review is on tropospheric ozone, it is worth noting that evidence supports substantial links between changes in

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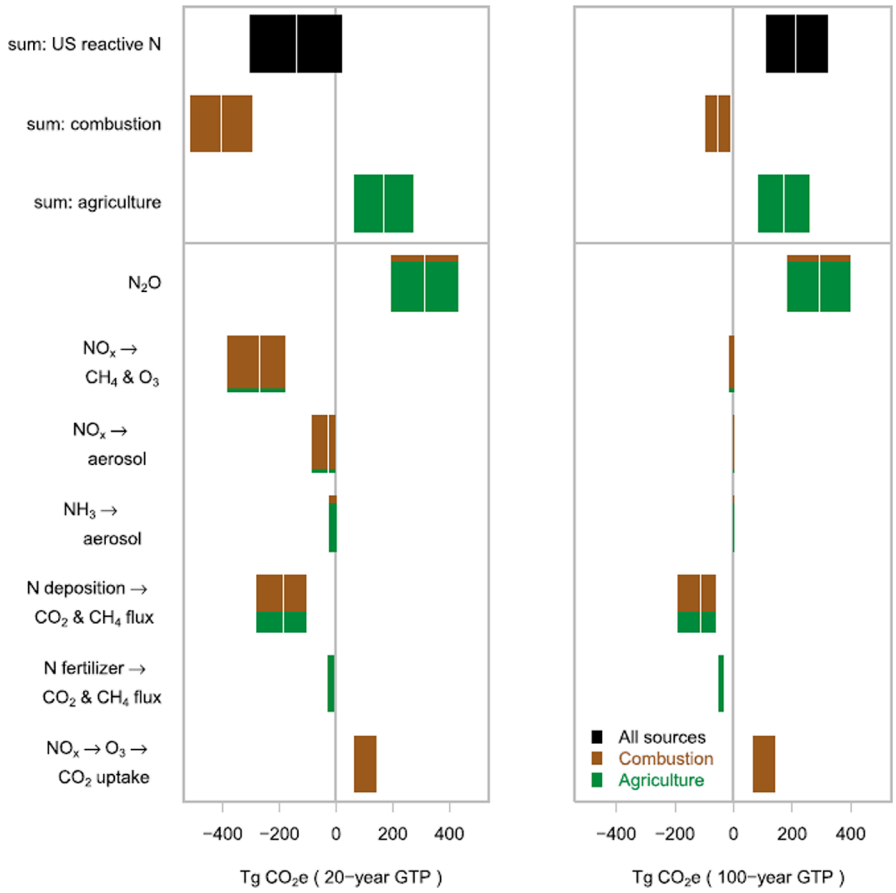

Figure 4. Climate change impact of U.S. reactive nitrogen emissions, in Tg CO_2 equiv, on a 20 year (left) and 100 year (right) global temperature potential basis. The length of the bar denotes the range of uncertainty, and the white line denotes the best estimate. The relative contribution of combustion (brown) and agriculture (green) is denoted by the color shading. Reprinted with permission from ref 43. Copyright 2012 National Academy of Sciences.

tropospheric and stratospheric ozone. The current +0.35 W m^{-2} results from a total O_3 RF of +0.50 [+0.03 to +0.70] W m^{-2} that is attributed to increases in tropospheric emissions of the precursor compounds, NO_x, CO, NMVOCs, and methane, and −0.15 [−-0.30 to 0.00] W m^{-2} attributed to ozone depletion by halocarbons.[33] Methane, an important precursor to ozone, is also a strong greenhouse gas, with a greater RF than ozone, and is addressed in section 2.1.4. The remaining ozone precursors, NO_x, NMVOCs, CO, do not exert a direct influence on climate through radiative forcing, but still affect climate through a variety of indirect effects, not limited to their role in the production of ozone. For one, all ozone precursor emissions, except NO_x, oxidize to form CO_2 and therefore generate additional radiative forcing (warming), although this effect is generally relatively small, with +0.02, +0.03, and +0.09 W m^{-2} from methane, NMVOCs, and CO, respectively.[33,34] The attribution of RF to the emissions is depicted in the well-known IPCC figure, here Figure 3, where the latest version from AR5 attributes not only the emissions, but also the resulting atmospheric drivers. This presentation of the information is just one way that shows how closely air pollution and climate change are linked. Various feedback effects also indirectly affect climate change, such as temperature on emissions, ecosystem feedbacks, or the role of NO_x, NMVOCs, and CO on methane lifetime that will be discussed in the following sections.

In addition to the direct effect of ozone as a greenhouse gas, ozone also has an indirect effect on climate change through its adverse effects on vegetation that inhibit the uptake of CO_2, as in the example depicted in Figure 1. As a strong oxidant, ozone enters plants through stomata on leaves and initiates a chain of reactions that degrades plants' chlorophyll and reduces rates of photosynthesis, adversely affecting plant growth.[35−37] Earlier estimates of this effect found that the forcing due to O_3 from the plant feedbacks by 2100 (from 1900) attributed to a suppression of the land-carbon sink was estimated to range from +0.62 to +1.09 W m^{-2}.[35] A study by Collins et al.[38] investigated the role of this plant feedback indirect effect, finding that it contributes significantly to the climate impact of ozone precursors on a 20 year time scale, by reducing the amount of CO_2 uptake by the terrestrial biosphere, with results to be strongly dependent on emission region and the variation in photochemistry and vegetation response. For NO_x and VOC emissions, the contribution was found to be roughly equivalent to the remaining effects combined from changes in ozone, methane, sulfate, and stratospheric water vapor (and nitrate and nitrogen fertilization of vegetation for NO_x). This plant feedback contribution was found to decline in importance for a longer (50 year) time scale because of the recovery of the vegetation.[38] Unger and Pan[39] postulated that the interactions between O_3, aerosols, and biogeochemical cycles may possibly

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emerge to be the most important climate impact of the short-lived air pollutants that have a climate effect.

Recent work from Kvalevag and Mhyre,[40] however, indicates that the RF of the indirect effect of tropospheric O_3 on plant growth is lower in land model simulations including limitations on available nitrogen. They found that including this carbon−nitrogen coupling significantly decreased the impact of O_3 on the land carbon sink between 1900 and 2004 and mitigated the indirect impact of ozone on RF (attributing only 2−5% of the RF (+0.03 to +0.07 W m^{-2}) to effects on CO_2) by a factor of 6 less than previous studies, which did not include this coupling.[40] Results such as these indicate the complexity of the ecosystem feedback effects, and the need for greater coupling among different earth system processes to improve our understanding of these indirect effects.

2.1.2. Nitrogen Oxides. The vast majority of NO_x (NO_2 + NO) emitted to the atmosphere comes from fossil fuel combustion with the remaining emission sources, biomass burning, soils, lightning, contributing roughly one-third of the total amount of present day anthropogenic and natural emissions.[17] Global anthropogenic emissions of NO_x were estimated to be 57 Tg(NO_2) for the year 2000.[41] Of the 5 global emission inventories compared by Granier et al.,[87] the emissions for NOx were all in fairly good agreement with the maximum difference between inventory estimates for the year 2000 being 17%. Fossil fuel combustion sources of NO_x include gasoline and diesel vehicles, other transportation sources such as airplanes and shipping, industrial sources, including power plants, industrial boilers, and municipal incineration, and home heating. Atmospheric mixing ratios of NO_x tend to range from <1 ppb in remote marine or forest locations, to <1−10 ppb in rural locations, to 10−1000 ppb in urban areas. NO_x emitted from combustion processes tends to be emitted in the majority as NO (∼95%) with only a small amount of primary NO_2. Once in the atmosphere, however, NO_2 is formed from the oxidation of NO (as outlined in the ozone chemistry in section 2.1.1). Because of the increasing prevalence of diesel vehicles and the implementation of diesel particulate filters, a European study found that the amount of primary NO_2 emitted in the traffic sector is increasing and has been reported to be about 30−50% depending on conditions.[42]

Emissions of NO_x are greater in the northern hemisphere, reflecting the larger amount of anthropogenic sources, than in the southern hemisphere, with monthly total NO_x emissions estimated at 9.1−10.8 Tg and 1.5−3.4 Tg, respectively.[16] These emissions include anthropogenic sources, biomass burning, and lightning NO_x, and tend to peak in late winter/early spring due to the seasonality of the biomass burning emissions.[16]

Nitrogen dioxide emissions have adverse health effects; they can lead to airway inflammation and contribute to respiratory issues, specifically asthma. NO_x contributions to particle formation can also aggravate existing heart disease, and contribute to increased hospital admissions and premature death.[24] The health effects are especially relevant in vehicles and near roadways where concentrations can be elevated (30−100% higher) in comparison to the surrounding area (http://www.epa.gov/oaqps001/nitrogenoxides/health.html). In addition, NO_x emissions contribute to adverse ecosystem effects, including acidification.

The effect of nitrogen oxides on RF is more complex than that of the consistently warming influence of RF from NMVOCs and CO, due to a variety of opposing influences from, for example, NO_x effects on ozone versus methane, the location of the NO_x emissions, and ecosystem feedback effects.[43−46] An overview of the climate change impacts of NO_x and other forms of nitrogen is given in Figure 4.[43] A more holistic look at the effect of not only NO_x, but other forms of N, including reactive nitrogen, ammonia, and N_2O, can be found in Templer et al.[36] or Pinder et al.;[43] this section will focus on NO_x. Work from Shindell et al.[47] found that NO_x emissions resulted in a negative (cooling) RF of −0.29 W m^{-2} from 1750 to 2000. This value included effects attributed to sulfate, methane, nitrate, and ozone, all of the attributions contributing negative RF with the exception of a small positive RF from O_3.[47] More recently, attribution experiments as part of ACCMIP evaluated the changes in emissions of NO_x from the 1850s to the 2000s, found that NO_x had an overall cooling impact of −0.193 W m^{-2}, attributed to the resulting changes in methane and ozone.[34] However, as NO_x fosters ozone production, this part exhibits a positive RF (+0.119 W m^{-2}), while the effect on methane results in a negative RF (−0.312 W m^{-2}).[34] The methane forcing in response to changes in NO_x emissions results from the effect that NO_x has on OH and, thereby, methane lifetime. As NO_x emissions increase, OH production is fostered, which reduces the lifetime of methane, because OH is the dominant sink for methane in the troposphere. The latest IPCC (AR5) attributes −0.15 (−0.34 to +0.02) W m^{-2} to NO_x from 1750 to 2011, with a contribution of −0.04 W m^{-2} from nitrate, −0.25 W m^{-2} from the effect on methane, and +0.14 W m^{-2} from the effect on ozone.[33]

The lifetime of NO_x can vary from hours to days, which means that there can be large spatial variations in NO_x. This combined with the nonlinearities in the O_3 chemistry and convective activity means that large geographical differences can result.[45,46] Furthermore, the differences in temporal scales of these effects should be noted. The methane effect occurs on a global scale on a time scale of approximately one decade, while the ozone effect is much more regional and occurs on a time scale of weeks. These differences also mean that in the short term (<1 yr), NO_x emissions are warming, but are cooling in the long term (ca. 10 years or longer).[38]

The effect of regional 20% emission reductions of NO_x was evaluated as part of the Hemispheric Transport of Air Pollutant (HTAP) multimodel intercomparison study to evaluate source-receptor sensitivity. The results from this study show that these regional NO_x reductions produced global, annually averaged net positive RFs, ranging from +0.21 to +1.72 mW m^{-2} for the different regions.[48] These results attribute the NO_x emission reduction to the drivers of RF, including subsequent changes in methane, ozone, and sulfate, whereby the positive net RF from increases in CH_4 (+2.29 to +3.98 mW m^{-2}) outweigh the negative net RF from decreases in O_3 (−1.19 to −3.19 mW m^{-2}); changes to sulfate were minor (−0.16 to +0.53 mW m^{-2}).[48] In all but one region the uncertainty of the net RF overlaps zero. Although not included in the net RF estimate, changes in the CO_2 uptake by the biosphere through the influence of ozone on plants' ability to remove CO_2 from the atmosphere were also attributed; these contribute a negative RF, changing the overall sign of the NO_x reduction to net cooling for all regions (−0.83 to −4.28 mW m^{-2}).[48] The ecosystem

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feedbacks, specifically the effect of ozone damage to vegetation, can be significant in terms of the effect it has on the net RF. Collins et al.[38] found that the induced change in the carbon cycle is the largest single contributor to the global temperature potential metric (a metric relating the changes in RF from an emission pulse to the effect on global temperature; see also section 4.2) for NO_x and VOC emissions, although the estimates depend on assumption relating to the sensitivity of vegetation types to ozone damage. The latest IPCC assessment report concludes that nitrogen oxides "likely" cause a net negative forcing but uncertainties are large.[33] The indirect effects on RF, specifically the ecosystem effects, need more research.

2.1.3. Ammonia. Nitrogen is a major nutrient for life on the planet, but molecular nitrogen is unavailable to most biota, which require fixed nitrogen in their nutritional input. A range of bacteria fix molecular nitrogen as free living organisms in soil and in symbiotic action with specialized vegetation (legumes).[49] The fixed nitrogen in vegetation is present mainly as amino acids but also as NH_4^+ in cell fluids. The NH_4^+ present in intracellular fluids within plant tissues is also connected to the atmosphere via stomata and exchanges freely with the atmosphere, the net exchange being determined by the pH and NH_4^+ concentration in the fluid and atmospheric ammonia concentrations in the free atmosphere. The concentration close to external surfaces of the vegetation in equilibrium with NH_4^+ in the apoplast is termed the compensation point.[50] If ambient concentrations are in excess of the compensation point, ammonia is deposited to vegetation, and if ambient concentrations are smaller than the compensation point, then ammonia is emitted to the atmosphere. However, there is substantial recycling of ammonia in plant canopies between stomata, leaf surfaces, and the ground surface. The consequence is a distinction between the compensation point of the stomata and other compartments, and the compensation point of the canopy as a whole.

The exchange of ammonia with terrestrial surfaces is commonly described using a resistance analogy, in which the flux (F_t) toward or away from the surface is treated as an analogue of current flow in a network of resistances (see Sutton et al. for more detailed information).[50]

Ammonia is therefore present in the atmosphere as a consequence of emissions from vegetation, soil, and animal excreta and therefore has entirely natural sources. However, the industrial fixation of nitrogen from molecular nitrogen and hydrogen by the Haber Bosch process[51] represents an additional nitrogen fixation pathway and is due entirely to human activity. The quantity of nitrogen fixed by the Haber Bosch process is currently estimated at 120 Tg N annually, and the agricultural use of legume crops further enhances nitrogen fixation (by another 60 Tg N yr^{-1}).[52] These anthropogenic additions to global nitrogen fixation are similar in magnitude to natural nitrogen fixation in unmanaged ecosystems, estimated by Vitousek et al.[49] to be 58 Tg N yr^{-1}, and in oceans to be 140 Tg N yr^{-1}.[53]

The total amount of nitrogen fixed annually is approximately 413 Tg N yr^{-1}, of which approximately one-half (210 Tg N yr^{-1}) is anthropogenic.[52] The relative contributions of anthropogenic and natural ammonia and ammonium in the atmosphere vary greatly across regions and between continents due to both the spatial variability in human use of fertilizers and the very short atmospheric lifetime and reactivity of ammonia. It is useful to provide some perspective on these time and space scales. Ammonia has an atmospheric lifetime of a few hours and is very rapidly deposited to terrestrial surfaces, depending on the compensation points of the absorbing surfaces, and also due to the rapid uptake of ammonia into water droplets and onto aerosols, especially acidic aerosols. Thus, hot spots of ammonia emissions close to livestock farms generate local areas with concentrations in the range 10−100 ug m^{-3}. However, the concentrations decline by typically an order of magnitude within 200 m downwind of the source area to background concentrations, maintained by emissions from vegetation. Thus, an agricultural landscape is characterized by a very patchy concentration field for gaseous ammonia. By contrast, the aerosol NH_4 concentration field, and thus the deposition field for reduced nitrogen, is much smoother, with aerosol concentrations in polluted regions being 2−10 ug m^{-3} while in clean air regions of Europe, aerosol NH_4 concentrations are in the range 0.5−1.0 ug m^{-3}.[54]

The bidirectional nature of ammonia exchange, described above, shows a close coupling of the net flux with ambient temperature. This is driven by the physical chemistry of NH_4 in solution and ammonia in the gas phase and temperature dependence of the partitioning between gas and solution phases. Thus, the ambient ammonia concentration is closely coupled to ambient temperature as demonstrated by sets of field measurements of ammonia by Flechard and Fowler.[55] The effects of climate change on the partitioning of NH_3/NH_4 are somewhat more complex as the pool of available NH_4 in solution needs to be considered along with the climate data.

