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Review

A Review of the Representation of Aerosol Mixing State in Atmospheric Models

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Abstract: Aerosol mixing state significantly affects concentrations of cloud condensation nuclei (CCN), wet removal rates, thermodynamic properties, heterogeneous chemistry, and aerosol optical properties, with implications for human health and climate. Over the last two decades, significant research effort has gone into finding computationally-efficient methods for representing the most important aspects of aerosol mixing state in air pollution, weather prediction, and climate models. In this review, we summarize the interactions between mixing-state and aerosol hygroscopicity, optical properties, equilibrium thermodynamics and heterogeneous chemistry. We focus on the effects of simplified assumptions of aerosol mixing state on CCN concentrations, wet deposition, and aerosol absorption. We also summarize previous approaches for representing aerosol mixing state in atmospheric models, and we make recommendations regarding the representation of aerosol mixing state in future modelling studies.

Keywords: aerosol; mixing-state; black carbon; hygroscopicity; radiation; cloud condensation nuclei; liquid-liquid phase separation; air quality; climate; heterogeneous chemistry

1. Introduction

As will be treated in further detail later in this review, the aerosol mixing state significantly affects concentrations of cloud condensation nuclei (CCN), wet removal rates, thermodynamic properties, heterogeneous chemistry, and aerosol optical properties, with implications for human health and climate. Over the last two decades, a significant research effort has gone into finding computationally-efficient methods for representing the most important aspects of aerosol mixing state in air pollution, weather prediction, and climate models. In this review, we summarize the interactions between mixing-state and aerosol properties and processes relevant for human health, weather and climate, and the methods used to represent aerosol-mixing state in these models.

This paper is organized as follows: The remainder of the introduction attempts to disambiguate some terminology regarding aerosol mixing state, then describes the general evolution of aerosol in the atmosphere, and finally provides a brief overview of measurement techniques used to provide information about aerosol mixing state. Section 2 describes and attempts to quantify the effects of assumptions about aerosol mixing state on aerosol properties and processes. The properties discussed include aerosol hygroscopicity, and aerosol optical and radiative properties. The processes discussed include ice activation, equilibrium thermodynamics, and heterogeneous chemistry. Section 3 lists, describes, and discusses different modelling approaches used previously to represent aerosol mixing state in atmospheric models. Finally, Section 4 gives a summary and some recommendations for representing aerosol in atmospheric models.

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1.1. Terminology

The mixing state of a population of particles refers to the heterogeneity of the aerosol population. Most commonly, "mixing state" is used to refer to the distribution of component chemical species among a population of aerosol particles (sometimes referred to as the "population mixing state", e.g., [1]). A population is said to be fully externally mixed if each particle is composed of a single species. The population is said to be fully internally mixed if each particle in the population has an equal proportion of each species in the population.

The term "mixing state" has also been used to refer to the morphology of the particles in the population. This includes both the shape of particles and the distribution of chemical species within a single particle. Aerosol particles are assumed in most modelling studies to be spherical. However, particles can exhibit several morphologies [2–10], for example uncoated black carbon (BC) particles are known to have fractal-like structures, and dry sea salt or mineral dust particles can have crystalline structures. The distribution of chemical species within a single particle includes the distinction between a homogeneously-mixed particle and one where a hydrophobic core is coated by a layer or layers of more hydrophilic material (a core-shell configuration). In some studies, the terms "homogeneously-mixed" and "internally-mixed" have been used interchangeably. For clarity, we consider "internal mixing" to refer only to the distribution of chemical species across an aerosol population. Therefore, we would consider both homogeneously-mixed particles and particles with a hydrophobic core and a hydrophilic shell to be examples of internally-mixed particles.

We note that nearly every size-resolved aerosol module distinguishes the chemical composition of aerosol in different size regimes with the same degree of resolution as the size distribution. Aerosol in each size mode of a modal scheme or each size bin of a sectional scheme is considered to be externally-mixed with each other size mode or size bin. The chemical composition of each mode or size bin is tracked individually. The aerosol within a given size mode or size bin (i.e., the size-resolved mixing state) may be assumed to be externally-mixed or internally-mixed, or a more detailed representation may be used, depending on the module and the configuration used. It is important to note that even if the aerosol within each size bin or mode is assumed to be internally-mixed (size-resolved internally-mixed), aerosol in different size bins or modes will be externally-mixed: for example, freshly-nucleated sulphate and organic particles will be externally-mixed with large dust and sea-spray particles. Throughout this document, when any size-resolved aerosol module is discussed, it is the size-resolved mixing state that we will refer to, and it can be assumed that different size modes or size bins are externally-mixed, unless specified otherwise.

To quantify the extent to which an aerosol population is internally- or externally-mixed, Riemer and West (2013) [11] proposed a metric, which they denote as the mixing-state index. This is defined as the affine ratio between the population bulk diversity (which depends on the number of chemical species in the bulk aerosol population, and their mass fractions) and the average particle diversity (which depends on the number of chemical species in each particle, and their mass fractions). The mixing-state index ranges from 0 for a fully externally-mixed aerosol population to 1 for a fully internally-mixed aerosol population. This index has been applied to observations from the Carbonaceous Aerosols and Radiative Effects (CARES) [12] and Megacities: Emissions, urban, regional and Global Atmospheric POLlution and climate effects, and Integrated tools for assessment and mitigation (MEGAPOLI) [13] observation campaigns. It has also been used to characterize the effect of mixing state on human health [14]. Additionally, a related metric was applied to observations in London [15]. The relationship between this index and errors in CCN concentrations from a fully-internally-mixed assumption has been examined [16]. Additionally, by using machine-learning together with the output of a global chemical transport model, the mixing-state index has been estimated globally [17]. It should be noted that the value of the mixing-state index depends on the number and identities of species chosen for analysis: the mixing-state index of a population will be different if the species considered are the classes "inorganics", "BC", and "organics" compared to a case where the chosen species are "sulphate", "sea salt", "carbonaceous", and "other" [12]. Thus, care needs to be taken in comparing values of the mixing-state index between different studies.

1.2. General Evolution of Aerosol Mixing-State in the Atmosphere

A common idealized picture of the evolution of aerosol mixing-state would be that particles are emitted to the atmosphere from different sources as fully externally-mixed particles. These particles would then evolve towards an internally-mixed state as low-volatility compounds such as sulphates, nitrates, and organic matter condense onto them and as the particles coagulate with each other. This picture, however, is only partially correct. In many cases, particles contain multiple chemical components at emission. For example, sea-spray aerosol has been observed to contain sodium, chloride, sulphate, other salts, and organic compounds just after emission [18], and many studies have shown that BC emitted from biomass burning is typically internally mixed with organic species and salts (e.g., [19,20]). The mixing state of aerosols is typically not included in emissions inventories, and therefore assumptions must be made regarding the mixing-state of emissions (e.g., what fraction of BC from a particular source is emitted as hydrophobic vs. hydrophilic). These assumptions will depend, in part, on the representation of the mixing state used in a particular model. We consider the detailed treatment of the mixing state of emissions as beyond the scope of this review, but an important subject for future research. With these caveats in mind, it is true that particles from different sources can be expected to have different chemical compositions at emission, and it is also true that the chemical compositions of aerosol particles become more homogeneous with time through condensation and coagulation [10,21–23].

Special attention has been paid to the changes in mixing-state of mineral dust and especially BC, as these species are both hydrophobic and absorbing (strongly absorbing in the case of BC, and weakly in the case of dust). The formation of coatings on these particles composed of more hydrophilic, less absorbing species has been frequently referred to as the "ageing" of these particles. The ability of these particles to act as CCN, their removal by wet deposition, and their radiative properties all depend strongly on the nature and amount of coating material on these particles, as will be discussed further in Sections 2.1.1, 2.1.2, and 2.2, respectively. The morphology of both BC and dust also changes as they become coated with liquid or aqueous matter. The coatings themselves create a quasi-spherical shell on the dust and BC particles [5], but the fractal morphology of BC has also been observed to collapse into more compact forms as it becomes coated [8,24].

In addition to condensation/evaporation and coagulation, chemical redox and hydrolysis reactions would be expected to play a role in the ageing of BC [24,25], organic compounds [23], sea spray [26,27] and dust [28–30] particles. Regarding BC, the chemical ageing timescale for the transformation from hydrophobic to hydrophilic has been shown to be typically much longer than those due to condensation or coagulation, and does not contribute significantly to the ageing of BC [23,31,32]. In general, this process has therefore been neglected in recent studies.

1.3. Measurement Techniques

As the focus of this review is the representation of mixing-state in models, we restrict ourselves to a brief overview of measurement techniques here. We refer the reader to the following sources for further details: Single-particle measurement techniques were recently reviewed by Li et al. (2016) [4]. Further information on measurement techniques targeting optical properties of aerosol, including absorption, is available in Moise et al. (2015) [33]. The assessment of Bond et al. (2013) [34] contains a description of measurement techniques targeting BC, including those that provide information regarding its mixing state.

Particle morphology and direct information about population mixing state can only be obtained from single-particle measurement techniques. The resolution of these techniques generally limits them to the study of particles larger than approximately 100 nm, although at least one recent study describes the morphology of particles as small as 50 nm [35]. These techniques include methods of imaging particles deposited on a substrate, such as transmission electron microscopy, scanning electron microscopy, atomic force microscopy, and scanning transmission X-ray microscopy with near-edge X-ray absorption fine-structure spectroscopy (STXM-NEXAFS). Energy-dispersive X-ray spectrometry, secondary ion mass spectrometry and NEXAFS can provide chemical composition information for individual particles.

Analysis of mixing-state effects on hygroscopicity is possible through hygroscopicity tandem differential mobility analyzer (HTDMA) or volatility tandem differential mobility analyzer (VTDMA) measurements [36,37]. By themselves, these techniques offer evidence on whether an aerosol population is internally- or externally-mixed, based on whether the detected distribution of growth factors is monomodal or multi-modal. Together with measurements of the aerosol size distribution, closure studies can be performed, offering more information about the mixing state of species with differing hygroscopicities.

Different experimental techniques targeting BC will yield different quantities, and care must be taken to disambiguate between them for comparisons between different measurements and between observed and modelled quantities. A set of terminology regarding BC has been adopted by the atmospheric science community to maintain clarity regarding these different quantities [38]. The absorption of BC is directly measured using photoacoustic methods, aethalometers, particle soot absorption photometers (PSAP), multi-angle absorption photometers (MAAP), continuous soot monitoring systems (COSMOS), thermal optical reflectance (TOR), thermal optical transmission (TOT), and single particle soot photometry (SP2). The mass of BC can be inferred from the amount of absorption. If the BC is internally mixed with other species, then calculations of the mass through these methods will require the use of mixing rules (see Section 2.2) or other assumptions to relate the mass to the absorption. Several of these methods (COSMOS, TOR, TOT, SP2) attempt to mitigate this issue by heating the aerosol during or prior to the measurement, with the intent of removing all non-refractory mass from the particles. Ideally, the only mass remaining would be the BC mass, as BC is refractory. We direct the reader to Moise et al. (2015) [33] and Bond et al. (2013) [34] for further discussion of the potential errors and biases in these methods.

2. Effects of Mixing State on Aerosol Properties

As we have stated previously, aerosol mixing state significantly affects concentrations of CCN, wet removal rates, thermodynamic properties, heterogeneous chemistry, and aerosol optical properties. In this section, we describe the mechanisms of these effects in more detail. We also provide estimates of the errors related to these quantities that are introduced in atmospheric models by simpler representations of aerosol mixing state.

2.1. Effects on Particle Hygroscopicity

Mixing-state interacts with the hygroscopicity of particles both through their composition and their morphology. If the component species within the particle can be assumed to be homogeneously-mixed, then the resultant hygroscopicity of the particle is generally predicted using κ-Köhler theory [39], with the particle hygroscopicity approximated using volume-weighted average of the hygroscopicities of the constituent species. If a core-shell configuration is assumed, and if the shell is sufficiently thick that it can totally encompass the core, then the hygroscopicity of the particle is often approximated by that of the shell. In the cases of BC and dust, the particle generally becomes more hydrophilic as it becomes coated by other species. However, we note that reactions of dust with soluble condensible species, such as sulphuric acid, do not necessarily produce soluble products or increase the CCN-activity of the dust aerosol [40]. It is also possible for the more hydrophobic species to form the coating in the cases of organic-organic or organic-inorganic mixtures. We will discuss this particular case further in Section 2.4.2.

We describe in this subsection the effects of the interactions between mixing-state and hygroscopicity on CCN concentrations and wet deposition. These two subjects are well-studied because of their implications for climate, but we note also that changes in hygroscopicity may also affect the impact of soot on human health. Coating of soot aerosol by more hydrophilic species would increase the water uptake by the aerosol, increasing its wet diameter. This would reduce the degree of penetration into the human respiratory system, thus reducing the impacts on human health compared to uncoated soot [14,41]. Assuming internally-mixed aerosol underestimates deposition to human alveoli by up to 5% for aged soot, and by up to 20% for fresh soot.

2.1.1. Impacts on CCN Concentrations

Differences in hygroscopicity due to mixing-state directly alter the ability of particles to act as CCN, and parametrizations of cloud droplet activation for global models have been capable of incorporating multiple externally-mixed populations for many years now [42]. CCN concentrations are primarily of interest because increases in CCN concentrations generally increase cloud droplet number concentrations, which in turn result in increases in cloud reflectivity and lifetime, with implications for weather and climate. We note that it is well-known that a change or difference in CCN concentrations will lead to a smaller change or difference in cloud droplet number concentrations (e.g., [43–45]), due in part to supersaturation suppression by increased competition for water vapour. While variation in chemical composition is less important than size in determining CCN concentrations [46,47], heterogeneity in hygroscopicity still significantly affects CCN concentrations [48–50], particularly at low supersaturations [47]. If variation in particle composition with size is neglected, then a fully-internally-mixed assumption will frequently overestimate CCN concentrations, particularly at low supersaturations. This is because highly hydrophilic compounds are generally assumed to form coatings on less-hydrophilic species, such as BC and dust, increasing their hygroscopicity and allowing them to act as CCN. However, cases also exist where a fully-internally-mixed assumption has been shown to underestimate CCN concentrations [51,52].

CCN closure studies indicate that heterogeneity in hygroscopicity can be important for CCN concentrations in urban areas (e.g., [48]), but that CCN concentrations can be well approximated by assuming that the population is fully internally-mixed further from source regions (e.g., [51–53]). This is due primarily to the coating of hydrophobic species, such as BC and dust, by hydrophilic species through condensation and coagulation. Depending on location and local emissions, heterogeneity in hygroscopicity frequently decreases in the early afternoon, when photochemistry increases the available concentrations of condensible species (e.g., [48,53]). Mahish et al. (2018) [54] compared predicted CCN concentrations based on different simplifications of the mixing-state using long-term observations from the Southern Great Plains site in Oklahoma, USA. They found that a size-resolved internally-mixed representation of the aerosol mixing state performed modestly better (normalized mean bias (NMB) 1 to 2%, coefficients of determination (R^2) about 0.85) compared to either a fully internally-mixed, size-resolved externally-mixed, or a fully externally-mixed representation of the mixing state (NMB 10 to 21%, -9%, and 0 to 7%, respectively; R^2 about 0.8). It should be noted that only the assumed hygroscopicity was varied, the size distribution was assumed to be known in all cases. Another CCN closure study performed in the Yangtze River Delta region suggested that interstitial aerosol CCN concentrations could be best predicted by an internally-mixed assumption under low-supersaturation haze or heavy haze conditions, and by an externally-mixed assumption under other conditions [55]. However, it should be noted that all tested assumptions well predicted the CCN concentrations: Nearly all reported fitting factors were between 0.9 and 1.1, and nearly all reported R^2 values were greater than 0.9. Fitting factors differed between mixing-state assumptions by at most 0.12 for any given supersaturation and weather type combination, and R^2 values rarely differed by more than 0.02 based on mixing-state assumption.

We note that the differences in aerosol physicochemical properties due to differences in mixing-state can also result in differences in aerosol concentrations, hence affecting CCN concentrations. Notably, particle hygroscopicity influences rates of removal by wet deposition, discussed further in Section 2.1.2. These differences in removal rates strongly influence the remaining concentration and composition of aerosol after a wet deposition event, thus altering the CCN concentrations and aerosol radiative properties after wet deposition events. Differences in CCN concentrations due to mixing-state effects will also influence in-cloud microphysical processing and chemistry. In-cloud oxidation processes, including SOA formation and oxidation of SO_2 to form SO_4, typically result in an increase in soluble matter. If the cloud droplet evaporates, the resultant aerosol particle would therefore typically be more hydrophilic. Initial aerosol mixing-state will therefore have implications for CCN concentrations at later times if the cloud evaporates.

Many modelling studies have been performed to assess the impact of simplified representations of mixing state on estimates of CCN concentrations. For example, detailed particle-resolved modelling studies (see Section 3.5) were performed by Zaveri et al. (2010) [49], and Fierce et al. (2017) [56]. The former study showed that for an idealized urban plume, a size-resolved internally-mixed assumption would overestimate CCN concentrations by up to 25% at 0.2% supersaturation, and by up to 40% at 0.5% supersaturation. Fierce et al. (2017) extended this work by, in part, considering a large range of scenarios. They found that a size-resolved internally-mixed representation would overestimate CCN concentrations within fresh plumes by, on average, 17%, but that this error becomes negligible as the plumes age. These studies estimated the errors in CCN concentrations due to the assumption of internally-mixed aerosol by binning and averaging the results of the fully-resolved mixing-state simulations, and therefore would not include the effects of mixing state on wet removal rates and transport.