The likely response of ammonia emissions to a changing climate has been considered by Sutton et al.[50] and by Fowler et al.[56] In the recent review of emission and deposition of ammonia by Sutton et al.,[57] they argue that emissions should explicitly include climate in the methodology, rather than prescribed emissions for agricultural sectors due to the strong effect of temperature on the liquid/gas-phase partitioning. The consequence of a global surface temperature change of 5 °C is shown to increase global ammonia emissions by 42%, from 65 Tg NH_3−N yr^{-1} in 2008 to 92 Tg NH_3−N yr^{-1} in 2100, in the absence of other drivers of nitrogen use. Considering both changes in global temperature and anthropogenic activity, it is likely that ammonia emissions would increase to 132 Tg NH_3−N yr^{-1}. The largest uncertainties associated with estimating future emissions of ammonia to the atmosphere are associated with drivers of consumption.[56]

Emissions of SO_2 have declined significantly in Europe and North America over the last two decades, with regional and intercountry differences.[58,59] This important change in emissions has driven changes in the chemical and physical characteristics of aerosols. The main difference is that NH_4NO_3 is now the dominant inorganic aerosol, and, unlike $(NH_4)_2SO_4$, NH_4NO_3 is volatile, and in warm climates readily dissociates to ammonia and HNO_3, both of which deposit rapidly, unlike their aerosol precursor. Thus, the atmospheric lifetimes of the two aerosols change due to the change in chemical form, and as climates warm the difference is amplified, effectively shortening the travel distance of the pollutants concerned.[57]

2.1.4. Methane. After carbon dioxide, methane is the most important greenhouse gas. It has a radiative forcing of +0.5 ± 0.05 W m^{-2}, about 28% that of non-CO_2 atmospheric

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constituents in 2010[60] (updated at http://www.esrl.noaa.gov/gmd/aggi/). CH_4 is a powerful infrared absorber; over a century it is 28 times more efficient per mass as a greenhouse gas than CO_2.[61] In addition, CH_4 is also important to the chemical state of the atmosphere, because its chemical destruction by reaction with the hydroxyl radical (OH) initiates a chain of reactions that can affect tropospheric air quality and ozone formation. The theoretical maximum yield of O_3 from one CH_4 molecule oxidized all of the way through to CO_2 and H_2O is 5 O_3 molecules. This maximum yield is never realized under actual atmospheric conditions because of competing reactions, but reality is closer to theory when NO_x levels are sufficiently high that the peroxy radicals (HO_2, CH_3O_2) react exclusively with NO and all of the formaldehyde (HCHO) formed is photolyzed by the radical path.[17]

$$\mathrm{HCHO} + h\nu \xrightarrow{2O_2} \mathrm{CO} + 2\mathrm{HO}_2 \tag{13}$$

HCHO and CO are important stable intermediates in the atmospheric chemistry process. The lifetime of CH_4 in the atmosphere is about 10 years, with estimates ranging from 9 to 11 years, with CO_2 the eventual product of its oxidation.[62−64] The atmospheric methane oxidation chain is depicted in Figure 5.

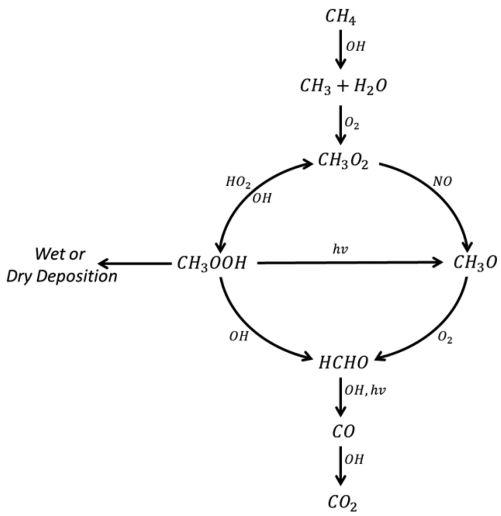

Figure 5. Methane oxidation mechanism. Reprinted with permission from ref 17. Copyright 2006 John Wiley & Sons, Inc.

The main sink for methane is reaction with OH. This chemical coupling leads to a significant amplification of emissions, because increased methane emissions decrease tropospheric OH, which increases the methane lifetime and thereby its concentration.[62,64] This then involves further climate and emission factors that influence the interannual variability of methane lifetime and/or the OH budget, such as temperature, water vapor, stratospheric ozone column, biomass burning, and lightning NO_x.[62] Global emissions of CH_4 are between 500 and 600 Tg yr^{-1}; see Kirschke et al.[65] or Prather et al.[63] Of the total emissions, 36% has been attributed to natural sources, mainly wetlands, while the other 64% of global emissions are due to microbial emissions associated with rice agriculture, livestock, and waste, and fugitive emissions from fossil fuel production and use.[63,66,67] From the late 1990s through 2006, global emissions were approximately in balance with global sinks, mainly chemical destruction by reaction with OH, but also from oxidation by soil microbes, and atmospheric reactions with O^1D and Cl in the stratosphere.[68]

Since preindustrial times, the global CH_4 mixing ratio has increased from 722 ± 4 ppb[69] (after conversion to the NOAA 2004 CH_4 standard scale[70]) to current values of about 1800 ppb in 2010 (an increase of 2.5 times). There is a very high level of confidence that anthropogenic activities caused the increase in atmospheric methane during the industrial era.[67] Current levels are unprecedented over at least the last 800 thousand years.[71] NOAA atmospheric network observations cover the last several decades, and show that global CH_4 increased rapidly through the late 1990s, leveling off during the early 2000s. This slowing of atmospheric concentrations prompted speculation that CH_4 was approaching chemical equilibrium, possibly earlier than could be accounted for given estimates of sources and sinks at that time.[72] However, CH_4 has recently started to increase in the atmosphere again since 2007.[68,73] The cause of the recent increase is not well understood and has been the topic of much recent work. Atmospheric inverse models suggest that increased emissions from tropical wetlands as well as increases in anthropogenic emissions are behind the recent increase.[74−76]

Emissions of CH_4 from natural wetland emissions are likely to be very sensitive to climate change. Some of the key drivers influencing wetland methane emissions are water table depth, soil temperature, and substrate availability and quality, as well as air temperature.[77] To model wetland ecosystems, and thereby estimate predicted changes under a future climate, the fundamental processes need to parametrized and modeled at an adequate level of complexity. However, many of these wetland ecosystem processes have not been studied in sufficient detail to allow them to be parametrized reliably, resulting in widely differing results from the limited number of studies carried out so far.[77]

Emissions from the Arctic, in particular, have the potential to increase significantly as soil temperatures rise and the vast stores of soil carbon thaw, releasing significant amounts of methane into the atmosphere (e.g., Harden et al.[78] or Schuur and Abbott[79]). Schaefer et al.[80] pointed out that these potential carbon emissions from the Arctic could have important implications for policies aimed at cutting emissions from fossil fuel use and production for a number of reasons. These reasons include that the permafrost carbon feedback loop is irreversible once initiated, and while the Arctic permafrost is currently a significant sink, the region could end up as a significant source with cumulative permafrost carbon flux estimates of 42−88% of the estimated cumulative global land sink for carbon. Furthermore, the release of permafrost carbon would continue for many years, even if atmospheric warming were to stop due to its huge thermal inertia, although the strength of this feedback loop very much depends on the amount of permafrost degradation that is predicted.[80] On the other hand, drying of tropical wetlands could lead to reductions in emissions.[67] For a more in depth discussion of expected changes in methane with regard to wetlands and permafrost under a future climate, please see O'Connor et al.[77]

A wide range of human activities affect atmospheric levels of CH_4. These range from food production (ruminants and rice) to disposal of food and other waste (sewage and landfills). Energy production from coal, oil, and gas results in

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varying amounts of CH_4 emissions during production, processing, storage, transmission, and distribution processes, as it is the primary component of natural gas, and often found alongside fossil fuels. Future increases in population could increase emissions from agriculture and waste as demand for food production rises, while the current boom in shale oil/gas exploitation has focused attention on activities related to the associated exploitation processes, such as leakage from drilling, storage, and transport of fossil fuel (e.g., Karion et al.[81] or Petron et al.[82] or Allen et al.[83]).

Currently, source and sink processes are not quantified accurately, and there are still large uncertainties on estimated emissions and losses. However, progress has been made using inverse modeling to quantitatively link regional sources and sinks, where emissions of CH_4 are inferred, along with photochemical sinks (OH concentrations), and matched to atmospheric observations, thereby reducing uncertainties.[84] For example, Bergamaschi et al.[74] recently used inversion techniques to evaluate changes in the methane cycle over the past decade, and found that global methane emissions have increased significantly since 2006, with much higher emissions during the 2007−2010 period as compared to the average emissions during the 2003−2005 period. Furthermore, inversion techniques allowed for the attribution of these increases spatially, to the tropics and midlatitudes of the Northern Hemisphere, and to largely anthropogenic sources.[74] In addition, significant interannual variations in CH_4 emissions from wetlands and biomass burning were identified that were superimposed on the increasing trend in anthropogenic CH_4.[74] It is clear that maintaining long atmospheric time series is crucial for trend detection, while increasing the spatial coverage of observations will improve the ability of atmospheric inversions to discriminate CH_4 sources (e.g., Bruhwiler et al.[76]).

2.1.5. Anthropogenic NMVOCs and CO. Total anthropogenic NMVOC emissions have been estimated at 129 Tg for the year 2000, although the quantification and attribution of sources can vary significantly depending on the estimate.[41,85] Road transportation, industrial sources, solvent use, and biomass burning are all significant contributors to NMVOC emissions. The adverse health effects of NMVOCs result from their contribution to ozone, but also from the toxicity of certain NMVOCs themselves. Certain NMVOCs, such as formaldehyde, benzene, or styrene, among others are (potentially) mutagenic or carcinogenic.[24,86] The majority of the toxic impacts of NMVOCs have been shown to be caused by a relatively few number of the NMVOCs (e.g., formaldehyde, acrolein, and furan), stemming from the transportation sector as well as residential sources, and often do not overlap with those that are the top ozone forming species.[86]

A comparison of different emission inventory estimates by Granier et al.[87] found that global CO emissions show similar patterns among the estimates with a variation in the spread among the total estimates, which for 2000 was about 28% between the lowest and highest value, ranging from ca. 500 to 600 Tg yr^{-1}. Combustion is the primary source of carbon monoxide emissions to the atmosphere, including both natural and anthropogenic sources, such as biomass burning and fossil fuel burning. Transportation and biomass burning are the largest contributors to anthropogenic emissions of CO.[24] Significant contributions also result from the atmospheric oxidation of methane and NMVOCs.

High concentrations (>1000 ppmv) of carbon monoxide may be lethal, with death resulting from asphyxiation. Lower concentrations have other adverse human health effects including headache, fatigue, nausea, and vomiting.[24]

Nonmethane volatile organic compounds and carbon monoxide contribute to positive RF (warming) through their role in ozone production, but also through an increase in methane lifetime. A number of studies have confirmed the relationship between increasing NMVOC and CO emissions and increasing RF via ozone and methane.[34,45−47,88,89] Given the general qualitative agreement among the published literature, only a few examples from more recent work are highlighted here, so as to provide quantitative information on the magnitude of the contribution to RF. The more complex role of NMVOCs from biogenic sources will be addressed separately. Shindell et al.[47] assessed emissions-based RF, and ascribed +0.25 W m^{-2} to CO and NMVOCs from 1750 to 2000, attributing this to changes effected in sulfate, methane, and ozone relatively equally, and a smaller contribution from resulting CO_2 changes, with a minor negative RF contribution from effects on nitrate. Aerosol indirect effects were not included. As part of the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP),[90] attribution experiments were done to attribute RF to the ozone precursor species. In these experiments, the change in RF from the 1850s to the 2000s was assessed. The RF for emissions of CO was attributed to the resulting influence that CO has on CO_2, CH_4, and O_3 for a total RF of +0.202 W m^{-2}, as shown in Table 1. The results from ACCMIP were the basis on which the latest IPCC RF values were based and therefore show significant similarities, but are not the same, as seen in Figure 3. It should be noted that the IPCC RFs covered a larger time span than those evaluated in Stevenson et al. (1750−2011 instead of 1850s−2000), which added 0.04 and 0.02 W m^{-2} to the period of 1750−1850 and 2000−2010, respectively.[33,34,64] For emissions of NMVOCs, a total RF of +0.090 W m^{-2} (as in Table 1) was attributed by the ACCMIP study, a somewhat smaller impact than that of CO.[34] Additional effects, such as changes in oxidants on secondary aerosol, were not included in the analysis.[34]

Table 1. Radiative Forcing Attributed to CO and NMVOCs over the Period from 1850 to 2000, As Reported in Stevenson et al.[34]

	total RF	from the resulting changes in		
		CO_2	CH_4	O_3
CO	+0.202	+0.087	+0.057	+0.058
NMVOCs	+0.090	+0.033	+0.022	+0.035

2.1.6. Biogenic NMVOCs. Volatile organic compounds (VOC) are emitted into the atmosphere from both anthropogenic and natural sources. It has been estimated that terrestrial vegetation emits about 1000 Tg of biogenic NMVOCs per year, which is roughly a factor of 8 higher than NMVOC emissions from anthropogenic sources.[41,91,92] Although vegetation produces thousands of different biogenic VOCs (BVOC),[93−95] species emitted in the largest amounts are isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$), sesquiterpenes ($C_{15}H_{24}$), and a number of oxygenated VOCs such as methanol, acetone, ethanol, and acetaldehyde.[91]

According to model estimates, the NMVOC global total expressed as emission of carbon consists of 70% of isoprene

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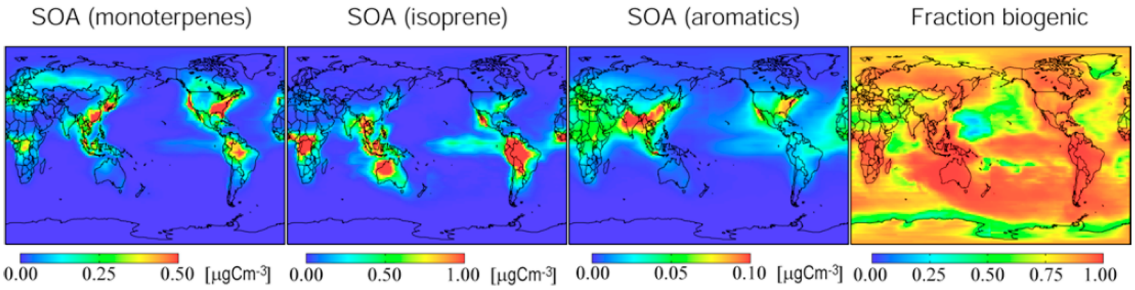

Figure 6. Comparison of modeled annual mean surface SOA concentrations (μg C m^{-3}) for the year 2000 formed from biogenic (monoterpenes and isoprene) and anthropogenic (aromatics) precursors. The fourth panel shows fraction of SOA from biogenic sources. Reprinted with permission from ref 18. Copyright 2012 Nature Publishing Group.

and 11% of monoterpenes. Methanol comprises 6% of the total, and sesquiterpenes together with acetone, ethanol, and acetaldehyde contribute with another 8%.[92] The uncertainty of BVOC emission totals is estimated to be within a factor of 2−3 based on different model approaches, variation of model input data, and comparisons of bottom-up to top-down inventories.[91,92] The surface ozone increase attributed to biogenic VOC emissions was identified by numerous model studies on both global[96−99] and regional[100−103] scales. The impact of biogenic VOCs is most evident in the vicinity of industrial and biomass burning areas where sources of BVOCs coincide with strong anthropogenic sources of NO_x.[98,103] Folberth et al.[96] estimate that the addition of surface O_3 induced by isoprene, the most abundant BVOC species, to the global O_3 budget increases global mean radiative forcing by +0.09 W m^{-2}. In the tropics, where BVOC emissions are most intense, the enhancement of radiative forcing can reach +0.17 W m^{-2}.

Under certain environmental conditions, reaction of peroxy radicals with NO produces organic nitrates, in particular peroxyacetyl nitrate (PAN). Because formation of PAN acts as a sink for both radicals and NO_x, it lowers the potential of surface ozone production in the source region.[14] However, as PAN is chemically more stable than NO_x, it can be transported over longer distances and thereby distribute NO_x to clean, remote environments. Thermal and chemical decomposition of PAN in such environments serves as an important source of nitrogen, which activates O_3 formation in locations distant from the original source of pollution.[104,105] Biogenic VOC emissions are a significant contributor to PAN formation.[106] A model study from Pfister et al.[98] showed that almost one-third of an annual global PAN burden is a product of isoprene oxidation, and at some locations isoprene chemistry contributes up to 60% to the total PAN column. The contribution is most profound in isoprene emitting regions (Amazon, Equatorial Africa, Southeastern U.S.) during summertime with significant increase of PAN over the oceans.[96] However, the mechanism of isoprene oxidation is not yet fully understood, and reaction rates and fate of isoprene nitrates in the atmosphere remain uncertain. Studies with global and regional chemistry models show that selecting either high yields in isoprene nitrate and permission of NO_x recycling or redirecting nitrates to NO_x sinks (e.g., formation of HNO_3, deposition) causes either increases or decreases in surface O_3 by about 5 ppbv.[101,107] Measurements of isoprene oxidation products in the field[108] and in the reaction chamber[109,110] aim to provide more detailed information on the oxidation processes and isoprene nitrate yields; such updates are also being successfully implemented in models.[111,112]

In unpolluted air with low NO_x concentration but with sufficient VOC sources, typically in remote forested regions, the troposphere is in the NO_x-limited regime.[17] VOC oxidation produces peroxy radicals, but the lack of NO_x inhibits formation of ozone. The presence of biogenic VOCs then leads to a decrease in the ozone concentration as it is consumed in the direct (VOC + O_3) reactions. Furthermore, removal of atmospheric oxidants (mainly OH) during VOC oxidation, as well as the radical−radical reaction that takes over under the low-NO_x conditions, reduces the oxidizing capacity of the atmosphere.[113] This has important climate related consequences because OH is a significant sink for methane (CH_4), a potent atmospheric greenhouse gas. Removal of OH, in this case induced by BVOC chemistry, increases methane's atmospheric chemical lifetime.[96,114] Nevertheless, recent observations in a pristine environment of the Amazon tropical forest report the above-canopy OH concentrations to be much higher than would be expected with BVOC-driven chemical mechanism described above.[115] The experimental data suggest the existence of an additional chemical pathway that would be responsible for OH-recycling. Taraborrelli et al.[116] proposed a new chain of chemical reactions that follows the oxidation of isoprene by OH in low-NO_x environments with sufficient loading of isoprene. The OH is recycled via the photo-oxidation of unsaturated hydroperoxy aldehydes, oxidation products of isoprene. In this way, isoprene acts as a stabilization factor by sustaining the oxidation capacity of the tropical forest.[115] In addition, HO_x generation from the Criegee intermediates generated from the reaction of ozone with isoprene is also a source of OH.[117]

In addition to their role in the tropospheric gas-phase chemistry, biogenic VOCs contribute to the formation of atmospheric aerosol, which is discussed in section 2.2. The oxidation products of some BVOC species can go through the gas-to-particle partitioning to form secondary organic aerosol (SOA),[14] thereby affecting the Earth's radiation budget directly as organic aerosol scatters the incoming solar radiation, and indirectly by forming cloud condensation nuclei;[119,120] see also sections 2.2.3 and 2.2.4. In earlier studies, only less volatile BVOC species such as monoterpenes and sesquiterpenes were identified in the smog chamber experiments to produce oxidized compounds that can transform to SOA.[121,122] Later experiments demonstrated that isoprene oxidation also contributes to the atmospheric SOA formation.[123,124] Even if the SOA yield for isoprene is small (1−3%), given the strength of the emission source, its

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contribution to global SOA total can be large.[125] Model studies attempted to estimate the global SOA totals and to determine the apportionment of anthropogenic and biogenic sources,[118,126−130] as shown in Figure 6. However, the global SOA budget remains uncertain, ranging from 12 to 1820 Tg(SOA) yr^{-1}. Spracklen et al.[131] constrained the SOA global total using measurements from a network of aerosol mass spectrometers and estimated the source strength of 140 Tg(SOA) yr^{-1} with about 13 Tg(SOA) yr^{-1} purely from biogenic sources. They suggest that a large portion of the SOA total (ca. 90 Tg(SOA) yr^{-1}) is anthropogenically controlled, that is, formed from biogenic precursors but due to enhancement from anthropogenic pollution. Higher concentrations of atmospheric oxidants (OH, O_3, or NO_3) in anthropogenically polluted regions amplify oxidation of biogenic VOCs to semivolatile species with SOA-forming potential. Also, primary organic aerosols (POA) serve as a medium for partitioning of biogenic VOC oxidation products from gaseous to a condensed phase. SOA production is therefore likely to be higher in regions with strong sources of POA, for example, from fossil fuel combustion. More detailed information on mechanisms of anthropogenic enhancement in biogenic SOA formation is reviewed in Hoyle et al.[132]

2.2. Aerosols

Aerosols are defined as the suspension of fine solid or liquid particles in a gas. Although not accurate, the term aerosols is often used to refer only to the particulate component of this suspension, used interchangeably with particulate matter (PM), which refers only to the particle phase.[17] Aerosols or aerosol particulate matter have a wide variety of anthropogenic and natural sources, and can be emitted directly or formed in the atmosphere from gaseous precursor species. Their lifetime in the atmosphere ranges from day(s) to weeks, and therefore their effects tend to be mostly local to regional.

In the context of air pollution and health effects, particulate matter is traditionally referred to and regulated using the operationally defined concepts of PM_{10}, $PM_{2.5}$ (fine particulate matter), and sometimes PM_1 (ultrafine PM), which stand for mass concentrations of aerosol particles with aerodynamic diameters of less than 10, 2.5, or 1 μm, respectively. However, some of the health and climate effects of aerosols are more closely related to or depend on the particle number concentration (PN). The largest number concentrations are typically encountered in ultrafine particle size range. Because the mass of a particle is coupled with the diameter to the power of three, especially the mass concentrations of PM_{10} and $PM_{2.5}$, but usually also PM_1, are typically determined by a relatively small number of particles at the larger ends of the corresponding size scales.

Aerosol particles and particulate matter are introduced to the atmosphere either directly as (primary) particles or indirectly in the formation of secondary aerosol from vapors in the air. Secondary formation indicates both condensation of vapors on pre-existing particle surface and new particle formation (NPF), that is, nucleation process, in which new particles with diameters below 2 nm are formed from clustering of vapor molecules (e.g., Kulmala et al.,[133] Weber et al.[134]). In this Review, we use terms primary emissions and particles for both the particles that are emitted to the atmosphere directly as particles and those that form, for example, in the exhaust plume immediately after emission, during the initial rapid cooling and dilution of the plume.

As a pollutant, PM is the cause of a variety of adverse human health effects, including premature mortality and morbidity, pulmonary disease, asthma, and other respiratory related illnesses, with chronic effect studies finding that long-term exposure to PM dominates the population health burden.[135] The relationship between particle mass concentrations (e.g., $PM_{2.5}$) and adverse health effects has been established (e.g., Dockery and Pope,[136] Pope et al.[137]). In addition to the traditional association between respiratory symptoms and fine particle mass concentrations, there is increasing evidence on the effects of ultrafine particles (aerosol number concentration) on the cardiorespiratory health and central nervous system.[138] New evidence linking the adverse health effects and the chemical composition of PM has also been presented.[138]

In addition to the health impacts, PM causes other adverse effects, such as damage to ecosystems and cultural sites, and reduced visibility. As climate forcers, aerosols can affect radiation either directly via aerosol−radiation effects or indirectly via aerosol−cloud effects. Aerosol−radiation effects result from the absorption or scattering of radiation by aerosol particles, whereby radiation absorbed by black carbon particles contributes to warming the atmosphere and the solar radiation scattered by the other aerosol components tends to cool the Earth's surface. Aerosol−cloud effects are based on the capability of aerosol particles with diameters over 50−100 nm to act as cloud condensation nuclei (CCN), which are activated to form cloud droplets in rising air masses. Because a larger number concentration of cloud droplets leads to higher cloud albedo (i.e., back scattering of solar radiation back to space) and longer cloud lifetime, the concentration of CCN sized particles is a driver for cooling mechanism shading the planet from solar radiation by clouds.[139,140] Hygroscopicity is an important characteristic for particles acting as CCN. The hygroscopicity parameter, κ, indicates the relative hygroscopicity, or relationship between particle dry diameter and CCN activity, of individual aerosol constituents, known mixtures, or complex atmospheric aerosols; κ values typically range for inorganic salts from 0.5 to 1.4, for organic species and their mixtures from 0.01 to 0.5, and for atmospheric particulate matter from 0.1 to 0.9, with 0 indicating nonhygroscopic components and 1.4 indicating highly-CCN-active.[141]

The emissions of aerosol particles and their precursors to the atmosphere have increased significantly after industrialization, simultaneously with increasing greenhouse gas emissions.[4] The resulting increase in aerosol concentrations has masked the global warming to some extent.[33,142] More specifically, a recent study estimated the changes from preindustrial to present day in tropospheric ozone and aerosols finding that overall the aerosol changes dominate the positive forcing of the ozone increases, resulting in a masking of nearly one-half the forcing from long-lived GHGs.[143] Furthermore, two studies recently investigated the impact of emission reductions following RCP4.5, finding that in this scenario approximately one-half the warming (or ca. 1 °C) by the end of the 21st century is due to reductions in anthropogenic aerosols.[144,145] Overall, the latest IPCC estimate of effective RF attributes −0.9 [−1.9 to −0.1] W m^{-2} to anthropogenic aerosols, which reflects both the warming and the cooling contributions, and includes the aerosol−cloud effects. (Effective RF is defined as the change in net top-of-the-atmosphere downward radiative flux after

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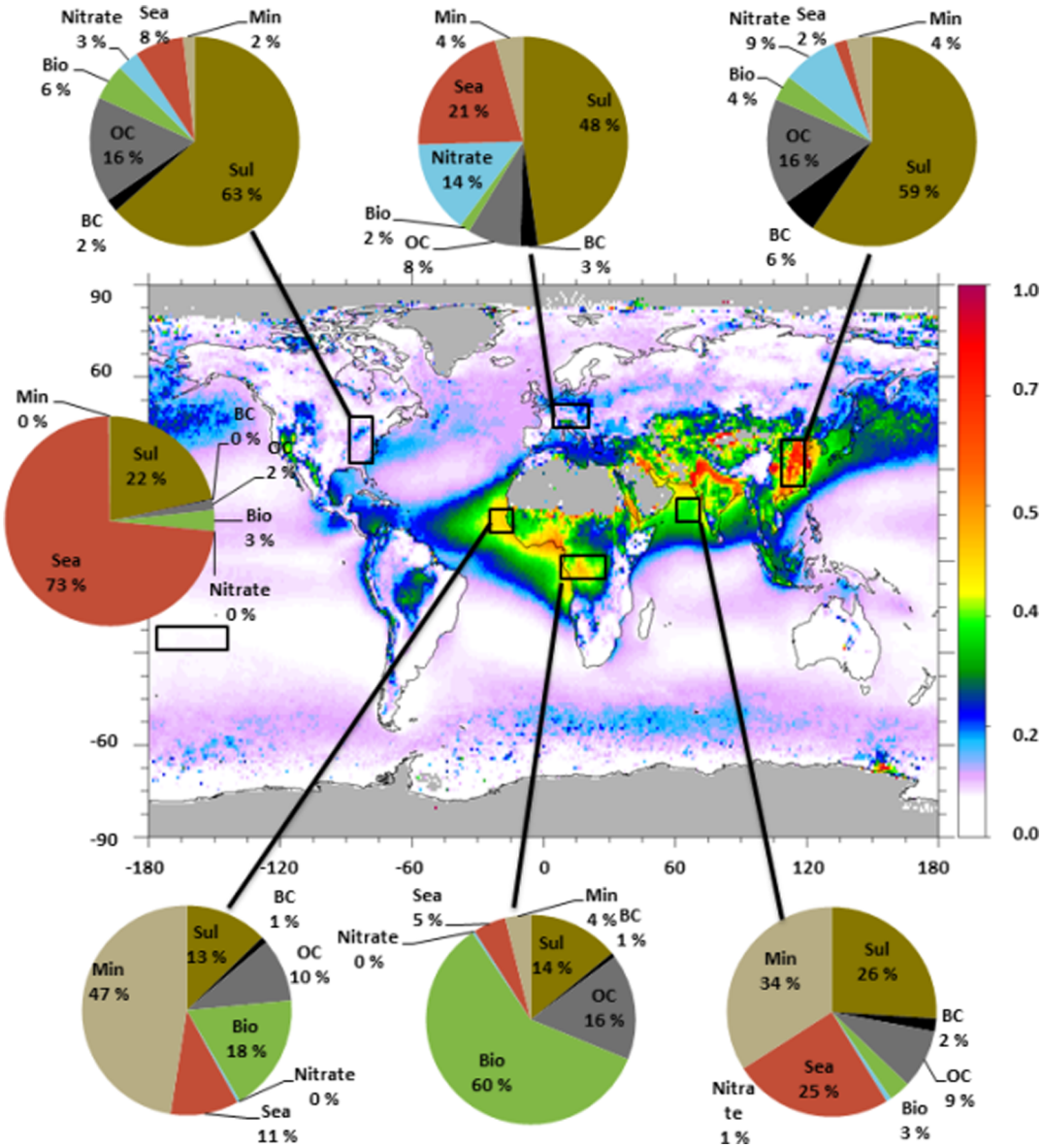

Figure 7. MODIS aerosol optical depth and contributions of the various aerosol types to the total AOD for different regions. MODIS aerosol optical depth [AOD (550 nm); dimensionless] averaged over the 10-year period 2001–2010.[147] Pie charts indicating relative aerosol-type contributions as estimated by a global aerosol model.[148] Aerosol types are Sul (sulfate), BC and OC from fossil fuel usage, Bio (OC and BC from biomass burning), Nitrate, Sea (sea salt), and Min (mineral dust). Gray areas indicate lack of MODIS data. Some aerosol types, for example, sulfate, have enhanced contributions to AOD due to hygroscopic growth. The contribution from OC is likely underestimated as in most of the global aerosol models.[149] Reproduced with permission from ref 150. Copyright 2013 Nature Publishing Group.

allowing for atmospheric temperatures, water vapor, and clouds to adjust, but with surface temperature or a portion of surface conditions unchanged.[64]) The anthropogenic negative radiative forcing (i.e., cooling) due to the aerosol–cloud effects and scattering is estimated to exceed the positive (warming) aerosol–radiation effect of black carbon aerosols. There is a high amount of uncertainty associated with the impact of aerosols on climate change overall.[33]

The health and climate effects of aerosol particles depend on the chemical composition and physical properties, that is, concentration and size distribution, of the aerosol. The depth of penetration and penetration efficiency of aerosols into human lungs depend greatly on particle size (e.g., Alföldy et al.[146]). The ultrafine particles can enter especially deep into the alveoli in the lungs, and from there affect the cardiorespiratory health and central nervous system. On the other hand, the aerosol–cloud (climate) effects depend on the number concentration of particles with diameters close to or over 100 nm, which is typically dominated by particles with diameters well below 1 μm in the boundary layer. The variation in aerosol composition influences both the climate impacts and the health effects, adding a layer of complexity. Figure 7 presents an overview of the variation in aerosol composition. In this Review, more detailed discussion has been split up by aerosol component.

2.2.1. Sulfate. Together with organic aerosols (section 2.2.3), sulfate aerosol is a key component of fine particulate matter ($PM_{2.5}$). The main sources of sulfate aerosol in the atmosphere are SO_2 emissions from fossil fuel burning, mostly from industry, power plants, and shipping, with a minor

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contribution from biomass burning,[41] and from natural sources, including dimethyl sulfide (DMS) oxidation from the ocean[151] and volcanic emissions.[152] Global anthropogenic emissions of SO_2 were estimated to be 51.5 (49−55) Tg(S) for 2010, with the largest contributions coming from the energy sector and industry, followed by international shipping.[58] Natural emissions of DMS amount to 10−40 Tg(S) yr^{-1},[153] whereas volcanic emissions of SO_2 are in the range of 4−20 Tg(S) yr^{-1}.[154] Given its relatively short residence time, on the order of a few days,[155] the global distribution of aerosol sulfate closely matches the pattern of emissions. Global model simulations as well as observational data from several networkstations in the Northern Hemisphere (Pringle et al.,[156] Righi et al.[157] and references therein) report the highest surface-level sulfate concentrations (∼5−10 $\mu g\ m^{-3}$) in East Asia and significantly high values in the other urbanized regions of the world (Europe and Eastern U.S., ∼2−5 $\mu g\ m^{-3}$). For emissions over the open ocean, shipping is the main anthropogenic source, which is the source of significant sulfate emissions, along with DMS emissions; the role of shipping will be highlighted in this section because of the particular implications for climate, going so far as to inspire geo-engineering studies utilizing SO_2 emissions from shipping, within the broader context of sulfate aerosols.