Other modelling studies compared simulations using more-detailed representations of the aerosol mixing state to simulations using less-detailed representations. These studies therefore implicitly included effects of changes in wet deposition and transport, so long as these processes are included in the model. Oshima et al. (2009) [57] used the MADRID-BC box model to investigate the effects of mixing-state representation on predicted CCN concentrations for a case of BC particles ageing by condensation of sulphate and secondary organic aerosol (SOA). They represent the mixing state using several BC mass fraction categories (see Section 3.2), and compare results using ten categories, three categories (BC-free, and hydrophilic and hydrophobic BC-containing particles), two categories (BC-free and BC-containing particles), or only one category (internally-mixed). They find that, compared to the ten-category representation, the internally-mixed assumption overestimates the fraction of BC mass that would activate at 0.05% supersaturation by 8–34%, depending on the age of the plume. Using a two-category representation provided very little improvement in the CCN-activated BC mass fraction. The three-category representation reduced the error in the CCN-activated BC mass fraction to 2–17%.

Ching et al. (2016) [58] modelled CCN concentrations using MOSAIC-mix (see Section 3.2) with different levels of complexity (up to 35 BC mass fraction categories and 30 hygroscopicity categories per size bin) for urban plumes ageing for up to 36 hours under a variety of scenarios. They found that normalized root-mean-square errors (NRMSE) in CCN concentrations using a size-resolved internally-mixed assumption would be up to 80%, with a mean across all scenarios tested of 14%. The use of two hygroscopicity categories ($\kappa < 0.2$ and $\kappa > 0.2$) reduced the mean NRMSE across all scenarios to 7%. Matsui et al. (2014) [59] compared modelled CCN concentrations for the East Asia region using the ATRAS model (see Section 3.2) using eight BC mass fraction bins to simulations where the aerosol was internally-mixed, and did not find significant differences based on the representation of mixing-state. This may be due to the large amounts of soluble condensible material in this region which quickly coats the BC particles, rendering them hygroscopic. However, subsequent work with ATRAS [60] also found only small differences in global mean CCN concentrations based on the number of BC mass fraction bins used. Lee et al. (2016) [61] examined a case of radiation fog in the San Joaquin Valley using Source-Oriented WRF-Chem (SOWC; see Section 3.4). They found that a size-resolved internally-mixed approach would overestimate CCN concentrations, due to the artificial coating of insoluble aerosol with soluble material. This increased the domain-mean fraction of aerosol that activated as CCN by 18%, resulting in increases in cloud liquid water by 5%.

In summary, when subsequent effects on wet deposition, transport, and other processes are neglected, a size-resolved internally-mixed representation of the mixing state results in overestimates of CCN concentrations that range from negligible to 40%, depending on supersaturation, aerosol composition, and the true aerosol mixing state. When effects on wet deposition and transport are included, these overestimates range from negligible to 80%. In all cases these errors are most frequently between 10% and 20%, are greatest near source regions and become negligible as aerosols age, primarily through condensation of hydrophilic species. The overestimates in CCN concentrations can be greatly reduced by using two separate mixing-state categories based on particle hygroscopicity, as shown by the results of Oshima et al. (2009) [57] and Ching et al. (2016) [58].

2.1.2. Wet Deposition

Changes in hygroscopicity also alter wet deposition rates, subsequently impacting on aerosol mass concentrations. As fully internally-mixed representations tend to overestimate hygroscopicities, they tend to overestimate wet deposition, particularly of hydrophobic species which can gain hydrophilic coatings. This results in underestimates of burdens of hydrophobic aerosol, such as BC. This would also affect the amount of BC transported to snow or ice-covered surfaces, where it can reduce surface albedo and enhance the absorption of solar radiation into the surface.

The effect of mixing-state representation on wet deposition has been addressed by several modelling studies. For instance, Matsui et al. (2013) [62] simulated the East Asia region using ten BC mass fraction categories. They found that a size-resolved internally-mixed assumption would underestimate BC concentrations by 15% to 20% in the planetary boundary layer, and by up to 35% in the upper troposphere. This was due to the resolution of uncoated BC, which is less-efficiently removed by wet deposition. Subsequent work [59] using the ATRAS aerosol module implemented in WRF-Chem showed that resolving the aerosol mixing state through up to ten BC mass fraction bins increased the spatially and temporally-averaged mass concentration of BC by about 10%, compared to a size-resolved internally-mixed simulation. A subsequent study [60] with the ATRAS aerosol module in CAM5 similarly found that a size-resolved internally-mixed assumption would underestimate globally-averaged BC lifetime by 4% to 15%, depending on the size of the BC emissions.

Assuming that an aerosol population is externally-mixed tends to underestimate wet deposition of hydrophobic species. The resulting errors in aerosol burden are typically larger than if the aerosol population is assumed to be internally-mixed. Chen et al. (2017) [63] found that assuming BC was externally-mixed would overestimate BC mass concentrations over Central-Eastern China by 5–20%, compared to a simulation with two BC populations (hydrophobic and hydrophilic). Assuming that all BC was size-resolved internally-mixed resulted in differences from the two-BC-population simulation that were <5%.

We note that the effect of the mixing-state representation on wet deposition and transport depends on the particular implementation of the wet deposition process in a given model. For instance, Vignati et al. (2010) [64] compared simulations using bulk externally-mixed aerosol and using two mixing-state categories (hydrophobic and hydrophilic) in a total of seven lognormal modes (M7, see Section 3.1.1). In this study, the bulk externally-mixed approach resulted in increased wet deposition of BC, because 70% of BC was assumed to be incorporated into cloud droplets and wet deposited as efficiently as hydrophilic species. They found that the BC surface concentrations were similar using both approaches close to sources, but could differ by orders of magnitude far from sources, such as in the Arctic and Antarctic. The mixing-state-resolved aerosol led to much improved agreement with BC concentrations observed at polar stations. The authors performed a sensitivity study with the bulk externally-mixed configuration of the model where they reduced the fraction of BC assumed to be incorporated into cloud droplets to a more representative value (40%) based on the M7 results. However, the model still underestimated BC transport to the polar regions. This was because, in the M7 results, the fraction of BC that was hydrophobic increased with distance from source regions, due to preferential removal by wet deposition of the hydrophilic BC. Additionally, Liu et al.

(2012) [65] compared simulations using a size-resolved internally-mixed mixing-state representation with simulations using two categories (hydrophilic and hydrophobic, see Section 3.1.1). When using the initial value of the hygroscopicity of primary organic matter (POA, κ = 0.1), much of the POA and BC was wet-scavenged before ageing into the well-mixed mode. Therefore only modest differences in POA and BC concentrations were predicted. When this κ was reduced to 0 in the two-category simulation, global burdens of BC and POA increased by 7.5% and 10%, respectively.

These studies show that a size-resolved internally-mixed representation of the aerosol mixing state overestimated wet deposition of hydrophobic aerosol, leading to underestimates in global burdens of BC that are from less than 5% up to 15%, depending on details of the model setup. Underestimates in BC concentrations are much greater far from source regions, and have been reported to be up to several orders of magnitude in the Arctic and Antarctic. Fewer studies using a variety of mixing-state representations have examined wet deposition than CCN concentrations. However, based on the results of studies that investigated CCN concentrations, we expect that using two hygroscopicity categories would be sufficient to greatly reduce error in burdens of hydrophobic material compared to a size-resolved internally-mixed representation.

2.2. Direct Impacts on Optical Properties and Radiation

When an absorbing particle, such as BC, becomes coated by less-absorbing species, the coating can increase the absorption of the absorbing core, in what is known as the "lensing" effect. Theoretical calculations (e.g., [66,67]) have shown that the absorption, and hence the radiative forcing, of BC strongly depends on whether it is internally-mixed or externally-mixed with respect to scattering species such as ammonium sulphate. The optical and radiative properties of non-absorbing aerosol are generally found not to be strongly dependent on the mixing-state of the component species (e.g., [49,68]), and total aerosol optical depth (AOD) is also generally not found to be strongly dependent on mixing state (e.g., [59,62,68,69]), as aerosol scattering generally contributes much more to AOD than aerosol absorption. Due to its strongly-absorbing nature, the vast majority of studies regarding the effect of mixing state on optical properties and radiation have focused on BC. While we focus here on the implications for modelling studies, the effects of mixing state and morphology on optical properties is also important for remote-sensing of aerosol from both the surface (e.g., [70]) and from satellite instruments (e.g., [71]).

Similarly to BC, mixing state would also be expected to affect the absorption of brown carbon (BrC) aerosol. Brown carbon refers to organic matter that absorbs in the near-ultraviolet and blue wavelengths, but is weakly absorbing in the red and near-infrared wavelengths. The magnitude of this wavelength dependence can exhibit large variations, and so remains poorly quantified [72]. Saleh et al. (2018) [72] note that there exists a fraction of BrC that has only a weak dependence of absorption on wavelength, and is also refractory. Additionally, Liu and Mishchenko (2018) [67] note that wavelength dependence of the absorption of BC depends on the mixing state and morphology of BC, and can deviate significantly from an idealized inverse relationship. The attribution of absorption between BrC and BC in measurements can therefore be ambiguous, with differences up to a factor of 4.3 in the fraction of absorption due to BrC depending on the method used to distinguish BrC from BC [73]. Uncertainties regarding other aspects of BrC that would influence its radiative effect are much greater than for BC. In particular, large uncertainties remain in the value of the refractive index of BrC [74], due in part to large variations in the refractive index depending on burn conditions [72]. Organic matter may become either more absorbing [33,75–77] or less absorbing (known as photobleaching) [78] with time as it undergoes photochemical or other oxidation reactions in the atmosphere.

Additionally, a particle consisting of BrC internally-mixed with inorganic species may undergo liquid-liquid phase separation (see Section 2.4.2). In this case, the more absorbing component (BrC) would frequently form a shell around the less-absorbing component (the inorganic species). This would result in less absorption enhancement than if the absorbing component forms the core of the particle [68]. Detailed calculations of the optical properties of such BrC-inorganic mixtures were recently performed by Fard et al. (2018) [79]. They considered particles consisting of a spherical inorganic core inside a spherical BrC shell, with the inorganic core located at random locations within the BrC shell. They calculated the optical properties of a large number of such particles, and found that the optical properties averaged over a large number (10,000) of particles with a randomly-placed core were very similar (within 3%) of the optical properties of a particle with a concentric core. The concentric core-shell assumption is therefore an appropriate approximation for calculating the optical properties of such particles. This has been shown previously for particles with a BC core, provided that the core occupies a relatively large volume fraction of the aerosol [80]. Fard et al. (2018) then used the core-shell assumption to calculate how the optical properties of internally-mixed BrC-inorganic particles differed between liquid-liquid phase separated particles and homogeneously-mixed particles. The asymmetry parameter was not significantly different for wavelengths greater than 400 nm. The maximum relative difference in the SSA was 25%, which was found for the largest and most absorbing particles with the lowest organic to inorganic ratios at the shortest wavelengths tested. After integrating across the visible solar spectrum to obtain the difference in aerosol direct radiative forcing, the authors conclude that "the effect of liquid–liquid phase separation on shortwave radiative forcing is rather small". These results therefore suggest that it is not necessary to account for phase separation to realistically represent the radiative forcing of BrC.

Two additional related effects to the change in aerosol optical properties based on mixing state are the changes in optical properties of cloud droplets and other hydrometeors in air (e.g., [34,81–83]) and of snow grains deposited on the surface (e.g., [84]). While each of these effects have been considered in global climate models and snow surface models, respectively, and each has been shown to be significant for estimates of radiative forcing, we consider them outside the scope of this review, given our focus on atmospheric aerosol modules.

2.2.1. Enhancement of BC Absorption Due to Internal Mixing

The absorption due to aerosol particles can be included in climate models without an explicit optical model through the use of the mass absorption cross section (MAC, also known as the mass absorption coefficient). The MAC is the absorption optical cross section normalized by the mass of the absorbing component of the particle, which is BC in most of the studies referred to in this section. The MAC of fresh, uncoated BC was recently estimated to be 7.5 ± 0.18 m^2 g^{-1} at 550 nm based on a compilation of previous measurements [9], in agreement with an earlier estimate by Bond and Bergstrom (2006) [85]. This MAC increases with particle size [86,87], and is greater for lacey structures than compacted structures [67].

Increases in absorption due to the lensing effect of weakly-absorbing coatings can be included through the use of an enhancement factor (E). The enhancement factor is defined as the ratio of the MAC of the coated particle to the MAC of the uncoated particle. The enhancement factor will depend on the size of the BC particle, and the amount and nature of the coating. In addition to the lensing effect, the presence of absorbing material in the non-refractory coating (e.g., BrC) can also contribute to larger values of E, especially if measured at shorter wavelengths. We do not attempt to summarize here all reported values of E based on field observations, but we note that reported values from observations range from close to 1 (no enhancement) to 4, with the majority of studies reporting values between 1 and 2.5 [2,10,86,88–96]. This diversity is likely due in part to differences in measurement methods, including the wavelength of light at which absorption is measured, as E typically decreases with wavelength [67,96]. Regional and seasonal variation in the amount of coating material present on BC particles also contributes to this diversity.

Jacobson (2012) [97] calculated a globally-averaged enhancement factor of 2.41 using the GATOR-GCMOM model. He attributes the large value of the enhancement factor compared to observations to the large portions of the global domain at high relative humidity, including interstitial aerosol between cloud droplets. The aerosols swell at high relative humidities, leading to a thicker non-absorbing shell and enhanced absorption. Many observations, however, have been made at relatively low relative humidities, and interstitial aerosol is particularly difficult to measure. Chung et al. (2011) [98] performed detailed optical calculations of scattering and absorption by BC particles. They calculated values of *E* as large as 1.9, and they also calculated a large range of changes in aerosol backscattering based on the degree of internal mixing, from a factor of −5 to a factor of +10.

Fierce et al. (2016) [99] introduced a parametrization of *E* intended for global aerosol models based on the volume fraction of dry aerosol coating that is mixed with BC-containing particles, the hygroscopicity of the coating material and the environmental relative humidity (RH). They implemented this parametrization into a global aerosol model, and found that use of the parametrization decreased the global mean *E* of BC by 23%. This resulted in a BC-mass-weighted mean *E* of 1.5, although the value ranged from 1.1 to over 2 locally. The authors note that BC absorption depends strongly on RH: At high RH, water uptake results in twice as much absorption by BC particles compared to the absorption under dry conditions. However, neglecting the effect of water uptake led to an underestimate of the global mean absorption enhancement by only 5%.

2.2.2. Mixing Rule

Alternatively to using fixed MAC and *E* values, the optical properties of an aerosol particle can be calculated using an optical model. If the aerosol particle contains multiple species with different optical properties (i.e., different refractive indices), then a mixing rule must be applied to calculate the refractive indices of the aerosol particle from the refractive indices of the component species. These mixing rules are distinct from the aerosol population mixing state: if an aerosol population is fully-externally mixed, it is not necessary to apply any mixing rule to calculate the optical properties of the individual particles, as each particle consists of only a single chemical species. Also, for any given mixing rule, the optical properties of an aerosol population will depend on to what degree the aerosol population is internally-mixed. We will discuss sensitivities to population mixing state, including comparing model results with fully-internally mixed, fully-externally mixed, and more detailed mixing-state representations in Section 2.2.3. The choice of mixing rule depends in part on how the different species are distributed throughout the particle. Previous studies have approximated the refractive indices using a volume-weighted mean of the refractive indices of the constituent species, or by the Maxwell-Garnett or Bruggman mixing rules [100], or by the dynamic effective medium approximation [101]. Both Toon and Ackerman (1981) [102] and Yang (2003) [103] have also provided algorithms for calculating the refractive indices of a particle composed of a spherical core surrounded by a shell with different optical properties using Mie theory. An expanded discussion of mixing rules can be found in [104].