The main formation path of sulfate aerosol in the troposphere is via oxidation of sulfur dioxide (SO_2) to sulfuric acid. This can occur both in the gas phase (involving the OH radical or stabilized Crigee intermediate)[18] and in the liquid phase inside cloud droplets (involving H_2O_2 and ozone). Gas-phase sulfuric acid is a key element in atmospheric new particle formation processes.[133,134] Sulfate aerosol particles interact with incoming solar radiation via scattering processes, resulting in a global cooling effect. The recent IPCC AR5[64] reported a global sulfate-induced RF from aerosol−radiation interactions of −0.41 [−0.62 to −0.20] W m^{-2} (direct aerosol effect only). Sulfate aerosol particles can also mix with other compounds and grow through coagulation, reaching larger diameters where they can be activated as cloud droplets, given their relatively high hygroscopicity.[158] The RF derived from such aerosol−cloud interactions (from all aerosols, not just sulfate) produces a global cooling effect of −0.45 W m^{-2}, albeit with large uncertainties [−1.2 to 0.0 W m^{-2}].[33] Most of the current global climate models include online representation of the sulfur cycle and of particle formation and growth, as well as parametrizations of the cloud droplet activation.[155,159]

As a component of PM, the health effects outlined earlier for aerosols (section 2.2) also apply to sulfate. However, in addition, SO_2 emissions have adverse effects on ecosystems through acid deposition. Industrial emissions of SO_2 and deposition through precipitation to soils and water bodies lead to adverse effects on aquatic ecosystems, forests, and other vegetation, and damage to materials and structures, such as declines in fish populations and decreased forest growth.[17,24] (Adverse acidification effects similar to those of SO_2 can also result from NO_x emissions; see section 2.1.2.) Air pollution control measures have been implemented in North America and Europe since the 1970s, to reduce sulfur emissions and improve air quality, spurred in part by issues related to acidification from SO_2 emissions. An example is the U.S. Clean Air Act, addressing, among others, the SO_2 emissions from power plants and industrial sources.[160] Such measures led to a general decrease in the sulfate loading in Europe and North America in the last decades of the 20th century.[58,161] The Representative Concentration Pathways (RCPs) developed in support of the IPCC AR5[162] and used in the model simulations of the Coupled Model Intercomparison Project Phase 5 (CMIP5[163]) project a decrease in emissions in the developed countries for the next decades and throughout the 21st century.[164] Fast-growing countries in South East Asia, on the other hand, are still affected by substantially growing emission of SO_2, which are assumed to peak and eventually decrease at some point between 2010 and 2040, depending on the scenario.[164] This explains the large regional differences found by model simulations of sulfate aerosol concentrations trends under the RCPs.[161,165−167] However, it has been noted that short-lived species in the RCPs do not span the possible range of air pollution futures and are therefore not suitable to assess possibly future air-quality developments.[164,384] Alternative scenarios, such as the Shared Socioeconomic Pathways (SSPs), were also developed, which are built around the climate forcing as represented by the RCPs, and alternative plausible trajectories of future global development that considering socio-economic factors such as population growth by age, sex, and education, urbanization, and economic development.[168]

In the context of sulfur emission control measures, coal-fired power plants are significant sources, due to the relatively high sulfur content of coal, varying between 0.5% and more than 3%.[169] Coal is the single largest primary energy input to electricity generation, producing about 40% of world electricity.[170] In the past decade, coal production in China increased by about 50% driving the bulk of world increase.[170] Large reserves of coal will still be available for more than a century, resulting in an expected growth in coal-fired power plants for the next decades, with China and India sharing 80% of such projected growth.[171] Available technologies, such as postcombustion scrubbing, which can remove more than 95% of SO_2 emissions,[172] could reduce global anthropogenic SO_2 emissions by 80% as compared to 1990 if fully implemented.[173] Such methods are well established in U.S. power plants, which resulted in the steady decrease of SO_2 emissions from this source since 1990.[59] Scrubbers are now being increasingly implemented in China,[174,175] so that a significant decrease in SO_2 energy-sector-related emissions starting already in 2005 is expected.[58]

Another sector with a large pollution reduction potential is international shipping, which has received little attention until recently. Within the past 2 decades there has been growing recognition of shipping as a significant source of pollution.[176−178] Ocean-going ships of various types contributed about 13% of the global SO_2 emissions from all anthropogenic sources in 2010,[58] although they accounted for only 2.7% of global CO_2 emissions in the same year.[179] The reason for such a high share is the relatively low quality of ship fuels, characterized by a very high fuel sulfur content (FSC), typically ranging between 1.9% and 3.1%, with a global average of 2.7%.[180] For comparison, the FSC of aviation fuels ranges between 0.001% and 0.1%,[181] and the maximum allowed FSC for land transport is 0.001% by European regulations.[182] In pristine marine regions, shipping is the only anthropogenic source of sulfur and has therefore a large impact on sulfate aerosol concentration.[183] Moreover, nearly 70% of shipping emissions occur within 400 km of land,[176] hence significantly affecting the air quality and thereby ecosystems and populations near the coastlines. The modeling

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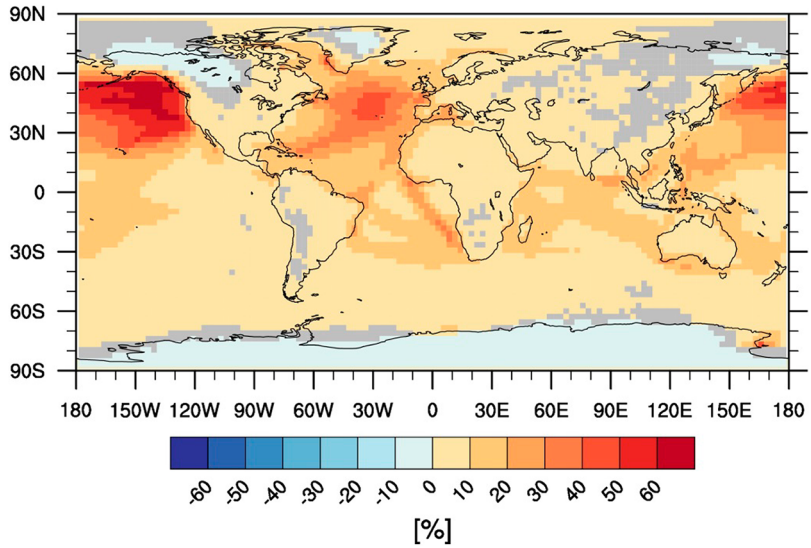

Figure 8. Multiyear average (1996−2005) of the relative contribution of shipping to aerosol sulfate, simulated by the EMAC-MADE global aerosol model using CMIP5 emissions for the year 2000. Nonsignificant grid points (according to a univariate *t* test with 5% error probability) are masked out in gray. Adapted with permission from ref 157. Copyright 2013 European Geosciences Union.

study by Capaldo et al.[184] showed that shipping contributes 5−30% of the nonsea salt sulfate concentrations near the coastlines of the Northern Hemisphere. Similar values were found more recently by Righi et al.,[157] using a global aerosol model with the CMIP5 emissions data[41,185] as input (see Figure 8). The assessment by Cofala et al.[173] showed that in many harbor cities ship emissions are a dominant source of urban pollution, which must be taken into account when addressing air quality threshold values for fine particulate matter. Using model-simulated ship-induced particulate matter concentrations and exposure functions, Corbett et al.[186] estimated a worldwide cardiopulmonary and lung cancer mortality between 19 000 and 64 000 for the year 2002, with the largest effects in Europe and East Asia, and a projected increase of 40% up to 2012 due to growing traffic volumes. Furthermore, sulfur emissions from shipping can damage the environment, due to sulfate deposition and consequent acidification of the ecosystems and water resources.[173]

Reducing sulfate concentrations has a positive impact on air quality and health issues, but also impacts on climate through changes to the radiative balance of the Earth. Sulfate aerosols have a negative RF, or cooling effect, which also means that reductions in sulfate aerosols could lead to rapid near-term warming (although this could be partially offset by reductions of short-lived warming species, such as BC). More specifically, sulfate particles from ship emissions are extremely efficient climate-forcers: due to the rapid coagulation process inside the ship emission plumes, sulfate particles can grow and reach sizes of about 100 nm within minutes after the emissions[187] where they can be activated as cloud droplets. They therefore have a large potential for perturbing the microphysical and optical properties particularly of low-level marine clouds such as marine stratocumulus clouds.[188] Ship-emitted sulfate particles thereby have a large potential for perturbing the microphysical and optical properties of low marine clouds.[188] Shipping-induced RF effect has been estimated to be in the range from −0.737 to −0.047 W m^{-2} by a number of modeling studies (including direct and indirect effects),[157,184,189−191] although large uncertainties exist and a supporting analysis from satellite data is still lacking.[192−194] Discrepancies in the different RF estimates result from a variety of factors including which effects are considered, as well as models and approaches, often making the different RF estimates difficult to reconcile and compare. This represents a substantial fraction of the total RF from aerosol−cloud interactions, which effectively counteracts the warming effect from CO_2 on the global mean, although with regionally disparate effects.[190]

2.2.2. Black Carbon. As the main component of soot, black carbon (BC) is a component of fine particulate matter ($PM_{2.5}$). BC particles are emitted from incomplete combustion of carbonaceous matter and carbon-based fuels.[195] Important sources include forest and savanna burning, residential biofuel burning, fossil fuel combustion, industrial processes, and power generation. The global annual total of BC emissions for the year 2000, estimated from bottom-up methods, amounts to 7.5 (2−29) Tg.[196] Major contributions come from open burning (about 40% of the global total), combustion of residential solid fuels (25%), diesel engines (20%), and industrial coal (9%).[196] Typical monthly mean concentrations of BC observed in the atmosphere range from 0.01 to 0.1 μg m^{-3} in the Arctic[197] to 10 to 15 μg m^{-3} in some polluted regions in Asia.[198,199]

BC particles are largely in the size range of the Aitken mode (i.e., less than 100 nm in diameter), and the accumulation mode (diameters between about 100 nm and 1 μm). Observed particle sizes range between 30 nm for particles formed by efficient and high temperature combustion such as aircraft engines,[200] 50−80 nm (count median diameter, CMD) in fresh urban plumes,[201] and about 120 nm (CMD) in plumes of wild fires.[202]

BC is characterized by its strong absorption of visible and near-infrared light and by its resistance to chemical transformation.[203,204] Common measurement techniques for carbonaceous aerosol use their optical properties or light absorbing characteristics (optical or light absorbing methods) to quantify the light absorbing component (often referred to as BC) or the thermal and chemical stability (thermal-optical methods) to determine the refractory (nonvolatile) component of these particles (commonly referred to as elemental

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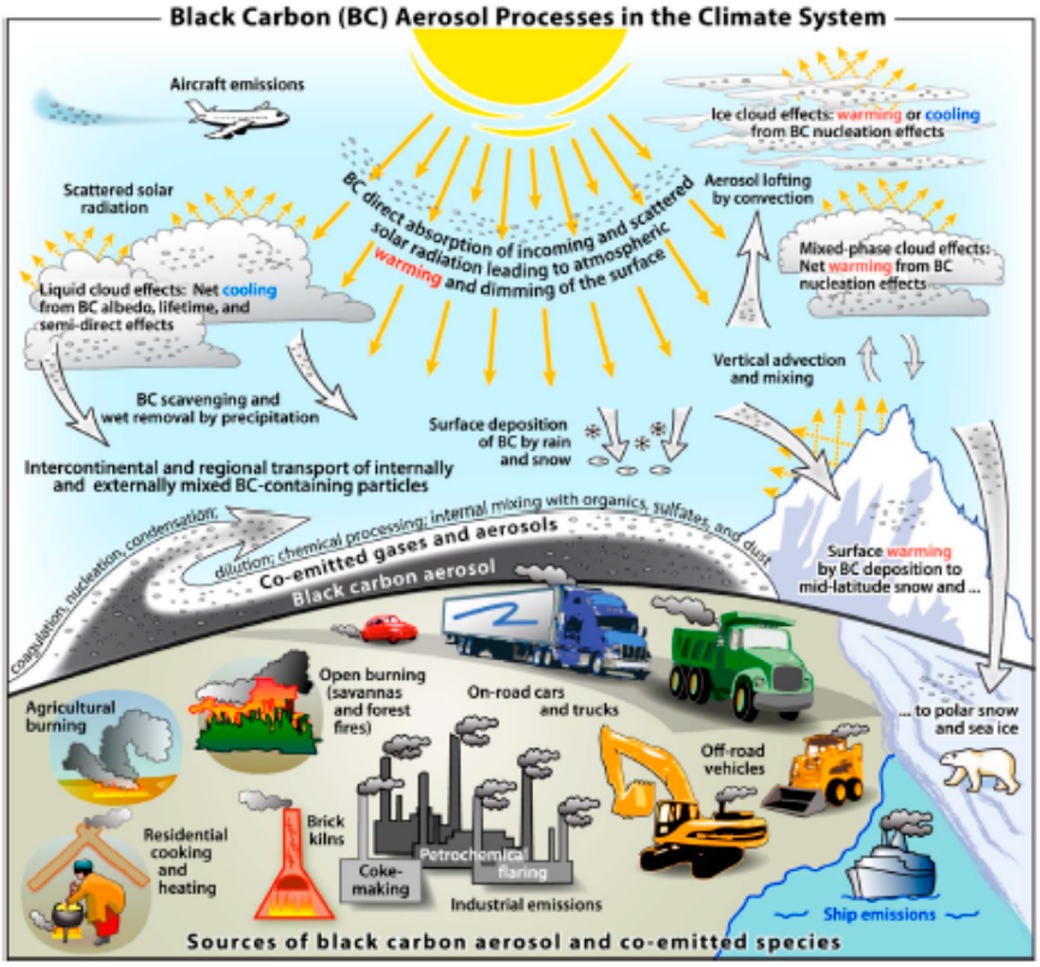

Figure 9. Schematic overview of the primary black carbon emission sources and the processes that control the distribution of black carbon in the atmosphere and determine its role in the climate system. Reprinted with permission from ref 196. Copyright 2013 John Wiley & Sons, Inc.

carbon, EC). Currently, there is no agreed and unambiguous terminology for quantifying carbonaceous matter in atmospheric aerosols in the scientific literature,[205] and all definitions used refer to a specific characteristic of the carbonaceous aerosol fraction or to the measurement method applied.[196,206,207]

Black carbon, as a component of fine PM, is associated with several adverse effects on human health (section 2.2). These include respiratory and cardiovascular morbidity, such as aggravation of asthma, respiratory symptoms, and an increase in hospital admissions as well as mortality from cardiovascular and respiratory diseases and from lung cancer, with links between the cardiovascular health effects and premature mortality from both short- and long-term exposures to black carbon particles specifically.[138,208] Some empirical evidence suggests that long-term exposure of $PM_{2.5}$ containing a high BC fraction may have larger mortality effects than other $PM_{2.5}$ mixtures.[209]

The efficient absorption of solar radiation by BC makes these aerosols the most important light absorber in the atmosphere. In addition to absorbing light while being suspended in the atmosphere, BC can reduce the amount of reflected sunlight when deposited on high albedo surfaces such as snow and ice, hence accelerating snow and ice melting, as depicted in Figure 1. By some estimates, emissions of BC are thought to be the second strongest contribution to the current radiative forcing driving global warming after carbon dioxide.[210] However, the exact climate forcing of BC is still under debate. In addition to highly uncertain anthropogenic emissions of BC, particularly the long-range transport and processes affecting the atmospheric lifetime of BC, are still poorly understood, resulting in a range of different estimates for the climate forcing of BC (e.g., Samset et al.[211]). The IPCC's AR5 reports a radiative forcing estimate for BC from fossil fuel and biofuel of +0.4 [+0.05 to +0.8] W m^{-2}.[153] For biomass burning such as forest and savanna burning, the IPCC includes both BC and organic aerosol (OA) species into the estimate for the RF, as large amounts of OA are coemitted with BC by these emissions sources. Sources emitting BC almost always emit OC as well, although the relative contributions of BC vs OC will vary significantly depending on the source. Of all major BC sources, diesel engines have the lowest coemissions of OC with a ratio of OC:BC of approximately 1:1; coemissions of SO_2 strongly depend on the fuel sulfur content.[196] In contrast, open burning has the highest average ratio of coemitted OC of all major source sectors. The ratio of OC:BC ranges between 4 and 14 (interquartile range) depending on the burning conditions and the material burned.[212] As BC and OA contribute to the RF with opposite signs, the resulting net RF in the case of biomass burning is close to zero.[64,196] The present-day RF from BC on snow including terrestrial snow,

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sea ice, and snow on sea ice is estimated as +0.01 to +0.08 W m^{-2}.[153] The forcing is largest on boreal terrestrial snow and during March to May because of the strong insolation.[213] The highest forcing in spring rather than in summer per unit mass of Arctic BC is a consequence of higher underlying albedo during spring because of greater snow and sea-ice coverage and brighter snow and ice albedo during the premelt season (e.g., Flanner et al.,[214] Perovich et al.[215]). Besides these interactions of BC with radiation (direct effect), BC particles may also interact with clouds changing cloud cover, emissivity, or cloud albedo (aerosol−cloud effects or semidirect and indirect effects). Absorption and local heating by BC can change the vertical temperature structure of the atmosphere, which can then affect the cloud distribution (semidirect effect).[216] In addition, aged BC particles can act as cloud condensation nuclei (CCNs) during cloud formation and change the number concentration of liquid cloud droplets as well as changing the ice particle concentration, which in turn affects the radiative properties of the clouds as well as their precipitation formation efficiency and lifetime (indirect effects).[217] Freshly emitted BC particles are generally hydrophobic,[218] which prevents them from acting as efficient CCNs. In the atmosphere, BC can become internally mixed with other aerosol components through condensation of condensable vapors such as sulfuric acid or certain organic compounds onto the particles, coagulation, and photochemical oxidation processes. These "aging" processes alter the optical properties of BC, its atmospheric lifetime, and its ability to act as cloud condensation or ice nuclei (e.g., McMeeking et al.[219]). For instance, internal mixing of BC with nonabsorbing compounds increases the absorption of solar radiation.[220] Internal mixing with water-soluble compounds converts the initially hydrophobic BC into hydrophilic particles, which are then able to serve as CCNs[17] and have a higher wet scavenging efficiency and thus a shorter average atmospheric residence time as compared to hydrophobic BC.[221] An overview of the processes outlined here is depicted in Figure 9.

Global model estimates for the combined RF of BC via semidirect and indirect effects on liquid clouds are −0.2 [−0.61 to +0.1] W m^{-2}; the ice cloud indirect effect has been estimated as 0 ± 0.4 W m^{-2}. The total impact of BC on clouds may cause either positive or negative RF, and all aerosol effects on clouds are still highly uncertain.[196]

Black carbon is an important driver for a number of impacts on the climate system, and at the same time emissions of BC are linked to premature mortality and disability making it of concern for local air quality.[222] Reducing the emissions of BC could therefore be not only a possible strategy to mitigate global warming,[223,224] but would also directly benefit human health by improving air quality.

2.2.3. Organic Aerosol. Organic aerosol (OA), referring to the carbonaceous particulate matter other than black carbon, is typically a significant fraction of PM in both polluted and pristine environments; the relative contribution to PM varies significantly depending on location (as shown in Figure 7). It is also commonly referred to as organic carbon (OC) or organic matter (OM), with the distinction being that OM contains other elemental components in addition to carbon, for example, hydrogen, oxygen, nitrogen, and sulfur. In polluted environments of the Northern Hemisphere, OA is often the dominant component with mass concentrations comparable to that of sulfate.[225,226] In more-pristine tropical and boreal settings, OA generally dominates, making up to 90% of the fine-mode aerosol mass burden.[227−229]

OA arises via both direct emissions to the atmosphere, referred to as primary OA (POA), and via chemical processes whereby gas-phase volatile organic compounds (VOCs) undergo oxidation reactions and condense to form secondary OA (SOA). On global scales, biomass burning represents the dominant source of POA and is characterized by strong seasonality and significant interannual variability.[212] In urban settings, POA is typically associated with traffic exhaust emissions, with initial particles sizes peaking below 100 nm.[230−233] Additional sources of POA include biofuels, cooking, bioarticles such as pollen, bacteria, and plant debris, sea spray, and soils. SOA is formed when condensable organic vapors form particulate matter either via condensation on pre-existing particles or via nucleation process. In both processes, the volatile organic compounds (see sections 2.1.5 and 2.1.6) go through atmospheric oxidation, which causes a decrease in volatility. The condensational growth due to SOA formation is the main player in the atmospheric growth of aerosol particles.[234−236] In the nucleation process, vapor molecules form small clusters of a few nanometres (<2 nm), which can grow via condensation and coagulation processes to form CCN-sized particles (>50−100 nm). Extremely low volatility organic compounds (ELVOCs) from oxidation of biogenic emissions have recently been shown to participate in the initial nucleation process together with sulfuric acid (and other) molecules in a number of environments.[22,133,237,238] Note that even in this instance only a small minority of SOA formed will participate in the actual nucleation, with the majority condensing onto existing particles, which may include those from a recent nucleation burst.

SOA is shown to outweigh POA in multiple field studies of OA composition that encompass urban, rural, and remote environments.[226,239] Furthermore, the dominance of SOA has been observed to increase with distance from major emission sources, which is consistent with continued chemical processing of VOCs downwind.[225,240] However, numerical models currently provide mixed results in terms of the dominance of SOA, which is linked to deficiencies in the understanding of its sources, formation processes, and evolution in the atmosphere.[128,241,242] The most recent AeroCom evaluation of the current status of global modeling of OA[241] showed that the modeled POA burden was relatively consistent across models as the concentrations are closely tied to emissions. However, there was much larger diversity in terms of the SOA burden due to the substantial differences in the chemical schemes applied.

OA is known to arise from both anthropogenic and biogenic sources, but the quantitative attribution to these emission sources is a significant deficiency in current understanding of OA.[128] So that these relative contributions can be determined with confidence, it must be demonstrated that processes governing both primary and secondary sources of OA are well represented in models. The median global POA source strength based on the AeroCom evaluation[241] was 56 Tg yr^{-1}, with a range from 34 to 144 Tg yr^{-1}. The combined biogenic and anthropogenic median SOA source strength was 19 Tg yr^{-1}, with a range from 13 to 121 Tg yr^{-1}. These estimates are in contrast to the statement that SOA outweighs POA, in this case because of the aforementioned reason that there are significant deficiencies in the under-

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standing of its sources, formation, etc., as well as a diversity in chemical schemes that provide SOA estimates. Furthermore, aerosol models typically attribute the majority of SOA to biogenic sources, with SOA formation from anthropogenic VOCs sometimes neglected by numerical models. However, known sources and processes relating to biogenic SOA formation are unable to balance the measured abundances of OA. Estimates of the anthropogenic contribution to SOA vary widely; an additional ~100 Tg yr^{-1} of anthropogenically controlled SOA would be required to match aerosol mass spectrometer observations from the Northern Hemisphere.[131,243] Numerous studies downwind of major urban conurbations have shown that substantial SOA formation occurs,[244−248] which would support an anthropogenically controlled contribution. However, observational studies[249−251] based on ^{14}C measurements in Europe and the U.S. have demonstrated that nonfossil carbon dominates outside of urban areas, which is suggestive of a biogenic source. Such studies potentially point toward SOA formation via a combination of anthropogenic and biogenic emissions, whereby biogenic VOC emissions reacts with anthropogenically perturbed oxidants to form SOA.[132] Such a process has previously been identified in the southeastern U.S.[252,253] The addition of anthropogenic or anthropogenically controlled SOA may be one means of addressing the inconsistencies between observations and numerical models, although constraining such processes presents a challenge and the uncertainties are currently large.

The global burden of biomass burning OA (BBOA) is substantially underestimated in models.[196,254,255] Factors ranging from 2 to 5 are typically required for model biomass burning aerosol, which is dominated by BBOA, to match aerosol optical depth observations.[254,255] A recent modeling study[256] focused on vegetation and peat fires in South East Asia found that comparisons with observations were improved when small fires observed by satellites were taken into account by emission inventories, although modeled concentrations were still biased low. Measurement studies of biomass burning in both the laboratory and the field have illustrated the vast range in BBOA emission factors at source.[257−259] In contrast to measurements downwind of urban emissions, BBOA shows limited mass enhancement downwind, which suggests that there is little net addition of SOA due to atmospheric aging. However, the BBOA does become progressively oxidized as the distance from the initial source increases.[258]

The semivolatile component of SOA has received significant focus as a means of potentially closing the gap between measurements and models. This class of organic compounds is not very well represented in explicit chemical schemes but can represent a large fraction of the particulate organic matter, particularly after they have undergone chemical processing that further reduces their volatility. The volatility basis set (VBS)[260,261] approach characterizes organic species by their volatility and treats POA emissions as semivolatile, which results in the initial particulate material partially evaporating upon atmospheric dilution and undergoing oxidation processes, resulting in the formation of so-called "intermediate" VOCs (IVOCs) in the gas phase. These IVOCs form a large reservoir of organic compounds that can repartition to the particle phase subsequent to chemical processing. Implementation of the VBS approach in atmospheric models has typically increased predictions of SOA formation and narrowed the gap between modeled concentrations and measurements. However, there are large uncertainties regarding the volatility profile of the wealth of POA sources that is required for this application, with model representations often highly tuned to the environment of interest.[262,263] The approach is highly sensitive to these initial assumptions regarding OA volatility, which is complicated by IVOCs being extremely challenging to measure quantitatively. As a result, evaluation of the VBS approach is lacking measurement input and constraint, although new measurement techniques are currently developing in this regard.[264,265]

Recently discovered rapid atmospheric auto-oxidation process of volatile organic compounds to form extremely low volatility organic compounds (ELVOCs) may partly explain the discrepancies between the measured and modeled amounts of SOA. Ehn et al.[22] reported that the initial oxidation reaction between common biogenic VOCs and ozone or OH-radical is followed by auto-oxidation reactions, in which oxygen molecules further oxidize the VOCs, thus forming highly oxidized ELVOCs in the time scale of seconds from the oxidation reaction.[23] In contrast to the previous understanding, these studies show that the ELVOC formation from ozone oxidation leads to significantly higher molar ELVOC yields (6−8%) in comparison to the yields from OH-oxidation (~1%). They also show that the ELVOC formation can explain the observed aerosol particle growth in rural boreal forest regions.

OA can both scatter and absorb solar radiation (depending on its composition), which complicates assessment of its overall climate impact. Of the optically absorbing types of OA, absorption is biased toward shorter wavelengths, with the OA being typically referred to as "brown carbon".[266,267] While the volume-weighted strength of the absorption is relatively weak as compared to BC, the overall abundance of brown carbon in atmospheric aerosol may elevate its impact from a warming perspective. Quantification of the absorptive properties and abundance of brown carbon is challenging with current measurement techniques; ground[268] and airborne measurements[269] in the U.S. suggested brown carbon contributed 20−40% of the total absorption. Furthermore, the airborne measurements indicated that its relative abundance increased with altitude, suggestive of a secondary formation process. OA is typically weakly hygroscopic as compared to inorganic species, with the hygroscopicity parameter, κ, typically ranging from 0.0 to 0.22.[141] Some studies have suggested that the hygroscopicity of OA increases with atmospheric aging,[225,270,271] although conflicting results are present in the literature[272] and the relationship appears to be system dependent.

Overall, the radiative forcing due to aerosol−radiation interactions for POA and SOA in AR5 of the IPCC was −0.12 [−0.4 to +0.1] W m^{-2}.[33] The level of radiative forcing estimated by numerical models is strongly dependent upon the mass burden of OA, which varies greatly across model simulations. OA emissions and precursors are often associated with numerous other coemitted species; POA is often coemitted with BC during fossil fuel and biomass burning, while NO_x and SO_2 are often coemitted with anthropogenic VOCs. This complicates estimates of OA radiative forcing (and atmospheric aerosol in general), as the individual chemical species typically have common parent sources and may undergo atmospheric processes in parallel. A further complication regarding OA radiative forcing is the estimation

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of the preindustrial background, which will have been dominated by biogenic SOA. Estimates of the natural SOA background are highly uncertain and have a large impact on estimates of both OA radiative forcing and all-aerosol radiative forcing.[273]

While OA is a major contribution to the global aerosol burden, because of the large uncertainties relating to OA itself and its coemission with other anthropogenic emissions and precursors, strategies to reduce OA-dominated sources would currently have a poorly constrained impact on climate. From an air quality and human health perspective, OA is a major fraction of $PM_{2.5}$; thus reductions in OA would be beneficial in terms of premature mortality and morbidity. Associations between specific sources/classes of OA and health effects such as respiratory and cardiovascular mortality have been demonstrated.[274−277] However, quantitative assessment of the health impact that is directly attributable to OA is challenging.[278]

2.2.4. Aerosol−Cloud Effects. Our understanding of the interactions between aerosol air pollution and climate effects is complicated not only due to the interactions between biogenic and anthropogenic aerosol formation, but also due to different metrics causing and contributing to the impacts. The aerosol−cloud effects, which contribute to total aerosol effective RF by −0.45 W m^{-2},[33] are not dependent on mass, but on the number concentration of cloud droplets and thus of CCN-sized particles. The $PM_{2.5}$ mass concentrations within the boundary layer are typically dominated by particles with diameters over or of the order of 1 μm, which originate often from sources different from CCN-sized and smaller particles.[279] Furthermore, larger particles act as a sink for ultrafine particles (UFP) and condensing vapors, and thus very high $PM_{2.5}$ concentrations even suppress the formation of CCN from UFP.[280,281] These interactions, although well understood qualitatively, have not yet been quantified due to the lack of comprehensive studies allowing for comparison of several locations with varying levels of $PM_{2.5}$, UFP, CCN, and condensing vapor concentrations.

Although the absolute levels of primary biological emissions of CCN-sized particles, for example, viruses, bacteria, and plant debris, contribute only a minor fraction to atmospheric number concentrations,[282−284] biogenic SOA is a significant contributor to the global CCN budget.[236] After atmospheric oxidation by ozone, and hydroxyl radicals (and possible subsequent auto-oxidation reactions), the volatility of these vapors is decreased radically allowing them to condense even on the smallest aerosol particles.[22,23] Because of the strong temperature dependence of the emissions of VOCs, this growth to CCN sizes forms a negative feedback mechanism: increasing temperature increases the number of CCN-sized particles and cloud droplets, which increases cloud albedo and lifetime, that in turn moderates the increase in temperature.[285,286]

Even though the mechanistic nature of the aerosol−cloud interactions is physical, several steps in the process are pushing the current boundaries of our understanding in atmospheric chemistry: oxidation and atmospheric auto-oxidation of VOCs to ELVOCs (e.g., Donahue et al.,[287] Ehn et al.[22]), formation and atmospheric relevance of stabilized Criegee radicals for sulfuric acid and ELVOC concentrations,[18,19,288] formation of molecular clusters from sulfuric acid, ELVOCs and amines to initiate atmospheric NPF,[133,238,289,290] and the effects of particle/liquid phase chemistry and hygroscopicity on cloud droplet activation (e.g., King et al.,[291] Prisle et al.[292]).