A volume-weighted mean of the refractive indices has repeatedly been shown to overestimate absorption of BC aerosol, as compared to a more realistic spherical BC core surrounded by a weakly-absorbing shell [105–109]. Kim et al. (2008) [106] found that core-shell and homogeneously-mixed mixing rules resulted in the same AOD. However, the choice of mixing rule did have an effect on the coated BC aerosol top-of-atmosphere (TOA) aerosol direct radiative forcing (DRF): The core-shell clear-sky and all-sky TOA aerosol DRFs were less (smaller positive values) than the homogeneously-mixed values by 32% and 10%, respectively. The total clear-sky and all-sky TOA DRF decreased (became more negative) by 2% and 14% respectively. The Maxwell-Garnett and Bruggman mixing rules yield optical properties more similar to a core-shell calculation than volume-averaged refractive indices [105]. Adachi et al. (2010) [2] calculated the optical properties of BC-containing particles using volume-weighted mean refractive indices, core-shell Mie theory, the Maxwell-Garnett mixing rule and detailed calculations using the discrete dipole approximation. They found that the Maxwell-Garnett mixing rule most closely approximated the detailed calculations of the absorption of BC-containing particles. They found that core-shell Mie theory and volume-weighted mean refractive indices overestimated the BC radiative forcing and MAC by similar amounts (26% and about 35%, respectively). Other studies have shown that the choice of mixing rule has smaller effects on optical properties than the representation of the population mixing-state: Klingmuller et al. (2014) [68] found that SSA and net shortwave fluxes were much less sensitive to the choice of volume-weighted means of refractive indices, volume-weighted means of dielectric constant, the Maxwell-Garnett mixing rule, or core-shell Mie theory than to whether or not BC was internally-mixed with respect to other aerosol components. Liu et al. (2017) [110] found that the sensitivity of BC-containing particle scattering cross sections to the choice of Maxwell-Garnett mixing rule, Bruggman mixing rule, core-shell Mie theory or Rayleigh-Debye-Gans model was insignificant, while an externally-mixed assumption resulted in smaller scattering cross sections by up to a factor of two. Matsui et al. (2018) [60] found that the sensitivity of aerosol absorption optical depth (AAOD) to the choice of core-shell Mie theory, Bruggman mixing rule, or dynamic effective medium approximation was about one third of the sensitivity to the choice of an internally-mixed or detailed BC mass-fraction mixing-state representation, but that this depended on the size of the BC emissions. These differences between choice of mixing rule can be smaller than uncertainties due to uncertainties in refractive indices and BC density [111].

2.2.3. Effects of Aerosol Population Mixing-State Representation on Radiation

Here, we describe how the choice of aerosol population mixing state representation as externally-mixed, internally-mixed, or using a more detailed population mixing state representation affects the radiative properties of the aerosol population and calculated aerosol radiative effects. Many global and regional modelling studies have shown that whether BC is assumed to be internally or externally mixed strongly affects estimates of aerosol SSA [57,68,69,107,108] and aerosol radiative fluxes [68,69]. Changes in the amount of absorption by aerosols have implications for climate through multiple pathways [34,112]. If the amount of incoming radiation scattered by aerosols is unchanged, increased absorption implies less radiation reaching the Earth's surface, and a decrease in temperature at the surface. Increased absorption also implies a local increase in temperature in the atmospheric layer containing the absorbing aerosol. This increase in temperature can reduce local relative humidity, decreasing cloud cover, or change atmospheric stability, leading to either increases or decreases in local cloud cover, depending on the relative location of the absorbing aerosol to the cloud layer (known as aerosol semi-direct effects). These changes in cloud cover can have large impacts on the Earth's radiative balance, and hence climate, and may also affect precipitation. Many modelling studies have shown strong sensitivities of the aerosol direct radiative effect (DRE) to the assumed mixing state of BC aerosols [1,113–117], and some have shown that even the predicted sign of the aerosol radiative forcing depends on the assumed mixing state [118–120].

Studies using more detailed representations of the aerosol mixing state have frequently used a size-resolved internally-mixed representation for comparison. Assuming that a BC-containing aerosol population is internally-mixed when some of the particles in the population are BC-free would overestimate the coating thickness on the BC particles, and hence overestimate the absorption. Detailed particle-resolved modelling studies (see Section 3.5) to estimate differences in radiative properties due to the assumption of internally-mixed aerosol (without including changes in processing, such as wet removal rates) have been performed by Zaveri et al. (2010) [49], and Fierce et al. (2017) [56]. The former study showed that for an idealized urban plume, a size-resolved internally-mixed representation would overestimate absorption coefficients by 14% to 30%, compared to the detailed particle-resolving model. Fierce et al. (2017) extended this work by, in part, considering a large range of scenarios. They found that a size-resolved internally-mixed representation would overestimate absorption coefficients within fresh plumes by, on average, about 50%, compared to the detailed particle-resolving model, and that this error reduces to about 25% as the plumes age. Similarly, Ching et al. (2016) [58] found using the MOSAIC-Mix model that an internally-mixed assumption would result in NRMSE values in absorption coefficients of 21%, averaged across ten different urban plume scenarios. The maximum NRMSE in the asymmetry parameter, single scattering albedo (SSA, the ratio of scattered to scattered plus absorbed radiation), and scattering coefficients were all close to 10% or less, while the maximum NRMSE in the absorption coefficient was more than 30%. We note that the low NRMSE in SSA relative to the NRMSE in the absorption coefficient is expected because total aerosol scattering is generally large compared to aerosol absorption, yielding values of the SSA that are generally high. Observed SSA values, even in regions expected to be strongly affected by absorbing aerosols, are usually larger than 0.8 [111]. The relative error in SSA can therefore be deceiving. For example, a change in SSA from 0.95 to 0.90 is only a change of about 5% in the value of the SSA, but implies a doubling of the fraction of extinction due to absorption.

Oshima et al. (2009) [57] compared box model simulations of BC particles ageing by condensation of sulphate and SOA by changing the number of BC mass fraction categories used to represent the aerosol mixing-state. They compared the results using ten categories, three categories (BC-free, and hydrophilic and hydrophobic BC-containing particles), two categories (BC-free and BC-containing particles), or only one category (internally-mixed). They found that, compared to the ten-category representation, the internally-mixed assumption underestimates scattering coefficients by 11–19% and overestimates absorption coefficients by 35–44%, depending on whether the BC aerosol is fresh or aged. Using a two-category representation greatly improved estimates of scattering and absorption coefficients, reducing the errors to 1–3% and 3–4%, respectively. The three-category representation did not result in much greater improvement in radiative properties. This contrasts with the effects on predictions of CCN activation discussed in Section 2.1.1, where the two-category representation had little effect on errors in CCN activation, but the three-category representation showed significant reductions in errors.

Matsui et al. (2014) [59] modelled the East Asia region using the ATRAS model (see Section 3.2) with ten BC mass fraction categories, and found that a size-resolved internally-mixed assumption would overestimate AAOD by 20%, resulting in an overestimate of the heating rate within the planetary boundary layer of 21%, despite a reduction in the BC mass concentration due to increases in wet deposition. This is in contrast to the negligible effect found on CCN concentrations, as the hygroscopicity of the particles depends less on the thickness of the coating than radiative properties.

Several early studies have shown that if one assumes that BC is fully internally-mixed with other species, the positive radiative forcings of BC are 57% to 189% greater than if one assumes that BC is externally-mixed with other species [114,121–123]. However, these early studies used volume-averaging to calculate the refractive indices of the coated BC particles, which has since been shown to overestimate the absorption of the coated BC [105,107,108,114]. Jacobson (2001) [109] calculated that the global, all-sky, yearly-averaged DRE from anthropogenic BC would be greater by 96% for an internally-mixed core-shell morphology (more realistic than volume-averaging) compared to an external mixture. Ma et al. (2012) [116] found that assuming BC is externally mixed vs. modelling the mixing-state of BC using two populations (hydrophobic and hydrophilic, see Section 3.1.1) would overestimate the DRE of anthropogenic aerosol at the top of atmosphere by 49% due to an underestimate of aerosol absorption. A similar study [119] found that anthropogenic aerosol TOA radiative forcing would change sign from -0.175 W m^{-2} to +0.031 W m^{-2} as the mixing-state representations is changed from externally-mixed BC to allowing some BC to become internally-mixed with other species. Zuang et al. (2013) [120] found that the aerosol DRF over east Asia would change sign from -1.11 W m^{-2} to +0.45 W m^{-2} as the mixing-state assumption was changed from externally-mixed to fully internally-mixed. Chung et al. (2011) [98] applied calculated changes in optical properties of BC particles due to coating together with global estimates of BC AOD to estimate the sensitivity of BC DRF to whether BC is externally or internally-mixed. When including both the maximum absorption increase and the maximum positive or negative effect on aerosol backscattering, they estimated that the global TOA DRF of both natural and anthropogenic BC would be between 14% less and +80% greater if BC was internally mixed with scattering species than if it was externally mixed.

Some studies suggest that a size-resolved internally-mixed representation yields more realistic optical properties than an externally-mixed representation. Jacobson (2001) [115] found using a model with a detailed categorization by mass composition mixing-state representation that BC rapidly becomes coated with scattering material in the atmosphere, and calculated that the radiative forcing was therefore more closely approximated by an internally-mixed assumption than an externally-mixed assumption (0.55 W m^{-2} compared to 0.62 W m^{-2} or 0.31 W m^{-2}, respectively). Han et al. (2013) [69] found that a size-resolved internally-mixed representation yields SSA that compared better with surface-based remote sensing observations in China than an externally-mixed representation. Ghan et al. (2012) [83] found that the globally-averaged anthropogenic aerosol radiative forcing differed by less than 0.1 W m^{-2} between simulations using a size-resolved internally-mixed and a two-category representation (hydrophilic and hydrophobic). When decomposed into the shortwave and longwave direct, indirect, and semi-direct components, the differences in the global means were still less than 0.1 W m^{-2} and less than the standard error. However, an internally-mixed representation will still overestimate the positive radiative effect of BC: Matsui et al. (2018) [60] calculated that a size-resolved internally-mixed approximation would overestimate the DRE by up to 94%, compared to simulations with ten BC mass fraction categories. Kodros et al. (2018) [1] calculated the aerosol DRE over the Arctic using various treatments of the BC mixing state, including constraints on BC shell thickness or the fraction of particles that included BC based on observations. They found that the aerosol DRE varied by 19% between calculations with external and internal BC mixing state assumptions (−1.65 and −1.34 W m^{-2}, respectively), but that this range was reduced to 9% between the two observationally-constrained calculations (−1.59 and −1.45 W m^{-2}). They also found that using an externally-mixed assumption with absorption increased by a factor of 1.5, as recommended by Bond et al. (2006) [105], resulted in an aerosol DRE approximately halfway between the two observationally-constrained calculations (−1.52 W m^{-2}).

Most of the above studies focus on how the radiative effects of BC change depending on whether it is externally or internally-mixed with scattering species, but an alternate perspective is to examine how the radiative effects of scattering aerosol change depending on whether or not the scattering material is internally-mixed with BC. Zhu et al. (2017) [117] found that representing SOA as internally-mixed with other particles instead of externally-mixed reduced the magnitudes of the globally-averaged aerosol DRE and aerosol indirect effect of SOA from −0.688 W m^{-2} and −0.723 W m^{-2} to −0.280 W m^{-2} and −0.032 W m^{-2}, respectively. This was, in part, due to the increase in absorption by BC due to internal mixing with SOA. The authors therefore suggest that representing SOA as externally-mixed with other aerosols greatly overestimates the magnitude of its radiative effects.

The globally-averaged radiative effects of BC aerosol depend not only on the optical properties of the aerosol, but also on the lifetime of the aerosol in the atmosphere. Many of the same scattering compounds that increase absorption of BC through the lensing effect are also hydrophilic, and therefore enhance the removal of BC from the atmosphere through wet deposition, reducing its atmospheric lifetime (see Section 2.1.2). This can lead to compensating errors: if a model overestimates the time required for BC to become coated with scattering, hydrophilic compounds, then the MAC of the BC will be underestimated, but the atmospheric lifetime and hence the burden of BC will be overestimated. This effect has been demonstrated by Matsui et al. (2013) [62], through model simulations of the East Asia region with either a detailed mixing-state representation using ten BC mass fraction categories or a simpler size-resolved internally-mixed representation. When only the changes in optical properties were considered, the absorption coefficient, the heating rate by aerosols at 1 km, and the negative radiative forcing at the surface were all overestimated by the simpler mixing-state treatment by 38%, 31%, and by 12%, respectively. When the effects on wet deposition were also included, BC concentrations were reduced by between 15% and 20% in the planetary boundary layer, and the overestimations in the absorption coefficient and the heating rate were reduced to 19% and 10%, respectively. The differences in the radiative forcing at the surface became negligible. This effect is also noted by Boucher et al. (2016) [124], who show that the BC AAOD and DRE are insensitive in the LMDz-OR-INCA and OsloCTM2 global models to the BC ageing lifetime (see Section 3.1.3) due to these compensating errors.

Other aerosol properties may be tuned to compensate for errors due to mixing-state representation: Nordmann et al. (2014) [125] performed regional simulations of Europe using a model with a size-resolved internally-mixed mixing-state representation. They found that while the BC mass concentrations were underestimated with respect to observations, the absorption was weakly overestimated with respect to observations. They attributed this to the BC being primarily externally-mixed in this region, instead of internally-mixed, as assumed by the model. In a sensitivity study, they were able to reproduce observed BC MAC values by reducing the imaginary refractive index of BC to an unrealistically low value of 0.26 (originally set as 0.71).

The sensitivities of aerosol radiative properties and radiative effects to the representation of the mixing state depends on other aerosol properties that are sometimes poorly constrained. The sensitivity of aerosol radiative forcing to mixing-state representation calculated by Ghan et al. (2012) [83] increased from less than 0.1 W m^{-2} to 0.2 W m^{-2} when the hygroscopicity parameter of POA was reduced, due to reduced wet deposition of BC mixed only with POA. Matsui et al. (2018) [60] have also recently shown that sensitivities of aerosol properties to mixing-state representation depend strongly on the emitted size distribution of BC: a size-resolved internally-mixed approach slightly underestimated AAOD and BC DRE by 4% and 10% when a small emission size was used, but AAOD and BC DRE were overestimated by 109% and 94% when a large emission size was used. The authors also stress that the sensitivities of AAOD and aerosol DRE to BC emissions sizes are much greater when the BC mass fraction mixing state is resolved using ten BC mass fraction categories than when using a size-resolved internally-mixed or a two-category approach.

It is important to note that some of the above studies consider the chemical mixing state of aerosol population independent of other aerosol properties that change as an aerosol population evolves from externally-mixed to internally-mixed. Most notably, some studies do not alter the size distribution of the aerosol population. In the real atmosphere, the same processes that cause an aerosol population to become internally-mixed (primarily condensation and coagulation) also cause the aerosol size distribution to shift to larger sizes. This effect is highlighted by the study of Curci et al. (2015) [107], which compared fine-mode aerosol AOD, SSA, and asymmetry parameter (g) calculated at 440 nm and 870 nm assuming that all aerosol was either externally-mixed, homogeneously internally-mixed, or internally-mixed with an absorbing core and a scattering shell. Aerosol bulk vertical mass profiles were obtained from 11 air quality models. Unlike other studies, they found that AOD decreased significantly (by 37% on average), when the mixing-state assumption was changed from externally-mixed to homogeneously internally-mixed. However, this was not due to a change in the distribution of absorbing and scattering species among particles, but instead to a change in the size distribution: the assumed lognormal size distribution for each chemical species was divided among 100 size sections. Within each size section, the masses of each species were summed to yield the internally-mixed particle mass. In essence, each of the externally-mixed particles were instantly coagulated with all other particles of the same size, resulting in fewer, larger particles. These larger particles scattered light less efficiently (per unit mass) due to the change in size alone. In other studies referenced here (e.g., [1,68,110,111]), aerosol particle size would be preserved when transforming between externally-mixed and internally-mixed assumptions. This implies that BC cores would be larger when externally-mixed than when internally-mixed as the total particle size (core+shell) is held constant. This does not reflect the evolution of particles in the atmosphere, as BC particle cores would not be expected to reduce in mass during condensation or during coagulation with non-BC particles. But it does allow for an easier separation of effects due to either the distribution of absorbing and scattering component masses across the aerosol population, or changes in aerosol size. Curci et al. (2015) [107] also found significant differences in SSA and g based on whether the particles were homogeneously mixed or had a core-shell morphology. Similarly, Kim et al. (2008) [106] found that assuming that aerosols were externally-mixed decreased AOD by 42%, but this effect is also likely due to the smaller size of the aerosols, as no coating of BC or OC by SO_4 occurs in the externally-mixed simulation.

2.2.4. Aerosol Particle Shape and Radiation

Generally, due to constraints on computational resources, all particles are assumed to be spherical for radiation calculations in atmospheric models. However, fresh BC particles have a fractal morphology, and sea salt and dust can have crystalline morphologies. Several studies have investigated using different shapes to approximate dust, including distributions of elliptical spheroids (e.g., [70,126]), tri-axial ellipsoids [127], Poisson-Voronoi tessellation [128], and non-symmetrical hexahedra [129]. Compared to Mie theory, all of these shapes can provide improved agreement with observed optical properties, due to both more realistic particle shapes and an increase in the number of free parameters. The elliptical spheroid approximation for dust has been adopted for the AERONET retrievals [70], but we are not aware of other shapes being used to calculate optical properties in any atmospheric aerosol model. The elliptical spheroid approximation is an improvement over a spherical approximation, but is still limited in its ability to reproduce the optical properties of dust, particularly for larger particles [126].