3. CLIMATE EFFECTS ON AIR QUALITY

3.1. Ozone and Meteorology

There are a variety of ways in which climate change can affect ozone, including changes in temperature, meteorology (including precipitation, stagnation events, humidity, clouds, etc.), natural emissions, and stratosphere−troposphere exchange. A number of modeling studies have investigated projected changes in future ozone considering, and often isolating, the different conditions to understand what the drivers to the changes in ozone concentrations are (e.g., Coleman et al.,[293] Doherty et al.,[294] Langner et al.,[295] Wang et al.,[297] Young et al.[296]). Many of these studies use the Representation Concentration Pathways (RCP) or scenarios from the IPCC Special Report on Emissions Scenarios (SRES) for projecting changes in emissions and radiative forcing/climate warming.[164,298,384] In many cases, future climate conditions will make it harder to achieve a given air quality goal, resulting in a need for greater emission reductions. This concept has been dubbed the "climate penalty".[299]

3.1.1. Temperature, Humidity, and Emissions. The ACCMIP multimodel comparison study found that all models were sensitive to the changes in emissions and climate change parameters from the RCP scenarios; however, these sensitivities were not consistent across the models in their predicted effects on changes in ozone concentrations.[296] Net chemical production of ozone was overwhelmingly negative for all changes between historical (year 2000) and projected ozone, with the exception of RCP8.5, largely because changes in emissions are projected to be much larger than the projected changes from a changing climate, although the effects of climate change and emissions change cannot be disentangled in the ACCMIP experiments discussed in Young et al.[296] Because of a higher specific humidity in the warmer climates in the RCPs, water-mediated loss of ozone likely contributed to the decreases in ozone.[34,296] For RCP8.5 a large increase in methane concentrations through the 21st century is included, which all things equal would be expected to increase ozone; however, the nonlinear relationship and dependence on other ozone precursors means that the significant projected reductions in NO_x after 2030 lead to that the methane increase does not result in as great an increase in ozone as might otherwise be expected.[296] These results are in line with those from Clifton et al.[300] that found the doubling of CH_4 under RCP8.5 partially offsets the summertime surface O_3 decrease due to reductions in NO_x emissions. Furthermore, the effects of increased methane on ozone concentrations in the RCP8.5 scenario were found to be mainly due to atmospheric chemistry, rather than additional forcing from CH_4, and the global CH_4 abundance contributed to raising surface O_3 during all months, although the largest influence was during cooler months when O_3 lifetime was longer.[300−302] The effects of climate change add further complexity to the results of the RCP8.5 case, which show double the ozone increase expected relative to the changes in precursor emissions, thereby attributing one-half the increase to climate change impacts, including increased influx of stratospheric ozone, changing chemical loss of NO_x,

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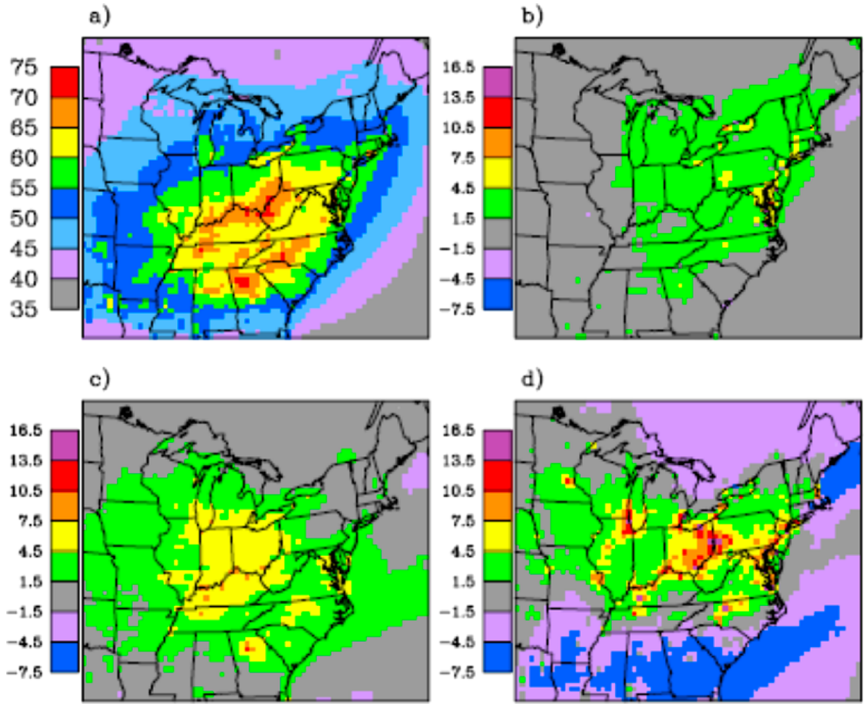

Figure 10. Summertime average daily maximum 8 h ozone for (a) the 1990s and changes in the summertime average daily maximum 8 h ozone for the SRES A2 scenarios relative to the 1990s for the (b) 2020s, (c) 2050s, and (d) 2080s. Values in ppb. Five consecutive summer seasons were simulated in each decade. Reprinted with permission from ref 306. Copyright 2004 John Wiley & Sons, Inc.

and changes to reaction rates from temperature and humidity changes.[296]

A study over China (2000−2050) isolated the effects of the change in emissions from those of climate change and found that the most pronounced climate driven ozone increase was found in summer (max 10 ppbv increase), although both positive and negative changes on surface ozone were observed due to climate change.[297] More specifically, the climate change penalty was attributed to enhanced natural emissions (increased bVOCs) of ozone precursors (∼40%) and changes in meteorological factors, such as higher temperature and higher water vapor content, lower PBL heights, and reduced ventilation rates. While ozone contributes to the formation of hydroxyl radicals, water vapor also provides a sink for ozone:

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \quad (14)$$

$$O(^1D) + H_2O \rightarrow 2OH \quad (15)$$

The expected increases in water vapor under a future climate are expected to decrease ozone lifetime and lower surface ozone over remote, less polluted regions, particularly over the oceans.[294,297] Some model studies have also found that increased water vapor leads to general decreases in ozone.[294] However, there are competing effects on ozone because OH plays an important role in a variety of atmospheric reactions, including the production of ozone from NO_x and VOCs, and in this way it may be possible that the subsequent reactions lead to greater O_3 formation, as was observed in a modeling study over the U.S.[303,304] There, increased humidity showed general decreases in ozone (found in hotter locations, e.g., the south), in agreement with other studies, but also isolated areas of increases in ozone (found in cooler locations, e.g., the north, where the responses were more mixed), highlighting the complexity of the hydroxyl radical chemistry.[304]

A multimodel study over Europe isolated the effects of climate change, comparing the 2000−2009 period with 2040−2049, finding that most models simulated increases in surface ozone over southern Europe and decreases in northern Europe. The increases were attributed to locally increasing temperatures affecting the chemistry, and to a certain extent changes in wind direction (transport), while the decreases in northern Europe were attributed to increases in cloudiness and precipitation, leading to increased scavenging of ozone precursors and less solar radiation to drive the photochemistry.[295] However, increases in the higher percentiles of hourly ozone concentrations in such studies indicate that climate impacts could be especially important in connection with extreme summer events,[295] or ozone episodes.[305] Earlier work found that both the number of exceedances and the duration of pollution events were expected to increase under a future regional climate (for the U.S.).[306] Doherty et al.[294] and Hogrefe et al.[306] also found that the relationship between increasing temperatures and increases in ozone concentration was exhibited across all three chemistry−climate models included in their study, and that these increased temperatures also led to enhanced isoprene emissions, resulting in increased surface ozone over most regions, a result supported by many other studies. An example of such results from Hogrefe et al.[306] for the predicted change in daily maximum 8 h O_3 concentrations over the northeastern U.S. under the SRES A2 scenario is shown in Figure 10. The role of isoprene and other biogenic emissions that are expected to increase under warmer climate conditions will be discussed in greater detail in the section on biogenic VOCs. The increased temperatures under a future climate will also have an impact on PAN concentrations, influencing the concentration of ozone. As a major reservoir species for long-range transport of ozone precursor species such as NO_x and HO_x, increased temper-

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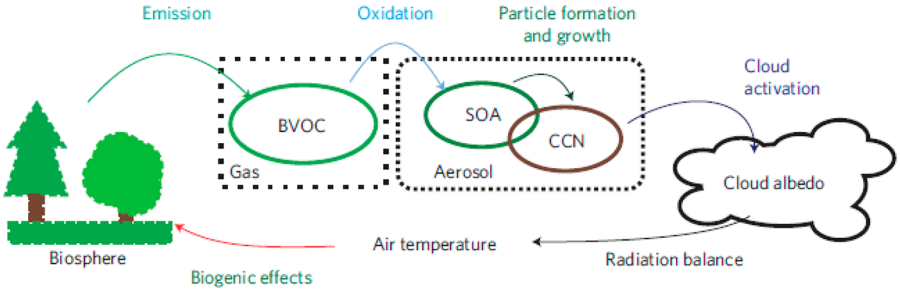

Figure 11. Schematic of a proposed climate feedback mechanism, in which the biosphere reacts to warming climate by emitting more organic compounds, leading to enhanced growth of aerosols and to an increase in the cloud droplet concentrations, thus diminishing the net radiative forcing. Reprinted with permision from ref 286. Copyright 2013 Nature Publishing Group.

atures leading to a greater thermal decomposition of PAN will result in changes to the long-range transport of ozone.[294] More specifically, model studies indicate that surface O_3 concentrations over land may show increases up to 6 ppbv over land, and decreases over the oceans.[294,307,308]

3.1.2. Transport Patterns and Mixing Height. The impact of climate change on atmospheric transport patterns did not show any consistent large-scale spatial responses, indicating that shifts in transport patterns are unlikely to have a major role of influence over the spatial patterns of annual mean ozone.[294] This conclusion is supported by earlier work from Racherla and Adams[309] who also did not find any conclusive evidence in their model runs showing systematic changes in circulation. Similarly, regional scale modeling was used to investigate the role of summertime midlatitude cyclone tracks on ozone pollution episodes in the northeast U.S. under future climate scenarios (RCP4.5 and RCP8.5) but also did not find strong evidence of cyclone frequency to explain variability in high O_3 events.[310] In contrast to these studies, Barnes and Polvani[311] demonstrated a robust response of the eddy-driven jets to climate change in the CMIP5 multimodel mean ensemble. Additionally, Barnes and Fiore[312] related surface ozone variability to jet latitude finding a strong dependence. These results would imply that understanding future changes in jet location could be used to derive changes in summertime surface ozone variability and ozone−temperature relationships.[312] Furthermore, climate-driven changes to transport patterns may have a greater role in peak (95th percentile or daily max 8 h) ozone.[294] Earlier work from Dawson et al.[305] evaluated the influence of meteorological parameters, such as wind speed and mixing layer height, but found that using domain average sensitivities (in this case regions of the U.S.) was not sufficient for predicting changes in ozone, given their heterogeneous response throughout the domain. Generally, decreased mixing heights and lesser wind speeds in the future scenarios were associated with higher levels of ozone, and vice versa, while changes in humidity led to more complex effects on smaller scales.[305] Murazaki and Hess[313] also identified effects suggestive of a more sluggish circulation in the future, resulting in longer lasting (ozone) pollution events. However, no significant differences in future boundary layer height were found, leading them to conclude that such effects were still very uncertain. While Lam et al.[314] also found no significant change in planetary boundary layer height for their study regions over the U.S. attributable to climate change, work by Hogrefe et al.[306] did attribute some decrease in ozone over the U.S. to an increase in convection and mixing layer heights from changes in the regional climate. Hauglustaine et al.[308] also found that more stagnant conditions over western Europe and the eastern U.S. favored the development of more intense pollution episodes. Recently, Horton et al.[315] investigated the occurrence and persistence of future atmospheric stagnation events, projecting increases in the occurrence of stagnation (1986−2005 vs 2080−2099) that would affect 55% of the current global population. Such differences among studies emphasize the uncertainty associated with changes to some effects, such as boundary layer height and circulation, in a future climate.

3.1.3. Stratosphere−Troposphere Exchange. A study comparing condition in the 1990s to projections for the 2090s found an increase in the net transport of ozone into the troposphere in the future climate. While confounding factors, such as greater humidity causing greater photochemical ozone loss, will counterbalance some of the increases, an increase in overall transport from the stratosphere and the role of stratosphere−troposphere exchange on radiative forcing and climate change should be considered.[316] A global model study comparing 2000 to 2100 found that a more intense Brewer−Dobson circulation would increase stratospheric ozone influx by 35%; furthermore, more vigorous convective activity induces an increase in lightning NO_x emissions by 50%, increasing ozone production in the tropics in the upper troposphere.[308] These effects were found to compete with those from a warmer and wetter climate leading to enhanced ozone destruction; cumulatively the study found that the overall tropospheric ozone burden from climate change was predicted to decrease slightly.[308] More recent work by Young et al.[296] found that an increase in stratospheric influx was likely masking what would otherwise be stronger negative changes in the overall ozone burden due to the decreases in ozone precursor emissions. Stevenson et al.[34] and Kawase et al.[317] confirmed these results, finding that most models indicate an increase in upper tropospheric ozone from increased stratosphere-to-tropospheric transport, as well as increased lightning production. Voulgarakis et al.[318] also find that changes in ozone depleting substances (e.g., CFCs) and stratospheric ozone can induce large-scale changes in tropospheric composition, with a non-negligible effect on radiative forcing, which should be considered within the scope of composition−climate interactions.

While studies have found that the climate penalty for ozone is projected to be a relevant factor in the number of air quality exceedances, projected changes in emissions (emissions reductions) tend to dominate future changes in ozone.[293,295,296] Furthermore, there are a greater number of studies that have evaluated the effect of temperature changes on ozone, but far fewer studies that have investigated the

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effect of, for example, mixing height; studies investigating the sensitivity of ozone to humidity often calculate changes only for positive changes in humidity.[304] Further research is warranted to tease out the effect of these different parameters.

3.2. BVOCs

Emissions of BVOCs from vegetation are strongly dependent on various environmental factors, most importantly on temperature and light, chemical composition of the air, vegetation type, and leaf area. Because these factors are likely to change under a future climate, the emissions of BVOCs will presumably be affected. Dynamic vegetation models have proven themselves to be a useful tool in the investigation of future changes in BVOC emissions as they can combine the simulation of the hydrological and carbon cycles, energy balance, and biochemical processes of the modeled ecosystem with temporal and spatial changes in fractional coverage of different plant functional types.[91,319−323] As a response to the 21st century climate changes, it is predicted that global isoprene emission will increase by 30−80% by the year 2100.[320,324−326] The studies associate most of the emission change with increase in air temperature and to a lesser extent with changes in land cover. While there is a clear positive link between temperature and isoprene emission, the impact of land cover changes reflects a combination of effects that can lead to an increase or decrease of emission depending on location. Future climate conditions are favorable for expansion of the temperate and boreal forests in the Northern Hemisphere, while loss of biomass is predicted in South America due to warming and drying of Amazonia.[320,325] Furthermore, human-induced changes such as deforestation and forest replacement by agricultural croplands will result in a decrease in isoprene emissions. Wiedinmyer et al.[326] estimated an increase in isoprene emissions of 70% under both future climate and land cover conditions, while an increase of only 2% was estimated for conditions where climate was fixed to present day values and land cover changes driven by future climate were considered (deforestation not taken into account). An even larger isoprene emission increase (factor of 2) was predicted by Guenther et al.[324] due solely to temperature rise at the end of the 21st century; they found a decrease in isoprene emissions of 30% and increase of 6% when future land cover with and without changes in cropland area was accounted for, respectively. To summarize, the effect of changes in land cover shows a greater variation in the effect on isoprene emissions depending on the different types of scenarios considered, while increasing temperatures due to climate change are all predicted to result in significant increases in isoprene emissions.

The role of CO_2 in the future estimates of BVOC emissions is not yet very clear. On one hand, higher CO_2 concentration enhances fertilization of the vegetation, stimulates the gross primary productivity and leaf growth, thus having positive feedback on BVOC emissions by increasing the emitting biomass.[103,327] On the other hand, series of experimental studies have shown inhibition of isoprene for some plant species grown in an environment with elevated CO_2.[319,328] Inclusion of this mechanism in the emission models either results in no change in future isoprene emission when compared to present-day estimates[319] or even causes a slight decrease.[329] Tai et al.[330] evaluated the impact of isoprene CO_2 inhibition on future air quality. They performed a series of chemical model runs with isoprene emissions calculated with and without the inhibitory effect of CO_2. The study shows that the future changes in surface ozone and secondary organic aerosols in 2050 with respect to present day are reduced by 50% when the inhibitory effect is taken into account. However, recent work by Sun et al.[331] suggests the ability of plants to accommodate to elevated CO_2, which would reduce the inhibitory effect on isoprene emission.

In addition, land cover changes induced by human activities may be of considerable importance for the amounts and species composition of future biogenic VOC emissions. As shown by Lathière et al.,[332] tropical deforestation and their replacement by the crop fields can significantly decrease isoprene emissions. On the other hand, recent trends replacing agricultural land by plantations of woody biofuel species or replacement of tropical forests by oil palm plantations lead to higher isoprene emissions because these tree species have generally higher isoprene potential than the original vegetation.[333,334]

As shown by the model studies, future changes in BVOC emissions may impose feedbacks on Earth's climate through impacts on formation of surface ozone[308,325,335] and organic aerosol,[118,285,286] as shown in Figure 11. However, the character as well as the magnitude of future changes still remain unclear. Even present day BVOC emission estimates are uncertain. Isoprene global totals modeled by bottom-up and top-down techniques vary within a factor of 2−3.[92,324,336] Interaction between the biosphere and atmosphere is a complex system with processes that have not yet been well described, for example, the influence of atmospheric chemical composition on plants and consequently on BVOC emissions, or the chemical mechanisms of new particle formation from BVOC oxidation products, and more understanding is needed to better evaluate the relationship between the BVOC emissions and the Earth's future climate.

3.3. Particulate Matter

Many of the factors influencing PM under a changing climate are similar to those outlined for ozone, such as changes in meteorology (including precipitation, stagnation events, humidity, clouds, etc.), temperature, and natural emissions. In addition, the influence of climate change on wildfires could have a significant influence on PM concentrations.[307,337] However, while there is a substantial literature basis for the "climate penalty" on future ozone, far fewer studies have investigated the effect of climate change on PM.[305,307,314,337−339]

A multimodel study of the regional impact of climate change on $PM_{2.5}$ concentrations over Europe found a slight benefit (decrease), due at least in part to increases in precipitation.[338] A model study comparing present day climate (1989−2009) to future climate (2060) over Europe found that changes in PM_{10} were small, and both positive and negative, with disagreements on the sign of the change found at many locations between two climate runs that differed in the meteorology used.[340] Hedegaard et al.[341] found that the impact of climate change alone resulted in a decrease in $PM_{2.5}$ at high latitudes (especially the Arctic), and a small increase over parts of the Atlantic Ocean and in subtropical and tropical areas. For the high latitudes, the effect of climate change and the projected change in emissions worked in unison to amplify the decreases in PM.[341]

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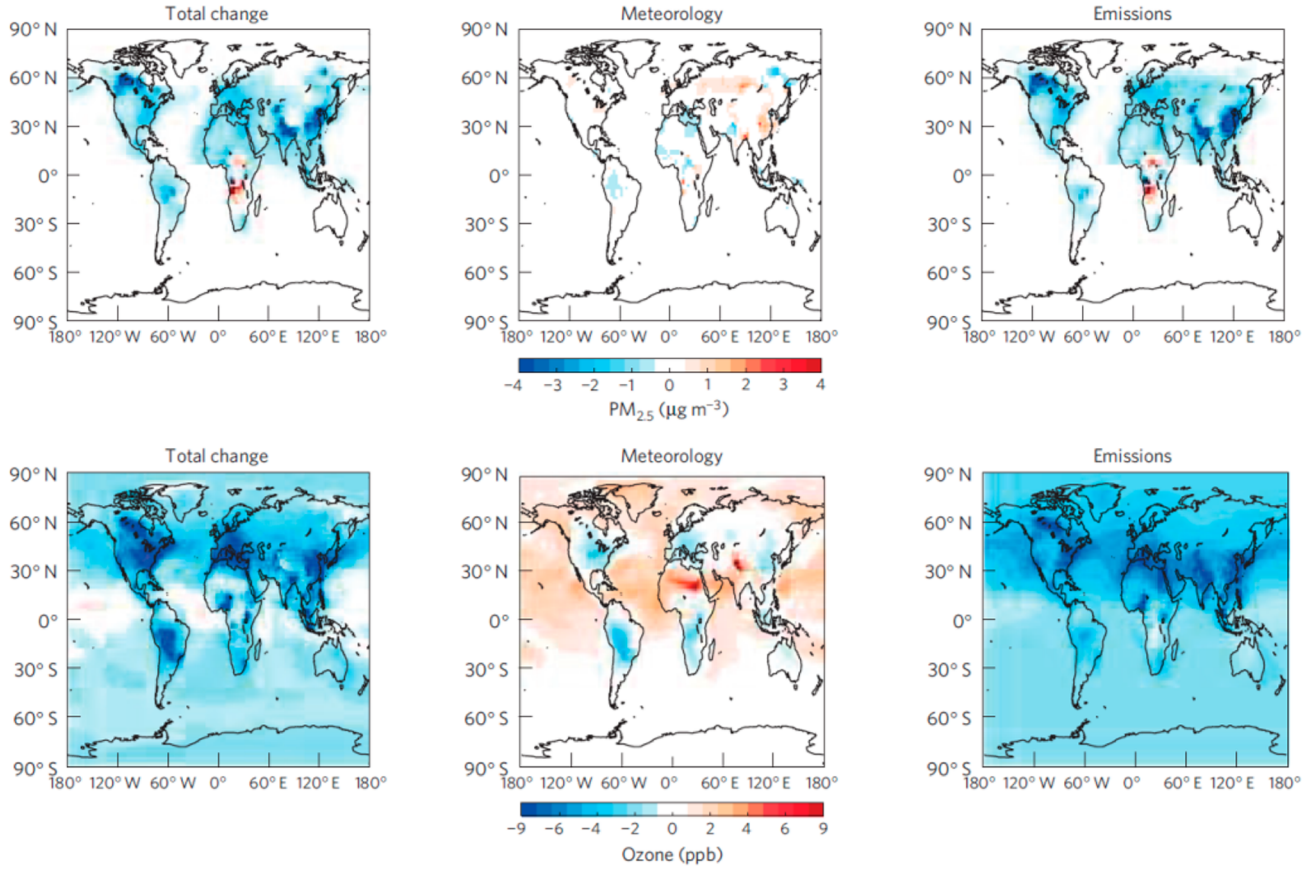

Figure 12. Effects of GHG mitigation on annual average PM2.5 and the 6-month ozone-season average of daily 1 h maximum ozone in 2100. Concentrations are averaged over four model years, for the total change (RCP4.5−reference scenario (REF)), and components due to changes in meteorology from climate change (REF emissions and RCP4.5 meteorology−reference scenario), and emissions (RCP4.5−REF emissions and RCP4.5 meteorology). Reprinted with permission from ref 344. Copyright 2013 Nature Publishing Group.

Tai et al.[342] found that from 2000 to 2050, weighted-average general circulation model results investigating the effect of meteorological modes under a changing climate projected a small increase (~0.1 μg m^{-3}) in $PM_{2.5}$ over the eastern U.S., due to less frequent frontal ventilation, while a small decrease over the Pacific Northwest U.S. in $PM_{2.5}$ was projected due to more frequent maritime inflows, although the variability in results from the different GCMs was greater for the latter case.

Liao et al.[343] investigated the effect of a changing climate comparing 2000 to 2100 following the SRES A2 scenario, and found that with no changes in anthropogenic emissions, CO_2-driven climate change would result in decreased burdens of all aerosol components considered (sulfate, nitrate, BC, primary organic aerosol), except SOA (+9%), ranging from −47% to −9%. The influence on the aerosol burdens was mainly from changes in wet deposition, climate-sensitive emissions, and aerosol thermodynamic equilibrium.[343]

Across a number of studies, it was consistently reported that the changes in emissions due to air pollution and/or climate policies dominated the resulting modeled changes in PM concentrations in comparison to the projected influence of climate change,[338,341,343,344] in agreement with what was found for ozone. The difference in these effects is shown in Figure 12 from West et al.[344] where the effect of climate change on meteorology is shown separately from that of changes in emissions.

The effects of a changing climate on wildfires and the influence that has on aerosol concentrations are often not considered in many of the studies that evaluate ozone and PM under a future climate. Instead, wildfires are often the focus of studies that look to evaluate this effect in particular, which can be very significant. Spracken et al.[337] evaluated the role of wildfires under a future climate on carbonaceous aerosols, comparing 1996−2000 to 2046−2050, and predicted that mean summertime OC and EC concentrations would increase by 40% and 18%, respectively, over the western U.S.; the vast majority of this increase (75% and 95%, respectively) was attributed to a 90% increase in wildfire emissions. The remainder of the increase was attributed to changes in meteorology (affecting atmospheric transport and aerosol deposition), as well as an increase in monoterpene emissions (from rising temperature) and thereby increases in SOA that affect the OC.[337]

Wildfires are a result of a complex set of interactions among the following major factors: weather (including temperature, relative humidity, wind velocity, and the amount and frequency of precipitation), fuels (including ignition agents and fuel conditions), topography, and human influence.[345−347] Under a changing climate, many of these factors will be affected, and increases in extreme events due to climate change are expected to have a significant impact on fire risk.[348] Although as Flannigan et al.[347] point out, increasing temperature alone does not guarantee greater fire disturbance

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because of the aforementioned multiplicity of factors and the complex interactions involved.

A number of studies investigated the influence of climate change on changes to future fire risk, or area burned, rather than the downstream impact on the effect on PM. However, implicit in these results are that more or larger fires would result in greater PM emissions from fires, as studies have shown increased PM or aerosol loadings associated with greater forest fire occurrence.[349,350] A number of studies observed higher risks of forest fires as a direct consequence of increasing temperatures (such as warmer spring and summer temperatures), decreased precipitation, or lower relative humidity, resulting in longer, drier fire seasons, as well as impacts from reduced or earlier snowmelts.[345,348,351] An increase in the number of ignitions from lightning is also expected under future climate change, due to more thunderstorms and more receptive fuels.[346] Counterintuitively, Westerling and Bryant[351] also found that wetter scenarios with more moderate temperature increases may actually result in more fire overall. To explain this, fire risk regimes dominated by variation in precipitation (as opposed to temperature) mean that hot temperatures and dry conditions could result in less fire risk if the conditions led to reduced growing season moisture availability and thereby less vegetation. The converse is also possible, that more moderate temperatures and wetter conditions could lead to greater vegetation that is subsequently available for fires.[351]

The changes to fire risk or projected area burned have significant spatial variation, depending not only on changes in weather patterns, and the location and density of forest cover, but also changes in land use, fire suppression, and fuel management activities, with some areas also showing decreases in fire risk.[348,351,352] Study areas that were identified as having increased fire risk or increases in burned area in the future due to climate change were large areas of North America, especially the Western U.S. and Canada, Finland, and the Mediterranean (this list is by no means complete, but is more a reflection of the areas that were considered in the studies cited here).[345,347,348,352,353]

The difficulty in projecting changes in PM under a future climate is the strong link of PM concentrations to meteorological influence. These studies show that the effect of climate change on PM concentrations is still uncertain, with different studies coming to different conclusions, and even within a single study emphasizing regionally disparate responses. The latest IPCC recognizes this difficulty, attaching no confidence level to the overall impact of climate change on $PM_{2.5}$ distributions.[33] In contrast, changes in ozone are most strongly linked to changes in temperature, which consistently shows an increase for the 21st century across general circulation models, even on regional scales.[343]

4. METRICS FOR ASSESSING IMPACT

4.1. Air Quality Metrics

Air quality metrics are a set of measurements used to quantitatively gauge efficiency, progress, or performance. Comparisons of air quality policies involve considerations such as cost, health, effects on vegetation, materials, and even aesthetics[354] and therefore can lead to a wide variety of metrics depending on what needs to be assessed. In general, for air quality the main metrics exist to quantify health or ecosystem impacts of air pollutants with different metrics established for human health and ecosystems.[355] Table 2 shows some typical air quality metrics.

Table 2. Example Metrics for Air Quality

air quality problem	metric
ozone	maximum hourly concentration
	maximum 8 h concentration
	running 8 h mean
	annual average concentration
	accumulated ozone exposure over 40 ppb threshold (AOT40)
particulate matter	maximum daily PM_{10}
	annual average PM_{10}
	maximum daily $PM_{2.5}$
	annual average $PM_{2.5}$
	maximum daily PM_{coarse}
	annual average PM_{coarse}
	ultrafine particle mass or number
deposition	nitrogen total
	nitrogen in excess of critical loads
	acid total
	acid in excess of critical load
air toxics	concentration or technology-based measures
health	premature mortality
	loss in life expectancy

The statistical distribution of pollutant concentrations often drives the formulation of metrics; in general, ambient concentrations of primary air pollutants have highly skewed distributions of (hourly) concentrations with the mode at low concentrations and a small number of hours with high concentrations. Whereas ozone, a secondary pollutant with a hemispheric background concentration[356,357] much greater than zero, has frequency distributions very different from those found for primary pollutants. For ozone metrics, there is often a need to distinguish from annual mean concentrations that can be made up from very different frequency distributions to shorter time scale periods. The annual mean does not capture all of the features of ambient concentrations that may be of concern in terms of the impact on human health, such as short periods of high concentrations. A range of different metrics are therefore used, and these metrics reflect different features of the frequency distribution of hourly concentrations (see, e.g., Pappin and Hakami[358] or Lin et al.[359]). These frequency distributions in turn vary with location and reflect the differing influences of local, regional, and global factors determining concentration (see, for example, Lefohn et al.,[360] Monks et al.[13]). Some typical ozone health metrics[361] are shown in Table 3.

Air quality metrics are often used to assess several levels of "standard" in use. These standards have differing legal status. In the health impacts area, fundamental health effect evidence is used to inform the setting of WHO Air Quality Guidelines (see, e.g., WHO[362]) below which the pollutant in question will not have adverse effects on public health. The guidelines are set without regard to the technological, economic, or social issues, which might affect their achievability. In translating these into legally based standards, some flexibility is introduced to allow for practical challenges in achieving the levels and/or to allow for year-to-year meteorological variability. For short-term standards, this usually takes the

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Table 3. Key Ozone Metrics of Relevance to Human Health[361]

metric	relevance	key influences on the values of this metric at urban locations
annual average	basic metric used to show long-term trends	includes all of the hours in the year; strongly influenced by the magnitude of local NO_x emissions and by topography through nocturnal depletion
annual average of the daily maximum of the running 8-h mean	used as "basic metric" for many of the health metrics; also used for Defra's air quality indicator	strongly influenced by the magnitude of local NO_x emissions
annual average of the daily maximum of the running 8-h mean with a 70 $\mu g\ m^{-3}$ cutoff	health impact, related to SOMO35	influenced by the magnitude of local NO_x emissions and by photochemical episodes
annual average of the daily maximum of the running 8-h mean with a 100 $\mu g\ m^{-3}$ cutoff	health impact	strongly influenced by photochemical episodes and to a lesser extent the magnitude of local NO_x emissions
maximum 1-h average (peak hour in the year)	used as the basis for some epidemiological studies, although has been suggested that 8 h is more representative; also an indicator of short-term peaks; note low statistical power, because it is the value for one single hour	the metric most sensitive to the magnitude of regionally generated photochemical episodes and thus likely to show a response to reductions in relevant precursor emissions
number of days with daily maximum of running 8-h mean exceeding 100 $\mu g\ m^{-3}$	equates to the number of exceedances of the UK ozone standard (AQS objective is no more than 10 exceedances per year)	strongly influenced by photochemical episodes and to a lesser extent the magnitude of local NO_x emissions
number of days with daily maximum of running 8-h mean exceeding 120 $\mu g\ m^{-3}$	equates to the number of exceedances of the EU target value (no more than 25 days, averaged over 3 years) and long-term objective (no exceedances) from the 3rd Daughter Directive	strongly influenced by photochemical episodes and to a lesser extent the magnitude of local NO_x emissions
SOMO35 (sum of means over 35 ppb)	used as a metric by IIASA, for CAFE and NECD revision, related to annual average of the daily maximum of the running 8-h mean with a 70 $\mu g\ m^{-3}$ cutoff	influenced by the magnitude of local NO_x emissions and by photochemical episodes

form of allowing a number of exceedances of a given concentration over a year, and/or averaging over several years.

In the area of short-lived climate forcers, there is a particular challenge in how to bring the climate effects of well-mixed, long-lived and short-lived components together. Fuglestvedt et al.[363] commented that there are "formidable difficulties" in developing metrics for short-lived species. These difficulties include the appropriate structure for the metric, which may be climate policy dependent, as well as contain value judgments as to the appropriate time periods. There are significant difficulties in the quantification of input parameters due to uncertainty in atmospheric processes, for example, for BC[196,364] and aerosols as well as feedbacks, for example, vegetation.[365] Further, with short-lived species the metric often depends on where and when the species was emitted.[48,363,365,366] An excellent overview of the challenges for short-lived climate forcers and metrics has been given by Peters et al.,[367] suggesting that "a more lively discussion of metrics for 'global warming' is needed".

4.2. Climate Change Metrics

Climate change since the 1950s has predominantly been driven by anthropogenic emissions of carbon dioxide (CO_2). Because of its ubiquitous emission from every sector and long atmospheric lifetime (typically decades to centuries), it is also expected to be the largest driver of future climate change.[33] Nevertheless, emissions of other greenhouse gases as well as air pollutants that have an effect on climate, often referred to as short-lived climate-forcing pollutants (SLCPs), have had appreciable effects on historical climate change, and their emission pathways can affect future climate.[61] The Kyoto protocol groups together a basket of greenhouse gas emissions and compares them to carbon dioxide using a CO_2 equivalent emission metric. Such an approach can aid options under climate agreements or emission trading and in some ways can be considered more comprehensive. Nevertheless, the CO_2 equivalent approach can remain problematic as, for example, not all aspects of CO_2 or methane-driven climate change would be equal. The Kyoto Protocol adopts a 100-year Global Warming Potential (GWP) metric, based on the equivalence of 100-year integrated radiative forcing from a pulse emission (e.g., Myhre et al.[61]). Another common climate metric that is increasingly discussed is the global temperature potential (GTP), which targets temperature at a given point in time (say 20 years in the future).[61,368] The choice of metric and time horizon can have a large effect on the perceived import of different emissions, and differences between metric values are particularly pronounced when comparing short-lived species to CO_2. For example, the current IPCC report lists a 100-GWP for CH_4 of 28, implying that 1 kg emission of methane is "equivalent" to a 28 kg emission of CO_2, whereas using a 100-year GTP metric would give CH_4 a value of only 4.3, implying that 1 kg emission of methane is "equivalent" to a 4.3 kg emission of CO_2.[61] The choice of metric and time horizon depends on the policy goals and is largely a societal value judgment.[369]

IPCC AR5 lists example GWP and GTP metrics for CH_4 and other short-lived species, for example, black carbon and NO_x. Although such metrics can be calculated, there are additional science and policy issues when applied to such emissions:

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(1) Large uncertainties: Uncertainties in the metric values for SLCPs are considerably larger than for greenhouse gas emissions.
(2) Geographical, seasonal, and sectorial variation in metric values: For example, NO_x emissions over Asia would be expected to generate more climate warming than the same emission in Europe. Another example is that NO_x emissions from aviation may warm the climate, whereas those from shipping may cool.
(3) Co-emitted species such as organic carbon that is often emitted with black carbon might lead to a cooling of climate: Should any policy consider these?