Uncoated BC generally has an aciniform (grape-like) fractal structure, consisting of chains of spherules around 30 nm in diameter (e.g., [9]). Each chain typically has tens of spherules per particle, resulting in a volume-equivalent diameter of around 120 nm (e.g., [2]), although single spheres have been observed as well [3]. As the BC particle takes up more hydrophilic species, these fractal chains collapse and become more sphere-like. During this initial stage, there is little enhancement of absorption by the coating [91]. In the absence of any scattering material, this collapse of the agglomerate would be expected to decrease the absorption of the BC particle [67]. If the coating is thicker, then the absorption is enhanced. This pattern of growth was found by Pei et al. (2018) [6], however they also note the importance of internal voids which may be filled after the particle is fully-coated. Due to the collapse of the fractal chains into a more sphere-like geometry, the absorption enhancement can be well-approximated by assuming a spherical absorbing core with a concentric spherical shell, once the shell is sufficiently thick [90,92]. Observations of highly aged particles indicate that the BC components are predominantly fully embedded in the coating material [95].

Even when a particle contains both BC and other species, the BC portion of the particle may not be entirely coated by the less-absorbing species. In the limit where the less-absorbing and BC masses are barely in contact with one another, the radiative properties would approach those of two externally-mixed particles. Liu et al. (2017) [110] showed through observations and calculations that for particles with a mass of 2 fg, the optical properties are best fit by an externally-mixed model if the ratio of non-BC mass to refractory BC mass was less than about 1.5. Peng et al. (2016) [91] similarly found that the observed absorption of BC particles showed only small changes until the mass-equivalent diameter increased by 50%, after which the absorption increased rapidly. Liu et al. (2017) ascribe this behaviour to the non-BC mass being too small to entirely coat the BC mass within this regime, and instead partially filling the space between BC cores or attached to them. For non-BC to refractory BC mass ratios >3, they find that the optical properties are best fit by an internally-mixed model, implying that the BC cores are generally entirely coated within this regime. They refer to intermediate mass ratios as the transition regime, where optical properties fall between the internally-mixed and externally-mixed limits.

Bond and Bergstrom (2006) [85] note that measured MAC values for fresh, uncoated BC are about 30% higher than those calculated using best estimates of the refractive index and density of BC. They suggest that this discrepancy is due to interactions between neighbouring spherules with the BC agglomerates.

The effects of mixing state and morphology on the optical properties of aerosol can be calculated in detail using, for instance, the discrete dipole approximation [130]. The large computational expense of these calculations prohibits the online use of these methods in global or regional aerosol models. Nevertheless, these studies provide important insights into the sensitivities of aerosol optical properties to mixing state and morphology, and insights into how to improve parametrizations of these optical properties in aerosol models. Such studies have shown that the MAC of uncoated BC is not sensitive to the aggregate size (e.g., [80,131]). The calculation of Chung et al. (2011) [98] suggest that for a realistic size distribution of uncoated BC particles, the mean MAC could be well-approximated by a volume-equivalent sphere. Using a rectangular prism in place of an ellipsoid for dust particles results in differences in mass extinction cross-section (MEC) as high as 60%, differences in MAC frequently between 10–15%, and differences in mass scattering cross-section (MSC) as high as 70% [131]. These differences are generally positive (rectangular prisms more scattering and more absorbing than ellipsoids), but may be negative depending on the wavelength of light, the particle size, and the particle aspect ratio. The differences in MEC and MSC are small at 550 nm for particles with volume-equivalent radii smaller than 700 nm, and at all wavelengths longer than 500 nm for particles smaller than 500 nm. For BC-dust mixtures, observations indicate that the BC particle lays on the surface of the dust particle, and so is not subject to lensing as the BC would be with a soluble scattering coating.

2.3. Mixing-State and Ice Activation

Mixing-state also influences the ability of aerosol to act as ice-nucleating particles (INP). Ice-nucleating particles can induce the freezing of cloud droplets (ice nucleation) that would not spontaneously freeze otherwise. The process of ice nucleation, and hence concentrations of INP, strongly impacts cloud properties, precipitation rates, weather, and climate [132]. Here, we summarize effects of mixing state on the ability of a given particle to act as an INP.

Mineral dust has been shown to be an effective INP. Treatment of specific mineral components of desert dust with NH_3 or O_3 have been shown to enhance their ability to act as INP [132], but further ageing of dust by O_3 exposure does not necessarily increase INP ability [133]. Coatings of HNO_3 have been shown to suppress the activation of dust through some ice nucleation physical pathways, but not others [132]. Laboratory studies have shown also that organic or sulphuric acid coatings can reduce the ability of dust particles to act as INP [132,134,135], but the physical mechanisms for this effect are unclear. In contrast, field observations suggest that coating of dust by ammonium sulphate increases the INP ability of dust [132]. Coatings of soluble and organic material have recently been shown to affect the ability of ambient dust to act as an INP in complex and inconsistent ways [136]. Atmospheric processing and ageing during the transport of mineral dust and the effect of coatings are not fully understood [135]. The importance of BC particles as INP has also been studied. Similarly to dust, it has been suggested that coatings on BC reduce its INP ability (e.g., [137]), but different laboratory studies on BC particles have shown complex and inconsistent effects of coatings on INP ability [34], often with no discernible effect on INP ability [132]. The effects of internal vs. external mixing of INP within cirrus clouds have been studied in a cloud box model [138]. However, this was done through prescribing a variety of threshold relative humidities for ice nucleation for otherwise inert particles, rather than by predicting ice nucleation ability based on chemical mixing state.

The above studies suggest that the scientific understanding necessary in order to appropriately represent the interactions between mixing state and INP concentrations remains elusive. A recent review on the topic of INPs [132] concludes that "Processes that significantly change the ability of a particle to act as an INP, are difficult to parameterize for IN [ice nucleation] without making significant assumptions. [...] Chemical processing can lead to varying effects, the reasons of which are poorly explored and therefore hard to parameterize based on current laboratory results". Due to the inconsistent effects reported in laboratory and field studies, we do not make any recommendations on the representation of interactions between mixing state and INP in aerosol modules at this time.

2.4. Equilibrium Thermodynamics and Heterogeneous Chemistry

In addition to condensation of low-volatility gaseous compounds, thermodynamic equilibrium of semi-volatile species and heterogeneous chemistry on the surface and/or in the bulk volume of aerosol also lead to the physical growth of particles [139]. Heterogeneous chemistry involves uptake and transformation of gaseous reactants into condensed-phase products via redox, hydrolysis and oligomerization reactions [29,140,141]. Gas-particle partitioning theory accounts for different volatilities of compounds and depends on aerosol composition and size. However, most models assume instantaneous equilibration in bulk aerosol mass, neglecting the impacts of size and composition mixing state of the aerosol population even in models which use size-dependent internal mixing state [142,143]. The impact of the mixing state on aerosol growth via thermodynamic equilibrium and heterogeneous chemistry was explored by a few 3-D modelling studies as described in following subsections.

2.4.1. Inorganic

Due to enhanced reaction rate of aqueous-phase S(IV) oxidation by O_3 at higher pH, sea salt and mineral dust particles can grow efficiently via heterogeneous chemistry (e.g., [26–28]). Oxidation of SO_2 in aqueous aerosol by NO_2 in the presence of sufficient neutralization by NH_3 has been shown as a mechanism for efficient sulphate formation in polluted environments in China (i.e., Chinese winter haze) [144,145]. The heterogeneous uptake of N_2O_5 onto aerosol particles has been shown to be important, as this reaction acts as a sink for NO_X and contributes to nitrate growth in aerosol [146,147]. These heterogeneous reactions are highly pH dependent; therefore, aerosol composition, water uptake properties as well as mixture of local gases are expected to impact aerosol growth.

Through heterogeneous reactions, mineral dust can enhance oxidation of organic compounds and it acts as a sink of O_3 in the atmosphere [29,118]. Heterogeneous reactions also lead to complicated interactions between mineral dust, NO_X and nitrate [29]. Enhancement of OH concentrations in the vicinity of dust enhances oxidation of SO_2, potentially leading to increased new-particle formation in vicinity of low dust concentrations [148,149]. SO_2 also reacts with mineral dust surfaces to form sulphate. These reactions are inhibited if the dust becomes coated with a layer of another substance. The oxidation of SO_2 by dust itself can be a source of this coating layer through the production of sulphate. Due in part to this self-inhibition, Manktelow et al. (2010) [150] estimated that heterogeneous reactions between SO_2 and dust particles do not greatly affect sulphate mass concentrations, which are instead dominated by uptake of H_2SO_4 formed through gas-phase or aqueous-phase oxidation pathways. Fairlie et al. (2010) [151] simulated uptake of nitrate and sulphate onto transpacific dust in GEOS-Chem. They found that the alkalinity of the dust was not titrated in the bulk during up to seven days of transport. Including this process greatly improves model agreement of NO_3 concentrations with observations, although other species are not greatly affected. The heterogeneous chemical formation of sulphate and nitrate enhances the amount of sulphate and nitrate internally-mixed with dust particles [30].

The acquisition of coatings on other aerosol species also affects heterogeneous chemistry. Soot particles with hydrophilic coatings act as sites for heterogeneous chemistry, increasing the uptake of N_2O_5 and decreasing O_3 concentrations [152]. Conversely, organic coatings have been shown to suppress uptake of N_2O_5 onto aqueous aerosols [153,154]. Parametrizations for this suppression have been described by Riemer et al. (2009) [153] and Gaston et al. (2014) [154]. However, an application of these parametrizations by Morgan et al. (2015) [155] to field observations found that the observations were better fit by neglecting suppression of N_2O_5 uptake by organics, and considering only aerosol water and nitrate content. Such parametrizations of N_2O_5 uptake require assumptions about the aerosol mixing state, specifically regarding what fraction of the aerosol population contains nitrate, chloride, or organic coatings [156]. It is therefore likely that their performance could be improved through more detailed representation of the aerosol mixing state, including to what degree inorganic and organic components are internally-mixed, and the phase state of the aerosol.

Jacobson (2001) [109] performed direct radiative effect calculations for sea-spray assuming that it is either externally or internally mixed with respect to other aerosols. The direct radiative effect was calculated to be -0.67 W m^{-2} for the externally-mixed case and -0.55 W m^{-2} in the size-resolved internally-mixed case. The effect was larger in the externally-mixed case due to greater aerosol water content when ammonium and sulphate were not permitted to partition into the sea spray particles. Similarly, the anthropogenic sulphate DRE was calculated to be -0.53 W m^{-2} when externally-mixed, and -0.32 W m^{-2} when size-resolved internally-mixed due to greater water uptake for H_2SO_4 vs. $(NH_4)_2SO_4$. However, it is not realistic to expect that ammonium and sulphate will be fully externally-mixed in the real atmosphere. The interactions of mixing-state with thermodynamic partitioning was explored in more detail by Jacobson (2002) [157]. By including thermodynamic partitioning, the amount of hygroscopic material condensing onto BC particles was increased, due to balancing of the pH by less acidic compounds than sulphate. The replacement of chloride ions in sea spray by sulphate was also captured by the model, and the subsequent condensation of chloride onto other particles. The net effect of including thermodynamic partitioning was to enhance growth rates, particularly of the smaller particles.

2.4.2. Organic

Organic aerosol matter has been shown to change viscosity with changes in RH and temperature, allowing it to exist in liquid, semi-solid, and amorphous solid or glassy phases in the ambient atmosphere [141,158,159]. These changes in particle phase of SOA have been parametrized by Shiraiwa et al. (2017) [160] based on O:C ratio and molar mass. This parametrization was implemented in the EMAC global chemistry climate model, and SOA was determined to be mostly liquid in tropical and polar air with high relative humidity, semi-solid in the mid-latitudes and solid over dry lands in the boundary layer. At higher altitudes, SOA was estimated to be semi-solid or solid.

The change in viscosity of organic aerosol has implications for heterogeneous chemistry: under low viscosity, the interior of the aerosol particles interact less with gases outside of the aerosol particle. For example, You et al. (2012) [161] carried out box model simulations of the Atlanta urban environment and found that liquid–liquid phase separation could result in increased concentrations of gas-phase NO_3 and N_2O_5 by up to 15% due to decreased particle uptake of N_2O_5. Gaston et al. (2014) [154] presents a parametrization of N_2O_5 uptake coefficients that includes the effect of LLPS on this process. However, Zhang et al. (2014) [162] found only small differences in the amounts of particulate nitrate predicted using either a source-oriented external mixture or an internally-mixed assumption. Additionally, Shrivastava et al. (2017) [163] explored the reduction in the oxidation of polycyclic aromatic hydrocarbons (PAHs) by gas-phase ozone due to organic phase changes. They introduced a parametrization for shielding of PAHs by OA: if the coating of the OA layer is greater than 20 nm and either the temperature is less than 296 K or RH is less than 50%, the PAHs are shielded from oxidation by the OA due to its low viscosity. They performed simulations using a global chemical transport model with this parametrization, and found that the resulting concentrations of PAHs were greater and much closer to observed values if the change in phase was taken into account. The authors estimated global incremental lung cancer risk due to PAHs, and found that the estimate increased from 0.6 to 2.0 deaths per 100,000 persons when the shielding effects were taken into account.

Additionally, even in the liquid phase, organic aerosol matter is not always miscible with other liquid or aqueous aerosol components, including other organic species [7,141,161]. This behaviour is frequently associated with differences in hygroscopicity of the component species. This can lead to liquid-liquid phase separation (LLPS): within an aerosol particle, two liquid species (or mixtures of species) separate, with organic species typically forming a shell layer around an inorganic core. Configurations with more than two layers are also possible. Bertram et al. (2011) [164] have shown that LLPS within particles containing organic matter depends on relative humidity and the O:C ratio of the organic species. Organic coatings on inorganic cores can suppress the hygroscopicity of the inorganic cores [165,166], thus impairing their ability to act as CCN. This has been shown to potentially reduce CCN concentrations in the high Arctic [167]. However, the presence of organic surfactants in the organic-rich phase can also lead to reduced surface tension, enhancing the ability of particles to act as CCN [168]. Recently, LLPS has also been shown to potentially impact the optical properties of particles containing brown carbon [79]. Therefore, the mixing state of particles may have additional effects on CCN activity and optical properties of organic-containing aerosols through changes in LLPS. However, the magnitude of these effects have not yet been investigated within global or regional atmospheric aerosol models. Also, thermodynamic calculations suggest that separation into organic-rich and inorganic-rich phases can increase the mass of organic material partitioning into the condensed phase by as much as 50% [169,170].

Gao et al. (2017) [171] showed that accounting for the partitioning of organic compounds between the gas and particle phases affects the mixing state of atmospheric aerosol. Semi-volatile organic species can evaporate from purely organic (externally-mixed) aerosol, and re-condense onto other aerosol particles, thus yielding a more internally-mixed aerosol population. Additionally, when organic species are internally-mixed with sulphate and nitrate, the inorganic species can alter condensed-phase processes such as oligomerization that form larger, lower-volatility molecules less likely to evaporate back to the gas phase [141]. This suggests that representing the mixing state of organic species with respect to inorganic species may be important for accurately simulating the yield of organic species and organic aerosol mass concentrations: if these processes are accounted for, and organics are incorrectly assumed to be internally-mixed with inorganic species, the yields would be overestimated. However, few climate or chemical transport models include these condensed phase processes [141].

3. Modelling Approaches

We compile published aerosol modules that include at least a partial representation of aerosol mixing state in Table 1. For context, we include in the table information on the representation of the aerosol size distribution, and the atmospheric models into which the aerosol module has been implemented. We classify these broadly as box models (0-D models), single-column models, and regional-scale or global-scale Air Quality Models (AQM), Numerical Weather Prediction (NWP) models, Chemical Transport Models (CTM), or General Circulation Models (GCM). We note that much of the information in this table depends on the specific implementation of the aerosol module. For example, the number of size bins or modes used to represent the size distribution and the number of mass species can often be easily modified by a user. In many cases, even the feature with which we are most concerned in this review, being the details of the representation of the aerosol mixing state, can be easily modified by the user. We have reprinted the module details as listed in the literature, but in any particular study, the modules listed may be modified from the form listed here. We include as a notable example of within-module diversity the configurations of GATOR used in Jacobson (2002) [157] and in Jacobson (2012) [97]. If the aerosol modes for representing aerosol within hydrometeors are excluded (as these represent cloud processing and transport of aerosol rather than mixing-state), the number of externally-mixed aerosol modes differs between GATOR 2012 and GATOR 2002 by a factor of six, and the number of aerosol tracers differs by nearly a factor of fifty. For all other modules, where the details of an aerosol module have changed over time due to continuing development, we have used the most recent description from the sources listed, as we believe that this is more representative of the state of the science. For all of these reasons, we advise the reader to take the information listed in Table 1 as indicative, but not absolute.

Table 1. Mixing state and size distribution representation in several aerosol modules. Please note that the listed information often depends on the specific configuration of each model, and should be taken as indicative only. Listed ranges of size distribution refer to particle diameters.