Carbon dioxide mitigation is needed to limit long-term climate change, and there is a growing view that while SLCP mitigation can help in the short-term, especially when combined with CO_2 mitigation, it is not that helpful to compare their emissions to CO_2 and it may be better to have separate short-term climate goals targeted at SLCPs.[370−372]

Figure 13 from Myhre et al.[61] nicely illustrates that on the sub-20 year time horizon, 1 year's emissions of SLCPs has a larger effect on temperature than 1 year's CO_2 emissions. However, after 20 years the climate warming from the year's emission of CO_2 will dominate the temperature response.

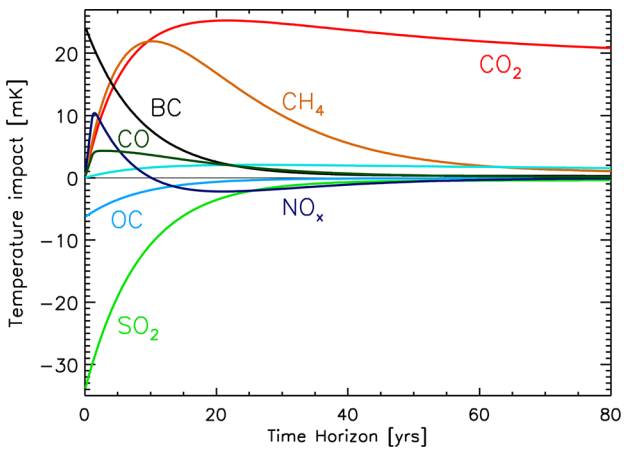

Figure 13. Temperature response by component for total man-made emissions for a 1-year pulse. Emission data for 2008 were taken from the EDGAR database and for BC and OC for 2005 from Shindell et al.[11] Reprinted with permission from ref 64. Copyright 2013 IPCC.

A key decision is the climate-related target. This is needed to define a climate benefit or a climate harm. Such decisions are needed to determine win−win situations for air quality and climate policy. In particular, it is by no means obvious if SO_2 emissions should be treated as beneficial for climate due to their global cooling influence, or if they should be considered a potentially harmful "dangerous anthropogenic interference with the climate system" (UNFCCC, 1992 Framework Convention on Climate Change) due to their ability to alter rainfall patterns. The climate target therefore very much influences the perception of trade-offs.

5. SCIENCE−POLICY CONTEXT AND OUTLOOK

Despite a growing recognition of the strong linkages between air pollution and climate change, both scientifically and politically, there is still significant work needed to fill knowledge gaps and coordinate mitigation and/or adaptation approaches. More specifically, mitigation approaches considered in the context of the bigger picture, the atmosphere as a limited resource/global common, and not just the consequence of a policy on only the intended target area (e.g., climate change) could avoid unintended consequences. Classically, this has been represented to date by the trade-off diagram as shown in Figure 14. As can be seen in Figure 14, encouraging diesel car usage to reduce CO_2 emissions (climate change) has led to detrimental effects for NO_x and PM emissions (air quality). Such connections and other more fundamental atmospheric chemistry feedback effects and linkages have been highlighted throughout this Review. Often the challenge in this area lies in effective understanding and metrics to assess impact coupled to "joined-up" policy decisions that weigh both the air quality and the climate change impacts.

One key challenge is understanding what air quality gains will be delivered by climate policy. For example, Smith and Mizrahi[374] have argued that "near-term climate benefits of targeted reductions in short-lived forcers are not substantially different in magnitude from the benefits from a comprehensive climate policy." To a large extent, many of the knowledge gaps are related to feedback processes and the coupling between and among different cycles, including wider ecosystem coupling. For example, the climate forcing of NO_x emissions is associated with significant uncertainty, as some of the processes lead to warming while others contribute to cooling, with many of these feedbacks not well quantified. NO_x emissions are also only one part of the much larger nitrogen cycle, where other forms of nitrogen, such as ammonia, also play important roles. Ammonia, in particular, is an area where significant potential for air quality mitigation via PM exists, but has not received as much attention as some other areas.

Ammonia currently contributes to effects on human health, through aerosol NH_4NO_3, which is becoming a dominant component of wintertime inorganic aerosols throughout Europe, to ecosystem effects and biodiversity loss in particular, as well as acidification now that sulfur emissions in Europe have been substantially reduced. The interactions with climate occur through aerosol direct and indirect effects and soil emissions of N_2O from nitrogen deposition. As substantial reductions in NO_2 emissions have been achieved, the role of ammonia has become gradually more important relative to emissions of oxidized nitrogen, as detailed in the recent European Nitrogen Assessment.[57] The overall social cost of nitrogen pollution in the EU 27 has been estimated to range between 75 and 485 billion Euros annually.[375] The lack of attention to control measures for ammonia is quite surprising given the low cost of emission controls relative to further measures to reduce NO_2 emissions, as shown in Figure 15.

The analysis of Van Grinsven et al.[375] shows that substantial cost-effective measures could be applied to reduce emissions of ammonia, and relative to measures for oxidized nitrogen emissions the marginal costs are smaller by a factor of 5. These could be achieved without reducing the productivity of European agriculture as the current losses of ammonia to the atmosphere represent inefficiencies in nitrogen use by agriculture. The economic benefit of agriculture has been estimated to range from 20 billion to 80 Billion Euros and is smaller than the annual costs of the pollution caused by the emitted nitrogen compounds, which

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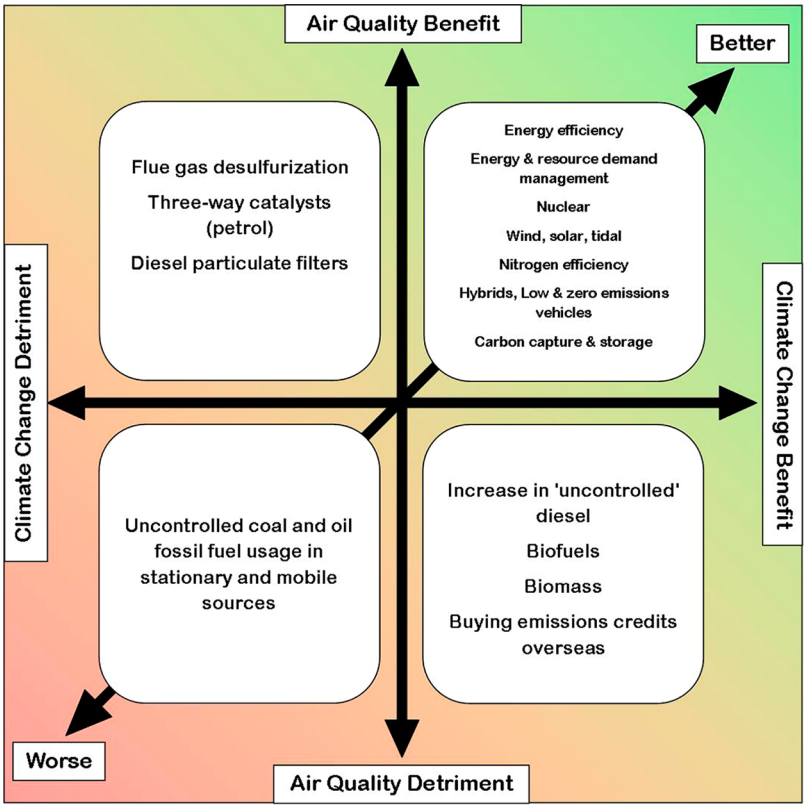

Figure 14. Synergies and trade-offs from policies and technologies to address climate change and air quality. Adapted from Williams,[8] as in von Schneidemesser and Monks.[373] Adapted with permission from refs 8 and 373. Copyright 2012 Taylor & Francis and 2013 Royal Society of Chemistry.

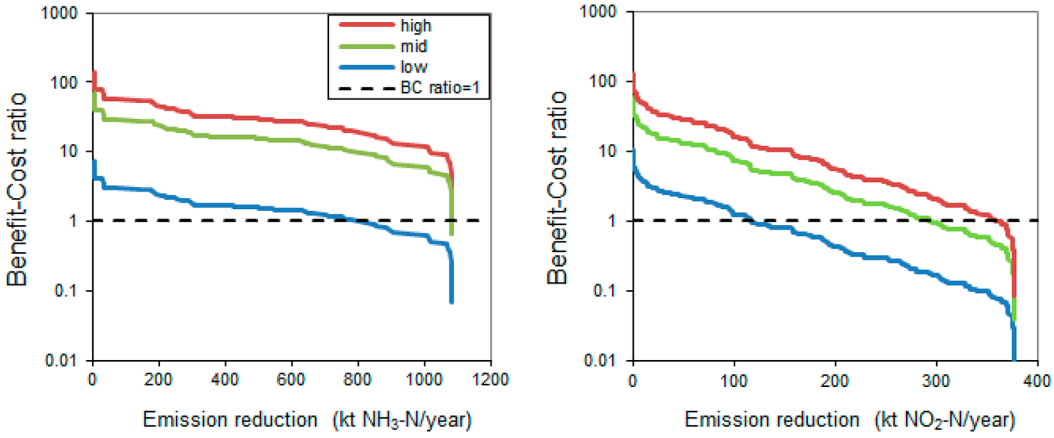

Figure 15. Ratio of marginal benefits of emission reduction over the costs of N-mitigation measures in EU27 for NH_3 and for NO_x from stationary sources, for emission reduction from 2010 beyond expected levels in 2020 by effects of current legislation. The comparison shows that there is a much larger potential for cost-effective mitigation of NH_3 emissions (800−1080 kt N) than for NO_x (110−370 kt N). Reproduced with permission from ref 375. Copyright 2013 American Chemical Society.

has been estimated to range from 35 billion to 230 billion Euros annually.[375]

The role of aerosols as CCN among other aerosol-climate feedback effects is another area adding to the uncertainty associated with how these feedbacks influence climate change. For instance, the response of clouds to global warming is still a research field with considerable uncertainties. Such a feedback has important implications for climate sensitivity and could either amplify or dampen global warming (e.g., Bony and Dufresne[376]). In turn, changes in clouds and the hydrological cycle have important implications on PM and other air pollutants through changes in, for instance, temperature and precipitation.

With respect to sources, additional concerns, in terms of both air quality and climate, may arise in the near future from increasing shipping in the Arctic. New polar shipping routes will be accessible in the summer months of the next decades after the melting of polar ice,[377−379] with consequent shifts in the regional impact of shipping emissions. Another emerging issue is fracking and its impacts both on methane emissions[380] and on local formation of ozone.[381]

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Improved quantification of the relative importance of the biogenic and anthropogenic fractions of SOA would be beneficial for both air quality and climate change. If a major fraction of SOA is anthropogenic, then this can be targeted to improve air quality, whereas if biogenic SOA is the dominant fraction, then its importance under future climate may increase. Furthermore, the various feedback effects associated with biogenic emissions are another area that have significant implications for both air quality and climate change, not only through SOA, but also in the effect on ozone, CO_2 and the carbon cycle, nitrogen, and biosphere−atmosphere dynamics. These processes are largely only poorly understood and therefore also remain poorly represented or left out of models.

Improved understanding of the role of coemitted species when assessing individual chemical components, which may have counteracting effects on air quality and/or climate, would be beneficial for future assessments. Policies typically target specific emission sources, rather than chemical components, and thus attempts to quantify the impact of proposed policies should reflect this. This is particularly pertinent regarding BC, which is typically emitted with a range of other particulate and gas-phase components that can either warm or cool climate (as well as their own consequences for health). For a subset of the BC emission sectors such as diesel engines and possibly also residential solid fuel burning, the net impact of emissions reductions from these sectors can be reduction in positive (warming) climate forcing. However, reducing the emissions from source sectors with a high ratio of coemitted species (cooling effect) such as open burning might result in a close to zero net effect on climate forcing. Modeling studies that accurately reflect the effect of mitigation policies by including reductions of all coemitted species, not just an idealized reduction of one chemical component, would provide more relevant information for policy, as some recent studies have demonstrated (e.g., the UNEP/WMO *Integrated Assessment of Black Carbon and Tropospheric Ozone*[222] or the World Bank Report *On Thin Ice*[382]).

Another important topic for future research is the effect of aerosol emission abatement regulations based on mass emissions on the number emissions and atmospheric number concentrations of aerosol particles. Even though in Europe the mass emission abatement technologies seem effective also for number emissions,[279] this might be different in other parts of the world where, for example, fuel sulfur content is different. Furthermore, if the emissions of particles in CCN- and micrometer-size scale, affecting especially the mass emissions, are reduced drastically, the coagulation scavenging of particles in nanometer size range might decrease. In the worst-case scenario, this would increase the concentration of ultrafine particles causing adverse health effects, but decrease CCN concentration, thus enhancing climate warming.

Despite the many areas where further research will help to reduce uncertainties and improve our understanding of atmospheric processes, the existing knowledge base can already be relied upon to make informed decisions to mitigate climate change and reduce air pollution. Climate metrics for short-lived species exist and could be used in policy decisions. Because of the many linkages between the two areas, including emission sources and atmospheric processes, coordinated mitigation options allow for simultaneous tackling of both issues, or at least an avoidance of trade-offs. A recent study quantified the air quality cobenefits of U.S. policies that reduce GHG (carbon) emissions, showing that monetized human health benefits associated with air quality improvements could offset 26−1050% of the cost of the carbon policies, depending on the flexibility of the carbon policy (flexibility in where/how the reductions are made, similar to cap and trade, as long as certain targets are met).[383] These results further indicate that significant gains remain, even in developed countries. A previous evaluation of mitigation options by UNEP in their *Integrated Assessment on Black Carbon and Tropospheric Ozone* focused on climate, but also included air quality effects, evaluated a variety of measures to reduce short-lived climate forcing pollutants and showed that the majority of the benefits would be in developing countries for those top measures considered.[11,222] As the diversity of these results shows, the results depend very much on the policies considered and the approach taken.

While both air quality and climate change are worth acting on individually, the potential for simultaneous benefits reflected in a coordinated approach that considers the linkages between the two areas is significant. An improved understanding of the fundamental physical and chemical processes that govern the interactions of the compounds involved, along with the effects on climate change and human and ecosystem health, will only aid in making smarter, informed decisions to address the environmental challenges of air quality and climate change.

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The authors declare no competing financial interest.

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Dr. David Fowler is the Senior Scientist at the Centre for Ecology and Hydrology (CEH) and is based in Edinburgh. He trained in Environmental Physics at the University of Nottingham, obtaining a Ph.D. from research on the dry deposition of SO_2 by micro-meteorological methods. He has worked at the Institute of Terrestrial Ecology (now known as CEH) on a range of atmospheric trace gases including SO_2, NO_2, NO, HNO_3, NH_3, O_3, CH_4, N_2O, as well as

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Dr. Axel Lauer studied meteorology in Munich (Germany) and obtained his Ph.D. on aerosols from the Free University of Berlin (Germany). Before joining the Earth system model evaluation group at the German Aerospace Center (DLR), Axel spent five years as a researcher at the International Pacific Research Center in Honolulu (U.S.) studying clouds, aerosols, and their interactions and two years at the Institute for Advanced Sustainability Studies in Potsdam (Germany), where he was heading a small modeling group investigating the impact of black carbon and of other aerosols on air quality and climate. His main research interests are aerosols, clouds, and cloud-climate feedbacks as well as their interactions and implications for air quality and climate.

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origin on regional air quality, primarily on tropospheric ozone. Her current research interest is the estimation of biogenic emissions on regional as well as global scales. In her work she focuses on the dependence of emissions on different environmental factors and the consequent impact of biogenic emissions on atmospheric chemistry. She is also interested in the development of anthropogenic emission datasets, air quality modeling, and relationships between atmospheric chemistry and climate.

Prof. Mark A. Sutton's interests focus on the emission, atmospheric transfer of atmospheric reactive nitrogen compounds, especially ammonia, including the interactions with greenhouse gas balance, and eutrophication. He is engaged in leading atmospheric flux measurements and developing a multipollutant approach for nitrogen, with special attention to the fate of emissions from agriculture. Prof. Sutton is Chair of the International Nitrogen Initiative (INI) of IGBP/SCOPE, and Co-Chair of the UNECE Task Force on Reactive Nitrogen (a body under the Geneva Convention on Long-range Transboundary Air Pollution). He was coordinator of the EU NitroEurope Integrated Project and led the European Nitrogen Assessment (ENA), the first continental multithreat assessment of nitrogen impacts on climate, air pollution, water quality, soil quality, and biodiversity, published in April 2011. He also led the "Our Nutrient World" report for UNEP, published in 2013. Prof. Sutton is currently coordinator of the EU ÉCLAIRE project, which addresses how climate change will alter air pollution threats to European ecosystems, and is a member of the Steering Group of the UNEP led Global Partnership on Nutrient Management (GPNM).

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