Module Name	Total # of Aerosol Tracers	# of Aerosol Number Tracers	# of Aerosol Mass Tracers	Size Distribution	BC Mixing State	Other Mixing State	Transfer Between Mixing States	Other Notes	Implemented in What Models?	Sources
APM	79	0	79 (SO_4, sea salt, BC, POC, dust, SOA , NO_3, NH_4)	hybrid: 40 bins for SO_4 (1.2 nm to 12 µm), 4 bins for dust (0.2 µm to 12 µm), 20 bins for sea salt (12 nm to 12 µm), lognormal modes for BC and POC, all one-moment.	4 modes: 2 fossil fuel (60 nm) and 2 biomass-burning (150 nm) split by hydrophobic and hydrophilic	"Secondary" particles (consisting only of SO_4, NH_4, and SOA) are predicted separately from coatings on other particles of these species. Dust has one population in 4 size sections, coating mass predicted as one bulk tracer for each species. POC same as BC.	BC and POC ages according to an e-folding lifetime of 1.2 days.		WRF-Chem regional NWP [152], GEOS-Chem global CTM [116,172], NAQPMS regional CTM [63]	[63,116, 152,172]
ATRAS	1280	128	1152 (SO_4, NO_3, NH_4, BC, OA, dust, Na, Cl, H_2O)	20 two-moment bins (1nm to 10 µm)	Up to 10 BC mass fraction bins for each size between 40 nm and 10 µm. No BC at smaller sizes.	non-BC species assumed to be internally-mixed with each other.	condensation and coagulation		WRF-Chem regional NWP [59,62]	[59,62]
ATRAS2	145	47	98 (SO_4, BC, POA, NH_4, HNO_3, dust)	12 two-moment bins (1 nm to 10 µm)	8 BC mass fraction bins for each size between 40 nm and 1.24 µm. No BC at smaller sizes, assumed well-mixed at larger sizes.	non-BC species assumed to be internally-mixed with each other.	condensation and coagulation	Aerosol variables are coarse-grained across size (to nucleation, fine, and coarse modes) for advection. Number and mass tracers here do not include VBS scheme (total of 26 tracers).	CAM5 global GCM [173]	(Matsui 2017) [173]
CanAM	108	0	108 (SO_4, NO_3, NH_4, POA, SOA, BC, sea salt, dust, H_2O)	12 one-moment bins (10 nm to 10 µm)	assumed internally-mixed	all species assumed internally-mixed	No transfer between mixing states.		GCMIII global GCM [174]; AURAMS regional CTM [175]; GEM-MACH regional AQM [176]	[174–178]

Table 1. *Cont.*

Module Name	Total # of Aerosol Tracers	# of Aerosol Number Tracers	# of Aerosol Mass Tracers	Size Distribution	BC Mixing State	Other Mixing State	Transfer Between Mixing States	Other Notes	Implemented in What Models?	Sources
CHIMERE	120	0	120 (SO_4, primary particulate matter, OC, BC, dust, salt, NO_3, NH_4, H_2O, SOA)	12 one-moment bins (10 nm to 40 µm)	assumed internally-mixed. primary particulate matter implicitly includes some BC.	all species assumed internally-mixed	No transfer between mixing states.		CHIMERE regional CTM [179]	[179,180]
CIT/UCD	1080	135	945 (NO_3, NH_4, OC, EC, SO_4, Na, Cl)	15 two-moment bins (10 nm to 10 µm)	Source-oriented mixing state categories; most BC is emitted in "diesel engines" source	9 source-oriented categories: fugitive dust, road dust, diesel engines, catalyst-equipped gasoline engines, non-catalyst-equipped gasoline engines, wood smoke, meat cooking, combustion of high-sulfur fuel, and other sources	none; condensation adds mass to each category	coagulation not represented	CIT/UCD regional AQM [181]	[181–183]
CMAQ	unclear	3	18 species (OC, EC, SO_4, NO_3, H_2O, Na, Cl, NH_4, non-carbon organic matter, Al, Ca, Fe, Si, Ti, Mg, K, Mn, and Other)	3 three-moment lognormal modes (Aitken, accumulation, coarse)	for radiation, fully externally-mixed. Otherwise, internally-mixed	assumed to be internally-mixed	No transfer between mixing states.	6th generation aerosol module also known as AERO6	CMAQ regional CTM; WRF regional forecast model	[184–187]

Table 1. *Cont.*

Module Name	Total # of Aerosol Tracers	# of Aerosol Number Tracers	# of Aerosol Mass Tracers	Size Distribution	BC Mixing State	Other Mixing State	Transfer Between Mixing States	Other Notes	Implemented in What Models?	Sources
DAMS	310	0	310 (two primary particulate species, two semivolatile species, one inert species)	10 one-moment bins (20 nm to 2.5 µm)	no BC simulated	For most detailed configuration, unary, binary, and each higher-level mixture tracked separately, with mass fraction threshold for transfer between categories (multiple thresholds tested, 1%–20%, default 5%). Different groupings of categories also tested.	Processes include gas/aerosol partitioning with aerosol composition-dependent rates, and coagulation.	More detailed treatment of semi-volatile organic partitioning that any other module listed in this table	box model [188]	[188]
GATOR 2002	32,400	1080	31,320 (H_2O, H^+, NH_4, Na, Mg, Ca, K, SO_4, NO_3, Cl, CO_3, combinations of the above, and BC, OA, and soil)	60 two-moment bins (1 nm to 120 µm)	3 modes for BC mixed with H_2O-NH_4-SO_4-NO_3-CO_3 (0–5% shell, 5–20% shell, and 20–100% shell). Also 4 modes for binary mixtures with each other component, and 1 mode for mixtures with all components.	Modes for each other components (sea-spray, soil, OA, SO_4) mixed with just H_2O-NH_4-SO_4-NO_3-CO_3, additional modes for binary mixtures, and a mode for mixtures of all components.	Deposition of non-BC material can move BC particles between the three BC-H_2O-NH_4-SO_4-NO_3-CO_3 bins. Particles move into the "binary" and "well-mixed" bins only through coagulation.	Please note that individual ions are tracked for H_2O-NH_4-SO_4-NO_3-CO_3 mixtures, so the actual list of species is 17, not 5.	GATORG global GCM [109]	[109,115,157]

Table 1. *Cont.*

Module Name	Total # of Aerosol Tracers	# of Aerosol Number Tracers	# of Aerosol Mass Tracers	Size Distribution	BC Mixing State	Other Mixing State	Transfer Between Mixing States	Other Notes	Implemented in What Models?	Sources
GATOR 2012	658	42	616 (BC, POA, SOA, H_2O(aq)-h, H_2SO_4(aq), HSO_4, SO_4, NO_3, Cl, H^+, NH_4, NH_4NO_3(s), $(NH_4)_2SO_4$(s), Na, tar balls, soil dust, pollen/spores/bacteria, NaCl(s), H_2O(aq)-c, H_2O(s))	14 size bins (2 nm to 50 µm)	3 modes: emitted fossil-fuel soot (EFFS), emitted biofuel and biomass-burning soot (BFBB), and ultimate internally-mixed. EFFS contains all aerosol species except Na, NH_4NO_3(s), NH_4SO_4(s), tar balls, dust, pollen/spores/bacteria, and NaCl(s). BFBB contains all aerosol species except soil dust, pollen/spores/bacteria, and NaCl(s).	3 additional modes for aerosol mass in liquid, ice, and graupel clouds and precipitation.	Only coagulation transfers particles from the EFFS and BFBB modes to the ultimate internally-mixed mode. Condensation adds aerosol mass within a mode.	Also tracks aerosol mass for each species in cloud liquid, cloud ice, and graupel. These tracers not included in numbers of aerosol tracers listed here.	GATOR-GCMOM global/regional GCM/NWP/AQM [189]	[97,189]
GEOS-Chem	15	0	15 (BC, OC, SO_4, dust, sea salt, NH_4, NO_3)	bulk	4 categories: fossil fuel hydrophobic, fossil fuel hydrophilic, biomass burning hydrophobic, biomass burning hydrophilic.	OC has 2 categories: hydrophobic and hydrophilic.	Hydrophobic OC converts to hydrophilic OC with an e-folding lifetime of 1.15 days. Biofuel and biomass-burning BC converts to hydrophilic with an e-folding lifetime of 4 h. Fossil fuel BC ageing is parametrized based on SO_2 and OH concentrations.		default aerosol scheme for GEOS-Chem global CTM	[93,190, 191]

Table 1. *Cont.*

Module Name	Total # of Aerosol Tracers	# of Aerosol Number Tracers	# of Aerosol Mass Tracers	Size Distribution	BC Mixing State	Other Mixing State	Transfer Between Mixing States	Other Notes	Implemented in What Models?	Sources
GLOMAP-bin	160	40	120 (SO_4, sea salt, dust, BC, POA, SOA)	20 two-moment bins (3 nm to 10 µm)	2 categories in each size bin: hydrophobic and hydrophilic.	Dust and POA also separated into hydrophilic and hydrophobic categories.	Condensation and/or coagulation of one monolayer of sulphate.		TOMCAT global CTM [192]	[150,192,193]
GLOMAP-mode	26	7	19 (SO_4, sea salt, dust, BC, POA, SOA)	7 two-moment lognormal modes (nucleation, Aitken, accumulation, coarse)	4 modes: insoluble in Aitken mode, soluble in Aitken, accumulation and coarse modes.	Dust in 4 modes: insoluble and soluble for accumulation and coarse. POA treated the same as BC.	coagulation and/or condensation of 10 monolayers of sulphate		TOMCAT global CTM [194], MetUM global/regional GCM/NWP/AQM [195]	[194,195]
GMXe	41	7	34 (H_2O, SO_4, NO_3, Cl, NH_4, Na, POA, BC, dust, sea salt)	7 two-moment lognormal modes (nucleation, Aitken, accumulation, coarse)	4 modes: hydrophobic in Aitken mode, hydrophilic in Aitken, accumulation and coarse modes	Dust in 4 modes: hydrophilic and hydrophobic for accumulation and coarse. POA treated the same as BC.	Coagulation with soluble mode moves mass to soluble mode, or condensation of 5 monolayers of sulphate		EMAC (ECHAM/MESSy) global GCM [196]	[196]
IMPACT	28	3	25 (SO_4, BC, OC, dust, sea salt)	Hybrid. 3 two-moment lognormal SO_4 modes, all other species one-moment bins with predefined size distributions. 4 dust bins, 4 sea-salt bins. 2 BC and 2 OC bins (fossil fuel and biomass-burning).	2 BC bins: fossil fuel and biomass-burning. Amount of SO_4 on each bin is tracked.	2 OC bins: fossil fuel and biomass-burning. All particles in all bins or modes assumed to be externally-mixed, but amount of SO_4 condensed on each bin is tracked.	SO_4 added to particles through condensation, coagulation, and in-cloud oxidation (this does not move non-SO_4 mass between modes). Soot and dust are assumed to be hygroscopic when coated with 10 monolayers of SO_4 (mass fraction 14%).		IMPACT also refers to the IMPACT global CTM [197]; CAM3 global GCM [198]	[197,198]

Table 1. *Cont.*

Module Name	Total # of Aerosol Tracers	# of Aerosol Number Tracers	# of Aerosol Mass Tracers	Size Distribution	BC Mixing State	Other Mixing State	Transfer Between Mixing States	Other Notes	Implemented in What Models?	Sources
M3+	13	8	5 (SO_4, BC, sea salt)	8 lognormal modes, some one-moment and some two-moment (nucleation, Aitken, and accumulation SO_4; pure fossil-fuel BC, mixed fossil-fuel BC, pure biomass-burning BC, mixed biomass-burning BC, and sea-salt)	4 modes: pure fossil-fuel and pure biomass-burning BC, and fossil-fuel and biomass-burning each mixed with OC and SO_4.	OC is always assumed to be internally-mixed with BC and SO_4, and to be in hydrophilic particles. Split into biomass-burning and fossil-fuel modes.	Condensation of 8 monolayers of SO_4 onto fossil-fuel BC; 2.5% per hour of biomass-burning BC	OC mass is included diagnostically as either constant ratio with SO_4 (mixed fossil-fuel BC) or BC (mixed biomass-burning BC)	TM2 global chemical transport mode [199]	[199]
M7	45 (29 for advection)	7	38 (Dust, BC, POA, SO_4, sea salt, 5 SOA types)	7 two-moment lognormal modes (nucleation, Aitken, accumulation, coarse)	4 modes: insoluble in Aitken mode, soluble in Aitken, accumulation and coarse modes	Dust in 4 modes: insoluble and soluble for accumulation and coarse. POA and SOA are treated the same way as BC: 4 modes: insoluble in Aitken mode, soluble in Aitken, accumulation and coarse modes.	Coagulation and/or condensation of one monolayer of sulphate.	20 SOA species, but these are advected as only 4 tracers	ECHAM5-HAM global GCM [200], TM5 global CTM [64]	[64,200–202]
MADE	27	3	24 (SO_4, NH_4, NO_3, BC, OA, sea salt, dust, and H_2O)	3 two-moment lognormal modes (Aitken, accumulation, coarse)	Assumed internally-mixed		No transfer between mixing states.		ECHAM4 global climate mode [203]	[203]

Table 1. *Cont.*

Module Name	Total # of Aerosol Tracers	# of Aerosol Number Tracers	# of Aerosol Mass Tracers	Size Distribution	BC Mixing State	Other Mixing State	Transfer Between Mixing States	Other Notes	Implemented in What Models?	Sources
MADE-in	42	7	35 (SO_4, NH_4, NO_3, sea salt, POA, BC, dust, H_2O)	7 two-moment lognormal modes (Aitken, accumulation, and coarse)	4 modes: 2 sizes (Aitken and accumulation), 2 mixing states (external and core-shell mixture)	Dust in 3 modes: external accumulation, core-shell accumulation, and internally-mixed coarse. Please note that pure soluble modes (no BC or dust) are included for Aitken and accumulation modes.	Condensation of SO_4 and organics, gas/aerosol partitioning of NO_3 and NH_4, aggregation following in-cloud processing, and coagulation. Particles are transferred if processes cause soluble mass fraction (including H_2O) to exceed 10%.		EMAC (ECHAM/MESSy) global GCM [204]	[204]
MADE3	90	9	81 (SO_4, NH_4, NO_3, Na, Cl, POA, BC, dust, H_2O)	9 two-moment lognormal modes (Aitken, accumulation, and coarse)	6 modes: 3 sizes (Aitken, accumulation, and coarse), 2 mixing states (insoluble and mixed). Insoluble state includes only BC, POA, and dust.	Please note that pure soluble modes (no BC, POA, or dust) are also included for Aitken, accumulation and coarse modes.	Condensation of SO_4 and organics, gas/aerosol partitioning of NO_3 and NH_4, aggregation following in-cloud processing, and coagulation. Particles are transferred if processes cause soluble mass fraction (excluding H_2O and POA) to exceed 10%.		EMAC (ECHAM/MESSy) global GCM [205]	[205,206]

Table 1. *Cont.*

Module Name	Total # of Aerosol Tracers	# of Aerosol Number Tracers	# of Aerosol Mass Tracers	Size Distribution	BC Mixing State	Other Mixing State	Transfer Between Mixing States	Other Notes	Implemented in What Models?	Sources
MADEsoot	30	6	24 (SO_4, NH_4, NO_3, SOA, soot, H_2O). Dust and sea spray treated separately.	6 two-moment lognormal modes (Aitken, accumulation, and coarse)	one mode for pure soot, and two modes for aged soot (Aitken and accumulation)	Dust treated separately, externally mixed. Please note that there are two modes for soot-free particles (Aitken and accumulation)	Condensation of SO_4 or SOA, threshold is soluble mass fraction of 5%. coagulation with soluble particle.		KAMM/DRAIS regional NWP [147], COSMO-ART regional NWP [207]	[22,147,207]
MADMS	39	5	30 (unidentified, BC, OA, dust, sea salt, SO_4, NH_4, NO_3, Cl, H_2O)	5 three-moment lognormal modes (Aitken, accumulation, coarse)	A BC-free accumulation mode is tracked separately from a BC-containing accumulation-sized mode. The number of BC-containing accumulation-sized particles coagulated by the coarse mode is also tracked.		Coagulation will move BC-free particles into BC-containing category. Please note that condensation physically would not move particles between states in this scheme.	Please note that surface area is also a transported tracer, unlike most modules. MADMS can be used to account for differences in condensation and coagulation due to non-sphericity, and to track fractal particle morphology. However, particles were assumed to be spheres in Kajino et al. (2012) [208].	RAQM2 regional CTM [208], EMTACS regional CTM [209]	[208–210]
MADRID-BC	3600	400	3200 (SO_4, NH_4, NO_3, Na, Cl, H_2O, BC, and OA)	40 bins (21.5 nm to 10 µm)	10 BC mass fraction bins.		Condensation of SO_4 and SOA only.	Coagulation not simulated.	Box model only [211]	[57,211]
MAM3	15	3	12 (SO_4, SOA, POA, BC, dust, sea salt)	3 two-moment lognormal modes (Aitken, accumulation, coarse)	Assumed to be internally-mixed	All species assumed internally mixed.	No transfer between mixing states.		CAM5 global GCM [65]	[65]
MAM4	18	4	14 (SO_4, SOA, POA, sea salt, BC, soil dust)	4 two-moment lognormal modes (aitken, accumulation, coarse)	2 modes: externally-mixed accumulation and internally-mixed accumulation.	POA treated the same as BC.	Coagulation or condensation of 8 monolayers of SO_4 or equivalent amount of SOA.		CAM5 global GCM [212]	[212]

Table 1. *Cont.*

Module Name	Total # of Aerosol Tracers	# of Aerosol Number Tracers	# of Aerosol Mass Tracers	Size Distribution	BC Mixing State	Other Mixing State	Transfer Between Mixing States	Other Notes	Implemented in What Models?	Sources
MAM7	31	7	24 (SO_4, NH_4, SOA, POA, BC, dust, sea salt)	7 two-moment lognormal modes (Aitken, accumulation, fine, coarse)	2 modes: primary carbon (only BC and POA) and mixed accumulation.	Sea salt and Dust in 2 modes each: fine and coarse. Both include tracers for masses of internally-mixed SO_4 and NH_4, but the modes are assumed to be externally-mixed with respect to all other species.	Coagulation or condensation of 3 monolayers of SO_4, NH_4, or SOA moves primary carbon particles to mixed accumulation mode.		CAM5 global GCM [65]	[65]
MATRIX	73	16	57 (SO_4, NO_3, H_2O, dust, sea salt, OC, BC)	16 two-moment lognormal modes (Aitken, accumulation, coarse)	BC is present in 7 of the 16 modes: 3 modes for different mass fractions of binary BC-inorganic mixtures (cutoffs at 5% and 20%), 1 mode BC-OC-inorganics, 1 mode BC-inorganics (formed by coagulation), 1 mode BC-Dust-inorganics, and 1 mode for higher order mixtures.	Inorganics-only in Aitken and accumulation modes, sea-salt-inorganic mixtures in accumulation and coarse modes, 2 modes in each of accumulation and coarse size ranges for binary dust-inorganic mixtures (cutoff at 5% inorganic fraction), OC-inorganic mixtures.	Coagulation, condensation of inorganics.		Box model [213] and GISS global GCM [214]	[171,213,214]
MOSAIC-Mix	1152	96	1056 (SO_4, NO_3, Cl, CO_3, NH_4, Na, Ca, OIN (other insoluble inorganics), BC, POA, SOA)	24 two-moment bins	Particles binned by black carbon mass fraction, up to 32 bins tested, 2 recommended.	Particles are binned by hygroscopicity, up to 30 bins tested, 2 recommended.	Condensation and coagulation.	Recommended configuration has 2 black carbon mass bins and 2 hygroscopicity bins, resulting in 96 number tracers.	Box model. [58]	[58]
MOZART	9	0	(SO_4, BC, POA, SOA, NH_4NO_3, sea salt)	Bulk, except sea-salt: 4 bins (0.1 µm to 10 µm)	Hydrophilic and hydrophobic categories.	POA also in hydrophilic and hydrophobic categories.	Fixed Ageing timescale of 1.6 days.	Dust not prognostic; taken from CAM climatology.	MOZART global CTM [215]	[215]

Table 1. *Cont.*

Module Name	Total # of Aerosol Tracers	# of Aerosol Number Tracers	# of Aerosol Mass Tracers	Size Distribution	BC Mixing State	Other Mixing State	Transfer Between Mixing States	Other Notes	Implemented in What Models?	Sources
OsloAero	23	0	23 (SO_4, BC, OA, dust and sea salt)	Calculated based on one-moment tagged sources; includes growth by condensation and coagulation of SO_4; similar to lognormal odes (nucleation, Aitken, accumulation, coarse)	Some BC is emitted as pure BC, and some is internally-mixed with OA. Condensation of SO_4 renders BC within the mode internally-mixed with SO_4; the same is true of coagulation with other species.	All emissions externally mixed; SO_4 condenses onto all emitted species; nucleation- and Aitken-mode particles can coagulate with accumulation- and coarse-mode particles to form internally-mixed particles. The mass of SO_4 condensed or coagulated onto each mode is tracked, but how that SO_4 is distributed across the size spectrum of each mode is re-calculated each time step. So it is possible for only some of the particles within a given mode to be internally-mixed, depending on what properties are considered.	Condensation of SO_4, coagulation. Particles are considered coated for cloud droplet activation if a 2 nm thick coating of SO_4 or OA is present. Mixing state does not affect wet deposition.	When aerosol mass is added, it is tagged by source (nucleation, condensation, coagulation, emissions, etc.) and size range. The size distributions are calculated a posteriori by adding the other tagged masses to the emission mass, and modifying the emitted size distribution appropriately.	CCM3 global GCM [216], CAM-Oslo global GCM [119], CAM4-Oslo global GCM [217]	[119,216,217]
PAM	20	7	13 (SO_4, BC, OC, dust, sea-spray)	7 two-moment piece-wise lognormal bins (20 nm to 20 µm)	Assumed internally-mixed with OC and SO_4 for microphysics, but assumed externally-mixed for radiation calculations.	Sea-spray assumed externally-mixed. OC and SO_4 internally-mixed w/ BC for microphysics, but all components treated as externally-mixed for radiation calculations.	No transfer between mixing states.		CCCma AGCM global GCM [218]	[218–220]

Table 1. *Cont.*

Module Name	Total # of Aerosol Tracers	# of Aerosol Number Tracers	# of Aerosol Mass Tracers	Size Distribution	BC Mixing State	Other Mixing State	Transfer Between Mixing States	Other Notes	Implemented in What Models?	Sources
PartMC-MOSAIC	19 per particle; of order 1e5	Not applicable	19 per particle; of order 1e5 (SO_4, NO_3, Cl, CO_3, MSA, NH_4, Na, Ca, other inorganic mass, BC, POA; 8 SOA species)	Size of each particle tracked independently.	Composition of each particle is resolved explicitly.	Composition of each particle is resolved explicitly.	Composition of each particle is resolved explicitly, so no transfer between states is necessary or possible. Processes that alter particle composition, including condensation and coagulation, are resolved.		box model [221] and WRF single column model [222].	[221,222]
RegCM	5	0	5 (SO_4, hydrophilic and hydrophobic BC, hydrophilic and hydrophobic OC)	Bulk	Hydrophilic and hydrophobic BC considered separately, assumed externally-mixed.	Hydrophilic and hydrophobic OC considered separately. All species assumed externally-mixed.	Fixed ageing timescale of 1.15 days.		RegCM regional climate model [223]	[223]
SALSA	65	20	45 (SO_4, OC, sea salt, BC, dust). SO_4 and OC lumped together as "water soluble" for D > 700 nm. Otherwise, mass concentration not tracked for particles larger than 700 nm.	7 two-moment bins (3 nm to 700 nm); and 3 one-moment bins (700 nm to 10 μm)	Split into soluble and insoluble bins. Insoluble bins contain no sea salt. Otherwise, all species present in soluble and insoluble bins.	Internally mixed for D < 50 nm; soluble and insoluble categories for 50 nm < D < 700 nm, soluble, fresh insoluble and aged insoluble categories for D > 700 nm.	Coagulation or condensation of a pre-defined mass fraction of soluble material, calculated using Kohler theory with a supersaturation of 0.5%.		ECHAM-HAM global GCM [224]; MATCH regional CTM [225]. A version of SALSA without separate mixing-state categories has also been implemented in UCLA-LES [226]	[224,225, 227]

Table 1. *Cont.*

Module Name	Total # of Aerosol Tracers	# of Aerosol Number Tracers	# of Aerosol Mass Tracers	Size Distribution	BC Mixing State	Other Mixing State	Transfer Between Mixing States	Other Notes	Implemented in What Models?	Sources
SALSA2.0	86	17	69 (SO_4, OA, sea salt, BC, and dust)	10 two-moment bins (3 nm to 10 µm)	No BC for D < 50 nm; two sets of externally-mixed bins (soluble and insoluble) for D > 50 nm. Sea salt only in soluble bins, but SO_4, OC, BC, and dust in both sets of bins.	Internally-mixed for D < 50 nm; two sets of externally-mixed bins (soluble and insoluble) for D > 50 nm. Sea salt only in soluble bins, but SO_4, OC, BC, and dust in both sets of bins.	Not stated.		ECHAM-HAM global GCM [228].	[228]
SCRAM	4340	140	4200 (HLI (Na, SO_4, NO_3, NH_4, Cl), HLO (BiA2D, BiA1D, BiA0D, GLY-OXAL, MGLY, BiMT, BiPER, BiDER and BiMGA), HBO (AnBlP, AnBmP, BiBlP, BiBmP, BiNGA, NIT3, BiNIT, AnCLP, SOAlP, SOAmP, SOAhP, POAlP, POAmP and POAhP), BC, and dust.)	7 bins (1 nm to 10 µm)	20 composition bins, including 1 for >80% BC, 8 for 20-80% BC and 11 for <20% BC	20 composition bins for five categories(inorganics (HLI), hydrophilic organics (HLO), hydrophobic organics (HBO), BC, dust), covering unary, binary, and higher-order mixtures. Generally, there is an unmixed (>80% mass faction) bin for each species, and bin limits for a given species are otherwise set at 0–20% or 20–80%.	Condensation and coagulation	30 detailed mass species: HLI (sodium, sulphate, nitrate, ammonium and chloride), HLO (BiA2D, BiA1D, BiA0D, GLY-OXAL, MGLY, BiMT, BiPER, BiDER and BiMGA), HBO (AnBlP, AnBmP, BiBlP, BiBmP, BiNGA, NIT3, BiNIT, AnCLP, SOAlP, SOAmP, SOAhP, POAlP, POAmP and POAhP), BC, and dust.	POLYPHEMUS regional AQM [229]	[229,230]
SOWC	880	40	840 (EC, OC, Na, Cl, NH_4, SO_4, NO_3, other, metals, unknown, Cu1, Cu2, Mn2, Mn3, Fe2, Fe3, SO3, air (in hollow particles), NO_3, H, H_2O)	8 two-moment bins (<78 nm to >5 µm)	Source-oriented mixing state bins. Most BC is emitted in "Diesel Engines" source.	5 source-oriented mixing state bins: Diesel Engines, Wood Smoke, High Sulfur Fuel, Food Cooking, and Other.	Condensation, coagulation adds masses of the smaller particle to the source bin of the larger particle.		WRF-Chem regional NWP [162]	[162]

Table 1. *Cont.*

Module Name	Total # of Aerosol Tracers	# of Aerosol Number Tracers	# of Aerosol Mass Tracers	Size Distribution	BC Mixing State	Other Mixing State	Transfer Between Mixing States	Other Notes	Implemented in What Models?	Sources
TM5	6	0	6 (SO_4, NO_3, NH_4, OC, sea salt, dust)	Bulk	Assumed externally-mixed.	SO_4, NO3, and NH4 assumed internally-mixed with each other, all other species externally-mixed.	No transfer between mixing states.		TM5 global CTM [231]	[64,231]
unnamed	90	30	60 (2 arbitrary species)	10 two-moment bins (1 nm to 10 µm)	No BC simulated.	Each species binned in 3 or 10 mass fraction sections.	Coagulation only.	Theoretical calculations of coagulation between arbitrary species with no chemical properties.	Box model only [232]	[232]

The simplest possible assumptions regarding aerosol mixing state are either that all aerosol particles are externally-mixed, or that all aerosol particles are internally-mixed. These assumptions continue to be frequently used in climate and air-quality models. For example, the regional climate model RegCM [223] assumes aerosol to be externally-mixed, although BC and OC age from hydrophobic to hydrophilic with a fixed ageing timescale of 1.15 days. We found many more examples of aerosol modules that assume aerosol to be internally-mixed, including the Canadian Aerosol Module (CanAM) [175–178], CHIMERE [179], the Community Multiscale Air Quality (CMAQ) model [184–187], the Modal Aerosol Dynamics module for Europe (MADE) [203], and the Modal Aerosol Module with three lognormal modes (MAM3) [65]. It is possible to assume that some species are always internally-mixed with respect to each other, while other species always exist as pure particles: For example, the bulk aerosol representation in the TM5 model [64,231] assumes that sulphate, nitrate, and ammonium are internally-mixed, while all other species are externally-mixed.

It is important to note that the vast majority of size-resolved aerosol modules implicitly track the differences in composition between aerosol of different sizes. For example, if an aerosol module tracks the masses of nucleation-mode aerosol and coarse-mode aerosol separately, whether through a modal or a sectional (bin) scheme, the nucleation-mode aerosol will be considered to be externally-mixed with respect to the coarse-mode aerosol, even if the aerosol within each bin is considered to be internally-mixed. Therefore nucleation-mode sulphate would not be internally-mixed with coarse-mode dust, even if no explicit representation of composition mixing-state was included.

We note also that when calculating microphysical and chemical process rates, cloud droplet activation, and radiative properties, it is possible for the same aerosol module to make different assumptions regarding whether particles are externally- or internally-mixed. For example, Wang et al. (2018) [191] assumes that all components are externally-mixed for radiative properties, but uses a constant absorption enhancement for BC (1.1 for fossil fuel BC and 1.5 for biomass burning BC) to account for coating by other species. The authors justify this approach by noting that, based on field measurements, most OA mass exists in particles that do not contain BC, even while most BC mass exists in particles that are coated with other species [89]. The aerosol scattering in the authors' cases of interest is therefore dominated by the BC-free OA particles, even while a lensing effect is present on the BC particle due to coating by OA. Regarding hygroscopic properties, separate populations of hydrophobic and hydrophilic BC and OC are represented in the model, with different ageing parametrizations for fossil fuel BC, biofuel or biomass-burning BC, and OC. Similarly, the Piecewise Lognormal Approximation (PLA) Aerosol Model (PAM) [218–220] assumes that aerosols are externally-mixed for the purposes of radiation calculations, but that BC, OC, and sulphate are internally-mixed for the purposes of aerosol microphysics.

3.1. Hygroscopicity-Based Representations

3.1.1. Two Hygroscopicity Categories

In this representation method, two populations of aerosol that are externally mixed from each other are tracked. In several aerosol modules, one population is hydrophilic, and the other is hydrophobic. This is likely the most widely-adopted approach for representing mixing state in atmospheric aerosol models, and has been implemented in GEOS-Chem [190,191,233], the GLObal Model of Aerosol Processes (GLOMAP) in both its bin [150,192,193] and modal [194,195] configurations, GMXe [196], the M3+ module [199], M7 [64,200–202], MAM4 [212], MAM7 [65], the Model for Ozone and Related chemical Tracers (MOZART) [215], the Sectional Aerosol module for Large Scale Applications (SALSA) [224,225,227], and SALSA2.0 [224]. The two populations are considered to be mixed externally with respect to each other, but particles within each population are assumed to be internally mixed. The hydrophobic population is generally assumed to consist primarily or entirely of BC and dust. Depending on the implementation, some organic matter may be considered to be part of the hydrophobic population as well. In the hydrophilic population, generally all or nearly all species are present, as the hydrophilic species typically form coatings on hydrophobic species, rendering them hydrophilic.

Depending of the representation of the size distribution, the hydrophilic and hydrophobic populations will be represented using separate bins or separate lognormal modes, or simply separate bulk mass tracers. To keep the following discussion sufficiently general and to avoid ambiguity, we use the word "categories" in place of bins or modes when discussing the model representation of mixing-state. We maintain this convention when discussing other mixing-state representations as well.

In general, size-resolved aerosol modules move aerosol number and/or mass from the hydrophobic to the hydrophilic category through model-resolved condensation and coagulation of hydrophilic species. Coagulation of a hydrophilic particle with a hydrophobic particle either always results in a hydrophilic particle, or a hydrophilic mass fraction threshold is used to determine if the resulting particle is added to the hydrophilic or hydrophobic category. Condensation of soluble material moves particles from the hydrophobic category to the hydrophilic category at a rate dependent on the minimum soluble mass fraction deemed necessary for a particle to be considered hydrophilic. Chemical ageing is generally not considered, as this has been shown to insignificantly affect the ageing rate of BC compared to coagulation and condensation [31,32]. In bulk aerosol modules, either constant ageing timescales or parametrizations of ageing are generally used. We will discuss this at length in Section 3.1.3.

The two-category approach has the advantage of being conceptually and computationally simple. If the hydrophobic category is assumed to contain no hydrophilic species whatsoever, then only the hydrophobic aerosol mass species need to be tracked within that category, reducing the total number of tracers. However, these simplifications prevent the representation of several potential scenarios. Hydrophilic particles with and without a hydrophobic mass component cannot be simulated in the same grid cell: Either all hydrophilic particles will contain some hydrophobic mass, or no hydrophilic particles will contain any hydrophobic mass. For example, if any hydrophilic BC-containing particles are in a grid cell, then all hydrophilic particles in the same grid cell and in the same size bin or size mode will be assumed to contain BC.

Sensitivity simulations performed using more detailed representations of the aerosol mixing state suggest that the use of two hygroscopic categories can greatly reduce errors in predicted CCN concentrations, compared to a size-resolved internally-mixed representation [57,58]. Based on these results, we expect that this also greatly improves the representation of aerosol wet deposition and therefore predicted burdens and mass concentrations of hydrophobic species. However, since a two-hygroscopicity-category representation does not separately represent primarily scattering particles without an absorbing component (e.g., BC-free particles), it will overestimate the thickness of coating on absorbing matter. This leads to an overestimate in the absorption by BC-containing particles [58,60].

3.1.2. Related Approaches

An approach similar to the two-hygroscopicity-category representation has been used by IMPACT [197,198] and the Modal Aerosol Dynamics model for multiple Modes and fractal Shapes (MADMS) [208–210]: In the accumulation mode, BC-containing particles and BC-free particles are tracked separately. The sensitivity studies performed by Oshima et al. (2009) [57] and Ching et al. (2016) [58] suggest that, compared to a size-resolved internally-mixed representation, this representation would greatly improve estimates of absorption by BC, but that there would be only modest improvement in predicted CCN concentrations and wet deposition rates.

In the Advanced Particle Microphysics (APM) module, hydrophilic and hydrophobic populations of both BC and POC are tracked separately, and "secondary" particles (composed only of SO_4, NH_4, and SOA) are tracked separately from the mass of SO_4, NH_4, and SOA that forms coatings on other particles [172]. A related but distinct approach is used by the OsloAero aerosol module [119,216,217], which is part of the CAM4-Oslo atmospheric module. In this aerosol module, emissions of SO_4, BC, sea spray, and dust are assumed to be externally-mixed. BC that is internally-mixed with organic matter is tracked separately from BC that is externally-mixed with respect to organic matter, but all organic matter is assumed to be internally-mixed with BC. The amount of SO_4 that is internally-mixed with each other externally-mixed category (through either condensation or coagulation) is tracked separately. The mass of coating species (SO_4 and, in the case of BC, organic matter) that is internally-mixed with each category is used in the calculations of the optical properties and for calculations of cloud droplet number concentration, but it does not alter wet deposition rates.

An extension to the two-hygroscopicity-category representation was used by MADE-soot [22,147,207], MADE-in [204] and MADE-3 [205,206]. In these models, three categories are used: one for purely hydrophilic particles, one for purely hydrophobic particles, and a third for particles with both hydrophilic and hydrophobic components. Condensation of soluble material will move particles from the hydrophobic category to the mixed category, but will not move particles in the hydrophilic or mixed categories into other categories. Coagulation of a hydrophobic particle with a hydrophilic particle, or of a mixed particle with a particle from any category, will result in a mixed particle. We expect that this mixing-state representation would resolve CCN concentrations and wet deposition as well as the two-hygroscopicity-category approach, but would reduce the overestimation of coating thickness, and therefore absorption, of BC particles.

3.1.3. Ageing Schemes

As stated previously (Section 1.2), particles emitted to the atmosphere will generally become more internally-mixed with other chemical species with time through condensation and coagulation. In many modelling studies, the primary concern is how to represent the transformation of hydrophobic particles, primarily consisting of BC, primary organic species, or dust, into hydrophilic particles through the acquisition of hydrophilic coatings.

In aerosol modules that distinguish between hydrophilic and hydrophobic particles (see Section 3.1.1), a choice must be made about how the transformation of hydrophobic particles to the hydrophilic category is represented. When the size distribution is resolved and condensation and coagulation are treated explicitly, this is frequently done by choosing a threshold amount of hydrophilic coating on the hydrophobic particles. This threshold amount can be expressed as a number of monolayers of hydrophilic species (e.g., [197,201]) or a ratio of coating diameter to hydrophobic core diameter (e.g., [63,234]), or a mass fraction of coating species to total particle mass (e.g., [22,32,147]). Sensitivity studies have shown that neither CCN concentrations [212,235] nor aerosol effective radiative forcing, either through aerosol-cloud interactions or through aerosol-radiation interactions [236], are sensitive to the threshold amount of soluble material needed to render a particle hydrophilic. However, the global burdens of BC and POA have been shown to increase by up to 41% and 52% as the threshold number of monolayers was increased from 1 to 8 [65,212]. This increase was associated with an increase in the global mean ageing timescale of BC from 0.24 days to 2.08 days, and an increase in the ageing timescale of POA from 0.37 days to 2.97 days.

Alternatively, a fixed or parametrized timescale for ageing can be chosen. This has the advantage of being less computationally intensive, but may not capture the actual spatiotemporal variation in ageing as with a more explicit representation. In particular, a fixed ageing timescale is inappropriate for global or regional studies, as multiple studies [22,32,63,91,234,237–240] have found that the ageing timescale of BC can vary from hours to days based on the concentration of condensible species and the concentration of hydrophilic coagulants. This is additionally supported by a study where fixed timescales were varied regionally and seasonally to best fit observations [241]: the resulting best-fit timescales varied from hours to days seasonally and regionally. A single fixed ageing timescale has also been found to be unable to reproduce the HIPPO-3 observations [242]. Koch et al. (2009) [243] found that reducing a fixed ageing timescale from one day to 0.5 days reduced the global BC burden and global AAOD by 19% and 9%, respectively. Concentrations of initially-hydrophobic aerosol are most sensitive to the choice of fixed ageing timescale in remote regions, far from source regions: Cooke et al. (2002) [244] found that halving or doubling an fixed ageing timescale of 1.15 days would change the global burden and atmospheric lifetime of BC by -25% or +7%, respectively, but changes in Arctic BC concentrations were $<-60\%$ and $>+75\%$, respectively. To more accurately represent the ageing of hydrophobic aerosols without greatly increasing computational cost, multiple parametrizations of ageing have been developed.

Before continuing, we note that there is some ambiguity about the distinction between "fresh" and "aged" particles, and therefore about the ageing rate. Different studies have variously considered "aged" particles to be those particles that have a particular thickness of coating species [22,32,234,245], have a particular hygroscopicity, or are CCN-active [238–240]. The first of these definitions is only appropriate for calculating ageing rates from hydrophobic to hydrophilic if the coating material is hydrophilic, and there are important differences between the latter two definitions as well. Importantly, larger particles are more likely to act as CCN, so the size of the particle has a significant effect on ageing timescales if the ageing timescale is defined as the time for the particle to become CCN-active. When choosing a parametrization, it is therefore important to ensure that the distinction between "fresh" and "aged" particles is consistent between the model (which will depend on model representations of the aerosol size distribution, of cloud droplet activation and of wet deposition) and the ageing parametrization.

Lui et al. (2011) [246] derived an ageing parametrization for BC, assuming that BC is aged primarily by condensation of low-volatility gases which are in turn formed by photochemical oxidation. This results in a parametrization of the form: ageing rate $k = a[\mathrm{OH}] + b$, where the $a[\mathrm{OH}]$ term accounts for condensation and the b term accounts for coagulation. They used $a = 4.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $b = 5.8 \times 10^{-7}$ s^{-1}. They showed that use of this ageing rate instead of a fixed timescale of 1.4 days improved both the amount and seasonal cycle of BC transport to the Arctic in comparison with observations. They also found low sensitivities (<10%) in BC burden, lifetime, and surface concentrations of BC in the Arctic to a doubling of either a or b. A later model study applied this parametrization and adjusted the a and b parameters to best fit the HIPPO flight observations of BC [241]. Their best-fit values of a and b were 2.4×10^{-11} cm^3 molecule^{-1} s^{-1} and 1×10^{-6} s^{-1}, respectively, and resulted in good agreement with both the HIPPO observations and ground-based observations.

This form is extended by Wang et al. (2014) [233] to also depend on the SO_2 concentration, under the assumption that BC is primarily aged by condensation of H_2SO_4, which forms via gas-phase OH-induced oxidation of SO_2. Their parametrization therefore has the form $k = a[\mathrm{SO_2}][\mathrm{OH}] + b$, where $a = 2 \times 10^{-22}$ cm^6 molec^{-2} s^{-1} and $b = 5.8 \times 10^{-7}$ s^{-1}. They restrict the application of this parametrization to fossil-fuel BC, and do not apply it to biomass-burning BC, as they expect that fossil-fuel BC is primarily aged by the oxidized products of co-emitted SO_2. They used a constant e-folding lifetime of 4 h for biomass-burning BC, as it is co-emitted with soluble organic compounds.

Cheng et al. (2012) [234] derived an ageing parametrization based on observations of refractory mass mixing state collected in Beijing. They considered the refractory mass to be internally-mixed if the ratio of the refractory particle diameter is between 45% and 82% of the total particle diameter, and they showed that the resulting fraction of internally-mixed particles correlates with observed particle mean hygroscopicity. They introduced parametrizations (equations 10-13 in their work) for the fraction of refractory mass that is internally-mixed based on other proxies for the age of the air mass since emission: $[\mathrm{NO}_z]/[\mathrm{NO}_x]$, where NO_x = NO (nitrogen oxide) + NO_2 (nitrogen dioxide) and NO_z is the total reactive nitrogen minus NO_x; [E]/[X], where E is ethylbenzene and X is m,p-xylene; and ([IM] + [OM])/[EC], where IM is inorganic matter, comprising NH_4^+, SO_4^{2-}, NO_3^- and Cl^-, OM is organic matter, and EC is elemental carbon. However, they note that the fitting parameters for their parametrization are not necessarily applicable to environments other than for the Beijing urban area, and that different emission sources could have different relationships between particle mixing state and the air mass age proxies. The first and third of these parametrizations were applied by Curci et al. (2019) [108] when calculating optical properties over North America and Europe using bulk aerosol mass concentrations and prescribed aerosol size distributions. They found that both parametrizations slightly improved estimates of SSA relative to AERONET observations over North America, but they note that SSA is significantly affected by the assumptions made regarding BrC absorption and the BC core size.

He et al. (2016) [32] represented the ageing of BC in a bulk aerosol model by performing simplified calculations of condensation, coagulation, and chemical oxidation. Lognormal size distributions of hydrophobic BC and other aerosol species were assumed, to determine the fraction of SO_4, NO_3, NH_3, and SOA condensing onto hydrophobic BC. They used a threshold mass concentration of 5% soluble material for the conversion of hydrophobic BC to hydrophilic BC. Coagulation was calculated by assuming monodisperse aerosol size-distributions, and chemical oxidation was calculated using the parametrization of Pöschl et al. (2001) [25]. The microphysics-based ageing scheme improved bias and correlation of modelled BC concentrations with HIPPO observations, as compared to a fixed ageing timescale of 1.2 days. Chemical oxidation ageing was shown to have a small (<0.5 %) impact on the global annual mean BC ageing rate. It led to only a small (<1%) reduction in BC column burden and zonal mean concentration globally as well as global BC lifetime. Additional sensitivity studies to the assumed aerosol size distributions and the coating thickness threshold had small effects (<10%) on BC concentrations and on the global annual mean ageing rate.

Riemer et al. (2004) [22] presented a parametrization for soot ageing based on regional modelling using the MADEsoot aerosol module. They recommended different ageing timescales during the day and night, and at different altitudes during the day. They found that during the day ageing by condensation of sulphuric acid resulted in an e-folding lifetime of two hours above 250 m, which increased to eight hours at lower altitudes (due to larger particle concentrations and greater condensation competition). During the night, coagulation dominated over condensation. The lifetime due to coagulation had the form $\tau = \frac{a}{N} + \frac{b}{N^2}$, where $a = 6 \times 10^4$ h cm^{-3} and $b = 3 \times 10^8$ h cm^{-6}, and N is the number concentration of soluble particles. This resulted in ageing timescales during the night of 10 to 40 hours. However, this parametrization was specifically formulated for urban environments, and the condensational lifetime in particular may not be appropriate in environments with lower concentrations of condensible species.

Jacobson (2010) [189] found using the GATOR-GCMOM global climate model that soot from fossil-fuel sources became internally-mixed with other aerosol through coagulation with an average e-folding timescale of only three hours. However, other studies (e.g., [22,238,239]) found that ageing timescales due to coagulation were much longer. This may be because Jacobson (2010) considered a particle to become internally-mixed after a single coagulation event with a particle from a different mixing-state category, but other studies have used a threshold of hygroscopicity or BC mass fraction to define the state "internally-mixed".

Riemer et al. (2010) [238] investigated the ageing timescale of BC in an urban plume using PartMC-MOSAIC. They defined "aged" particles as those that would activate as CCN at a given supersaturation. The study showed that a given mass fraction of particles generally becomes CCN-active 3–4 times more quickly than the same number fraction of particles. This is because the larger particles (which contain more mass) become CCN-active more quickly due to larger surface areas for condensation. They also found a difference of more than a factor of 20 in ageing timescales between critical supersaturation thresholds of 0.1% and 0.6%, with ageing timescales decreasing monotonically with increasing supersaturation. This work was extended by Fierce et al. (2015) [239], who found that the timescale of ageing due to condensation during the day was of the order of one hour, and depended primarily on the number size distribution of fresh BC particles, the condensational growth rate, and the hygroscopicity of the condensing species. The timescale of ageing due to coagulation was of the order of one day, and depended primarily on the wet diameter of non-CCN-active BC particles, and the number concentration of >100 nm diameter CCN-active particles.

Oshima and Koike (2013) [240] developed a parametrization of ageing timescales for BC based on simulations with a box model. Their parametrization provides the rate for uncoated BC particles to become CCN active, expressed as a function of the mass-normalized coating rate and the parameters of the fresh BC size distribution. It has the form $\frac{1}{\tau} = \frac{V_{BC}}{A(D_m,\sigma)} + \delta$, where V_{BC} is the rate of hydrophilic species condensation onto BC particles normalized by the BC mass, $A(D_m,\sigma)$ is a parameter that depends on the size distribution of BC, and δ is an optional term representing the ageing rate due to coagulation. The authors present a parametrization for δ, but suggest that a fixed term may also be used.

Chen et al. (2017) [63] estimate the ageing timescale as $\tau = 3f\nu\frac{\rho_c}{\rho}\frac{m}{\gamma_c}$, where f is a dimensionless constant equal to 0.63, ν is the ratio of soluble coating thickness to BC diameter necessary for the BC particle to be considered hydrophilic, ρ_c is the density of the soluble coating species, m is the mass of the BC particle, and γ_c is the rate at which soluble mass condenses or coagulates onto the BC particle. They estimate ν as equal to 5%.

While most of the above studies focused primarily on BC, we note that these same approaches can be applied to other hydrophobic aerosols. Fan et al. (2004) [247] represented the ageing rate of dust as depending linearly on SO_2 concentrations, with a rate constant of zero for RH <50%, and 0.001 s^{-1} for RH >60%, and linearly interpolating in between.

3.2. Categorization by Black Carbon Mass Fraction

As mentioned previously, the mixing state of BC is particularly important both due to the enhancement of absorption by scattering coatings and due to the increase in hygroscopicity from hydrophilic coatings, which in turn allows BC to act as a CCN and hastens its removal from the atmosphere through wet deposition. This has led some authors to focus on the representation of mixing state based on the BC mass fraction. This is the approach used by the MADRID-BC [57,211] and ATRAS [59,173] aerosol modules: aerosols are categorized into several (ten and eight, respectively) externally-mixed sub-populations based on the BC mass fraction. The lowest BC mass fraction category contains particles that contain no BC and the highest BC mass fraction category contains particles that are exclusively BC.

The greater detail allows for better estimates of CCN concentrations and BC optical properties. Using the MADRID-BC box model, Oshima et al. (2009) [57] performed simulations of a plume advecting off of the coast of Japan. They found that a size-resolved internally-mixed assumption overestimates the fraction of BC mass that would activate at 0.05% supersaturation by 8–34%, underestimates scattering coefficients by 11–19% and overestimates absorption coefficients by 35–44%, depending on the age of the plume. Additionally, by adjusting the number of BC mass fraction bins, it is possible to assess simpler representations of the aerosol mixing state. They performed further simulations with two mixing state categories (BC-free and BC-containing particles), similar to the IMPACT [197,198] and the MADMS [208–210] aerosol modules; and three categories (BC-free particles, and hydrophilic BC-containing particles and hydrophobic BC-containing particles), similar to the MADE-soot [22,147,207], MADE-in [204] and MADE-3 [205,206] aerosol modules. They found that using BC-free and BC-containing categories greatly improves estimates of scattering and absorption coefficients, reducing the errors to 1–3% and 3–4%, respectively, but provided very little improvement in the CCN-activated BC mass fraction. The three-category representation does not result in much greater improvement in radiative properties, compared to the two-category representation, but it reduced the error in the CCN-activated BC mass fraction to 2–17%.

However, studies performed using the ATRAS model [59,60] have found that a size-resolved internally-mixed assumption yielded only small differences in CCN concentrations, as compared to simulations with eight or ten BC mass fraction bins. This may be due to a greater contribution of BC-free particles to CCN concentrations in the East Asia region and globally, as compared to the plume case study examined by Oshima et al. (2009) [57]. The changes in hygroscopicity did affect wet deposition, leading the size-resolved internally-mixed case to underestimate BC concentrations by 9% for the East Asia region [59] and by up to 15% globally [60]. Matsui et al. (2014) [59] found that the size-resolved internally-mixed assumption overestimated AAOD by 20% in the East Asia region, resulting in an overestimate of the heating rate within the planetary boundary layer of 21%, despite the reduction in the BC mass concentration due to increases in wet deposition. Matsui et al. (2018) [60] also found that the size-resolved internally-mixed representation would overestimate the globally-averaged MAC of BC by up to 115%, depending on the emitted sized distribution of BC. This led to overestimates in AAOD by up to 110% and in the DRE of BC by up to 94%. They also performed simulations with a two-category ($\geq$90% BC and <90% BC by mass) representation of the mixing state, and this representation also generally overestimated AAOD and DRE, similarly to the size-resolved internally-mixed case.

The MOSAIC-Mix module [58] extends this type of representation by including two dimensions: both BC mass fraction and hygroscopicity. They simulated urban plumes ageing for up to 36 hours under a variety of scenarios. Compared to their most detailed representation of aerosol mixing state, they found that, on average, an internally-mixed assumption would yield NRMSE in CCN concentrations and absorption coefficients of 14.2% and 21.4%. Using three BC mass-fraction categories, these errors were reduced to 7.0% and 2.8%. The authors suggest the use of two hygroscopicity categories and two BC mass fraction categories: this yielded average NRMSE values in CCN concentration and absorption coefficients of 5.4% and 3.8%, respectively.

Together, the above results suggest that a great improvement in estimates of aerosol optical properties can be achieved by separating low-BC mass fraction (or BC-free) particles from high-BC mass fraction (or BC-containing) particles, but that improvements in CCN concentrations are more modest and less consistent across studies.

3.3. Detailed Categorization by Chemical Composition

The aerosol modules in the previous section categorized aerosol particles by the BC mass fraction. The modules listed in this section separate particles not only by BC mass fraction, but also by the mass fraction of many other species as well. These aerosol modules have previously been described as Mixing-State Resolved (MSR) [229]. However, we find this term ambiguous, as the particle-resolving (Section 3.5), source-oriented (Section 3.4), BC mass-fraction (Section 3.2), and even the two-hygroscopicity-category approach (Section 3.1.1) can all be said to be resolving the aerosol mixing state with different degrees of detail.

The GATOR 2002 module [157] used one category each for mixtures of sea-spray, OA, or soil dust with condensing inorganic species (aqueous H_2O, H^+, $NH_4{}^+$, $SO_4{}^{2-}$, $NO_3{}^-$, $CO_3{}^{2-}$, and 11 products of these ions), as well as an additional mode containing only the above condensing inorganic species. BC and condensing inorganic species were represented using three additional categories with different thresholds for the BC mass fraction. Ten additional categories contained binary mixtures formed by coagulation of particles in two of the above bins, and one final category contained ternary and higher-order mixtures, for a total of 18 categories. As the mass of condensible material was tracked within each category, condensation would change the mass within a category, but it would not transfer particles between categories. Only coagulation transferred particles between categories.

The Multiconfiguration Aerosol TRacker of mIXing state (MATRIX) module [171,213,214] used a similar representation. Pure categories were included for sulphate only. All other categories would include sulphate mass acquired through condensation of sulphate and coagulation with pure sulphate particles. Organic carbon and sea salt particles were therefore represented in categories that included both OC and sulphate or sea salt and sulphate, respectively. Depending on the tested configuration, dust-sulphate and BC-sulphate mixtures were represented with several categories with sulphate mass-fraction cut-offs of 5% and/or 20%; and mixtures of BC, sulphate, and either mineral dust or OC were tracked separately. Remaining combinations of species, including higher-order mixtures, were represented using a single “mixed” composition bin.

The Detailed Aerosol Mixing State (DAMS) module [188], the Dergaoui et al. (2013) module [232], and the Size-Composition Resolved Aerosol Model (SCRAM) [229,230] all include categories for mostly-pure, binary, and higher-order mixtures. However, they are distinguished from the GATOR 2002 module by allowing the mostly-pure and binary mixture categories to include small mass fractions

(5% in DAMS and Dergaoui et al. (2013), 20% in SCRAM) of other species. This is more expensive computationally, as it requires that one track the mass of multiple species within the "mostly-pure" categories, instead of just the mass of the pure species, and thus results in a larger number of tracers for the same number of total chemical species. Aerosol mass is moved between categories as coagulation (or also condensation in DAMS and SCRAM) changes the relative masses of different species within a category beyond the mass fraction thresholds.

The detailed chemical mixing state that can be represented in these schemes allows for studies on the interactions between gas-particle partitioning and mixing state. For example, Zhu et al. (2016) [229] found that an internally-mixed assumption would, on average, underestimate NO_3 concentrations by 38% and overestimate NH_4 concentrations by 8% over the greater Paris area, due to interactions between the mixing state of SO_4 across the aerosol population and gas-particle partitioning. The differences in inorganic mass fractions led to large differences in aerosol water and subsequently AOD for specific points in space and time (up to 72.5%), but these become insignificant when spatially and temporally averaged. However, such studies also require sufficiently-detailed representation of thermodynamic partitioning: if bulk equilibrium was assumed, then the representation of the mixing state would have little effect on NO_3 or NH_4 concentrations, or on AOD.

3.4. Source-Oriented

As stated previously, many particles are emitted containing multiple chemical species. Therefore, it can be beneficial to designate categories for particles by the emission source, rather than by the primary chemical species in the particle. Separating particles by source also facilitates studies of the impacts of different aerosol sources on air pollution and climate by maintaining information regarding the origin of aerosol number and mass. This is similar to tagging aerosol number or mass by source sector, but studies that tag by source sector often still consider the tagged mass to be fully internally-mixed or size-resolved internally-mixed with aerosol mass from other sources for the purposes or calculating radiative properties and hygroscopicity. We therefore consider the mixing state to be resolved with a source-oriented approach only if the emissions from different sources are externally-mixed for calculations of radiative properties and hygroscopicity.

This is the approach used by the University of California at Davis / California Institute of Technology (UCD/CIT) model [181]. A different category is used for each of the nine source types of interest included in the model: fugitive dust, road dust, diesel engines, catalyst-equipped gasoline engines, non-catalyst-equipped gasoline engines, wood smoke, meat cooking, combustion of high-sulphur fuel, and other sources. The size distribution is represented using 15 two-moment bins for each source type. Condensation changes the particle mass within a category, but does not move particle mass between categories, as it would for many of the other representations listed here. Coagulation is not included in this module, as it was assumed not to have a significant impact on the aerosol population over the distances of interest. Many studies were performed using this model focusing on air quality in California (e.g., [182,183]). However, it was found that the variables of interest to the authors of these studies, including EC, OC, $PM_{2.5}$, and nitrate concentrations, could be adequately resolved using a size-resolved internally-mixed assumption within the region of interest. The R^2 values between the size-resolved internally-mixed and source-oriented mixing-state mass concentrations of EC less than 1 $\mu g\ m^3$ was 0.645, and reported R^2 values for all other mass concentrations were greater than 0.84, and frequently above 0.95 [182,183].

The source-oriented mixing-state approach is also used by Source-Oriented WRF-Chem (SOWC) [162]. A different category is used for each of the five source types of interest included in the model: diesel engines, wood smoke, high-sulphur fuel, food cooking, and other sources. The mass of each species is tracked in eight size bins for each source type. Like the UCD/CIT model, condensation changes the particle mass within a category, but does not move particle mass between categories, as it would for many of the other representations listed here. Coagulation adds the mass of the smaller coagulating particle to the mass of the category including the larger coagulating particle.

Therefore, both condensation and coagulation change the composition of each category with time, making them more well-mixed.

While GATOR 2002 [157] binned particles by composition, the GATOR 2012 module [97] may be best understood as separating particles by source: two different categories are used for emitted fossil-fuel soot and emitted biofuel and biomass-burning soot, as well as a third category for "ultimate internally-mixed" particles, which included aerosol from all other sources as well as aerosols formed by coagulation of aerosol in two different categories. Three additional categories are used to represent aerosol within hydrometeors, but we consider this to be a representation of cloud processing of aerosols rather than mixing state, and beyond the scope of this review. The fossil-fuel soot and biofuel and biomass-burning soot categories contain many of the same chemical species, but differ in that the aerosol is emitted by different sources.

As particles do not move between external categories through condensation, there is a risk that such a scheme will not distinguish between particles that are freshly emitted or have undergone ageing through condensation if the particles are from the same source category (e.g., one aged biomass-burning plume advecting over another biomass-burning source). This risk should be mitigated through sufficient size resolution, as condensation of material and self-coagulation would grow particles to larger size bins, if the size distribution of the emissions is sufficiently narrow. We also note that particles with significantly different properties can be emitted from the same source, such as BC-containing particles and BC-free particles, both emitted by biomass-burning sources. These particles from the same source will be distinguished only if two categories for the same source are included.

3.5. Particle-Resolving

In the particle-resolving approach, the mass composition of each particle is resolved explicitly. Therefore, the degree of internal or external mixing across the aerosol population is known exactly. The optical properties and hygroscopicity can be calculated for each particle. Assumptions about particle morphology are still necessary, but this is true of nearly every other aerosol module described here, as well. We include only one example of an aerosol model using this approach, being the PartMC-MOSAIC model [221]. In practice, generally 10^5 individual particles are simulated in PartMC-MOSAIC simulations. Due to computational expenses, it is generally used only within a single-box model, but it has been operated within a single-column model [222].

Because of the explicit knowledge of the chemical mixing state in PartMC-MOSAIC simulations, it has been used in several studies to better understand the evolution of particle mixing state within an urban plume and the resulting effects of mixing state on CCN concentrations and aerosol optical properties [49,56,58,99,238,239].

4. Summary and Recommendations

Optimally, the mixing-state of aerosols would be resolved explicitly in models. However, for global and regional models, this continues to be prohibitively expensive. Many regional and global studies have shown that an internally-mixed assumption better represents aerosol hygroscopic and optical properties of BC compared to an externally-mixed assumption [63,69], with few exceptions [120]. Therefore, in global models with coarse spatial resolution (100s of km), if computational resource limitations prohibit the use of multiple mixing-state categories, we recommend that it is assumed that aerosols are internally-mixed. It must be recognized that this will still lead to an overestimate of CCN concentrations, wet deposition of initially-hydrophobic aerosol, and aerosol absorption. These errors depend on model spatial resolution, and on the representations of the aerosol size distribution, aerosol processes, and aerosol optical properties, in addition to the true mixing state of the aerosol population. With these caveats in mind, a size-resolved internally-mixed representation has been shown to frequently overestimate CCN concentrations by 10% to 20% [54,56–58,61], and absorption coefficients of BC by 20% to 40% [49,56–58]. In the case of CCN concentrations and BC absorption, these overestimates will be greater near source regions, while overestimates in wet deposition will lead to greater errors in hydrophobic aerosol concentrations far from source regions (e.g., [64]).

When the hydrophobic-hydrophilic two-category approach is applied, we strongly advise against the use of fixed timescales to represent the ageing of hydrophobic species by coating with hydrophilic species, as this ageing scale has been shown to vary from hours to days, depending primarily on the availability of condensible hydrophilic species [22,32,63,91,234,237–240]. Even where computational resources do not permit explicit calculation of ageing by condensation and coagulation, multiple parametrizations exist for particle ageing [22,32,63,233,240,241,246,247]. Ageing by coagulation is generally slower and less important than ageing by condensation, but is non-negligible during night-time conditions and where concentrations of condensible species are low relative to aerosol concentrations.

The two-category (hydrophobic and hydrophilic) approach has proven useful for better predicting CCN concentrations and wet deposition of initially-hydrophobic aerosol. More than a decade ago, Bond et al. (2006) [85] advised that this model representation of the hygroscopic properties of BC-containing particles could also be used to better predict the optical properties of BC-containing particles. While much progress has been made using this approach, subsequent research has shown some of its limitations. Low-hygroscopicity organic compounds, frequently co-emitted with BC, can enhance its absorption without dramatically increasing its hygroscopicity. Additionally, the representation of all scattering hydrophilic species as coatings on BC, instead of including BC-free particles separately, has the effect of overestimating the coating thickness on BC particles, and thus overestimates the enhancement of BC absorption [60]. The majority of BC mass in a given air parcel may be internally-mixed (i.e., coated) by non-BC mass, even while the majority of the non-BC mass in the same air parcel is externally-mixed with BC (i.e., contains no BC inclusions). This may frequently be the case in biomass-burning plumes [89]. This has also been observed in the Arctic, where more 95% of observed particles were BC-free, but the number fraction of uncoated BC particles was negligible [95]. Sensitivity studies with more and less complex representations of aerosol mixing state suggest that three [57] or four [58] mixing state categories based on BC mass fraction and particle hygroscopicity are sufficient to resolve CCN concentrations, wet deposition, and aerosol optical properties. We therefore suggest that global and regional models represent separately BC-free hydrophilic particles, BC-containing hydrophilic particles, and hydrophobic particles. We also advocate for further studies testing model sensitivity to mixing state representation, in order to better quantify the errors introduced by this simplification.

With the exception of a very few cases, the description of an aerosol population or individual aerosol particles as simply "externally-mixed" or "internally-mixed" is no longer sufficient. Even at emission, many aerosol particles contain multiple species, both hydrophobic and hydrophilic, scattering and absorbing. These terms conflate hygroscopic and radiative properties, which may not necessarily co-vary. An aerosol population may contain hydrophobic, absorbing particles (e.g., BC) where some are coated with hydrophilic scattering species (e.g., sulphate) and others are coated with more hydrophobic scattering species (e.g., POA). In such an example, the population is homogeneous with respect to radiative properties (all BC is coated with low-absorption species), but heterogeneous in its hygroscopic properties. Regarding radiative properties, the absorption of a black carbon particle depends not only on whether it is coated or uncoated, but on the amount of scattering material on the particle. Similarly, the terms "fresh" and "aged" are used by some authors to refer to the change in radiative properties of BC as it becomes coated, and by other authors to refer to an increase in hygroscopicity of multiple aerosol species. We therefore stress that authors need to be precise about the properties and species considered when describing aerosol mixing-state.

Much of the existing literature has focused on the effects of mixing-state on the radiative and hygroscopic properties of aerosol, specifically BC, due to the importance of these properties for estimating aerosol impacts on climate. However, the distribution of species across an aerosol population has implications for any process that depends non-linearly on the composition of an aerosol particle. We note in particular that interactions of chemical mixing state with thermodynamic partitioning have only been included in models by a small number of studies [157,188,229,230,232], but that this topic becomes more relevant as more models include nitrate as a resolved species and include more detailed representations of organic species. Nitrate is expected to become more important for accurately estimating radiative effects of anthropogenic aerosol in the future as emissions of sulphate decrease.

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Abbreviations

The following abbreviations are used in this manuscript:

AAOD	Aerosol Absorption Optical Depth
AOD	Aerosol Optical Depth
APM	Advanced Particle Microphysics
ATRAS	Aerosol Two-dimensional bin module for foRmation and Aging Simulation
AURAMS	A Unified Regional Air-quality Modelling System
BC	Black Carbon
CanAM	Canadian Aerosol Module
CAM	Community Atmosphere Model
CARES	Carbonaceous Aerosols and Radiative Effects
CCCma AGCM	Canadian Centre for Climate modelling and analysis Atmospheric General Circulation Model
CCM	Community Climate Model
CIT	California Institute of Technology
CTM	Chemical Transport Model
DAMS	Detailed Aerosol Mixing State
DRE	Direct Radiative Effect
DRF	Direct Radiative Forcing
EC	Elemental Carbon
ECHAM	European Centre HAmburg Model
GATOR-GCMOM	Gas, Aerosol, Transport, Radiation, General Circulation, Mesoscale, and Ocean Model
GATORG	Gas, Aerosol, Transport, Radiation, and General Circulation model
GCM	General Circulation Model
GEM-MACH	Global Environmental Multiscale model—Modelling Air quality and CHemistry
GEOS-Chem	Goddard Earth Observing System coupled to Chemistry
GISS	Goddard Institute for Space Studies
GLOMAP	GLObal Model of Aerosol Processes
GMXe	Global Model aerosol extension
HIPPO	HIAPER Pole-to-Pole Observations
HTDMA	hygroscopicity tandem differential mobility analyzer
INP	Ice-Nucleating Particles
LLPS	Liquid-Liquid Phase Separation
MAC	Mass Absorption Cross-section
MADE	Modal Aerosol Dynamics model for Europe
MADMS	Modal Aerosol Dynamics model for multiple Modes and fractal Shapes
MADRID-BC	Model of Aerosol Dynamics, Reaction, Ionization, and Dissolution with resolution of a mixing state of Black Carbon
MAM	Modal Aerosol Module
MATRIX	Multiconfiguration Aerosol TRacker of mIXing state
MEC	mass extinction cross-section

MEGAPOLI	Megacities & Emissions, urban, regional and Global Atmospheric POLlution and climate effects, and Integrated tools for assessment and mitigation
MESSy	Modular Earth Submodel System
MOZART	Model for Ozone and Related chemical Tracers
MSC	Mass Scattering Cross-section
MSR	Mixing-State Resolved
NEXAFS	Near-Edge X-ray Absorption Fine-structure Spectroscopy
NRMSE	Normalised Root-Mean-Square Error
NorESM	Norwegian Earth System Model
NWP	Numerical Weather Prediction
OC	Organic Carbon
PartMC-MOSAIC	Particle Monte Carlo model-Model for Simulating Aerosol Interactions and Chemistry
PLA	Piecewise Lognormal Approximation
PAM	PLA Aerosol Model
POA	Primary Organic Aerosol
POC	Primary Organic Carbon
RH	Relative Humidity
SALSA	Sectional Aerosol module for Large Scale Applications
SCRAM	Size-Composition Resolved Aerosol Model
SOA	Secondary Organic Aerosol
SOWC	Source-Oriented WRF-Chem
SSA	Single Scattering Albedo
STXM	Scanning Transmission X-ray Microscopy
UCD/CIT	University of California at Davis / California Institute of Technology
UKCA	United Kingdom Chemistry and Aerosols
VTDMA	Volatility Tandem Differential Mobility Analyzer
WRF	Weather Research and Forecasting model

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