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Key Points:
- Increases in assumed cloud water pH can improve simulation of sulfate aerosols
- Aerosol radiative forcing over the last 40 years is sensitive to the value of cloud water pH
- Global composition climate models assuming a fixed value of cloud water pH do not fully account for recent aerosol radiative forcing

Supporting Information:
- Supporting Information S1

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The Impact of Changes in Cloud Water pH on Aerosol Radiative Forcing

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Abstract Oxidation of sulfur dioxide (SO_2) in cloud water by reaction with ozone is an important sulfate aerosol formation mechanism and strongly dependent on the acidity of cloud water. Decadal reductions in Northern Hemisphere sulfur emissions have contributed to higher cloud water pH, thereby altering sulfate formation rates. Here we use a global composition-climate model to show that changes in cloud water pH over the 1970–2009 period strongly affects the aerosol particle size distribution, cloud condensation nuclei concentrations, and the magnitude of aerosol radiative forcing. The simulated all-sky aerosol radiative forcing (1970–2009) over the North Atlantic is +1.2 W m^{-2} if pH remains constant at 5.0, as in many climate models. However, the forcing increases to +5.2 W m^{-2} if pH is assumed to increase by 1.0 unit over this period. Global composition climate models need to account for variations in cloud water pH to improve the representation of sulfate aerosol formation and aerosol radiative effects.

Plain Language Summary Particles in the atmosphere (aerosols) can be harmful to human health at the surface and also affect the Earth's climate. Sulfate is a major component of atmospheric aerosols. It is formed from chemical reactions involving sulfur dioxide, which has large man-made sources in the energy and industrial sectors. This study investigates the sensitivity of sulfate aerosol formation in clouds to the assumed acidity of the cloud water. Large changes in man-made emissions over the Northern Hemisphere in the last 30 years have altered the acidity of cloud water. Here we used climate model simulations that include a representation of aerosols and chemistry to investigate the effect of changes in cloud water acidity on sulfate aerosol formation between 1970 and 2009. Our analysis shows that changes in the acidity of cloud water has a strong effect on the properties of aerosols and how they interact with the Earth's radiative balance. The impact is shown to be particularly important for cloudy regions like the North Atlantic that are sensitive to changes in aerosols. The results highlight that the impact of changes in cloud water acidity on aerosols should be included within climate models to improve our representation of aerosols and their interaction with climate.

1. Introduction

Sulfate is a major component of atmospheric aerosol particles (Zhang et al., 2007) that affects visibility, acid deposition, air quality, and human health (Fuzzi et al., 2015). Sulfate is largely present in the fine size fraction of aerosols (less than 2.5 μm diameter) where it can interact directly and indirectly (via the modification of cloud microphysical properties) with Earth's radiative balance, leading to a large but uncertain negative radiative forcing of climate (Myhre et al., 2013).

Sulfate aerosol mass is produced from the oxidation of sulfur dioxide (SO_2) in the gas phase by hydroxyl (OH) radicals and by aqueous phase reactions in cloud and rain water involving hydrogen peroxide (H_2O_2), ozone (O_3), O_2 catalyzed by transition metal ions, and other oxidants (Alexander et al., 2009; Dentener et al., 2002; Feingold et al., 2002; Harris et al., 2013). Globally, aqueous phase oxidation accounts for 60–80% of tropospheric sulfate formation (Barth et al., 2000; Chin et al., 1996; Faloona, 2009; Roelofs et al., 2001).

The rate of in-cloud dissolution and subsequent aqueous phase reactions of SO_2 depend on the pH of the cloud water, as well as cloud properties, processing times, and precipitation rates (Ervens, 2015; Gong et al., 2011; Pandis & Seinfeld, 1989; Rasch et al., 2000). Cloud water pH is determined by the dilution of the chemical components in the particles that form cloud droplets. These components are either acidic (sulfates, nitrates, and organics) or basic (ammonia, mineral dust, and sea salt) and originate from both natural and anthropogenic sources, meaning cloud water pH is spatially variable. The cloud water pH also varies within the size distribution of cloud drops; lower pH values tend to be associated with smaller drops (Gurciullo & Pandis, 1997).

Cloud water pH can have a strong influence on the efficiency of in-cloud sulfur oxidation. The oxidation rate of S (IV) by H_2O_2 is approximately independent of pH and is the preferential pathway at a pH <5.5, while oxidation by O_3 is highly sensitive to pH and is the preferential pathway for pH >5.5 (Seinfeld & Pandis, 2006). Increasing the pH by 1 unit can increase the oxidation reaction rate of S (IV) by O_3 by a factor of 100 (Kreidenweis et al., 2003).

Measurements of cloud water pH are limited to a few locations. The pH varies from 3 to 7 across coastal marine environments and continental areas of the United States, Europe, China, and India (Aleksic et al., 2009; Benedict et al., 2012; Budhavant et al., 2014; Collett et al., 1993; Murray et al., 2013; Plessow et al., 2001; Sun et al., 2010). Measurements show that since the mid-1980s cloud water pH has increased from 4 to ~5 in the northeastern United States due to reductions in emissions of acidifying gases (Aleksic et al., 2009; Murray et al., 2013; Schwab et al., 2016). However, there are no measurements over remote regions downwind of source locations where SO_2 oxidation is likely to take place after long-range transport.

There are substantially more measurements of rainwater pH, with the observed trend anticipated to correlate with that of cloud water, but have a different magnitude (Aleksic et al., 2009; Collett et al., 1993). Rodhe et al. (2002) used a global chemical transport model to calculate the spatial variability of pH in precipitation and showed that the lowest values (pH 4–5) occur in polluted continental regions and higher values (pH >6) over dusty and marine locations. Reductions in anthropogenic emissions of SO_2 since the 1980s over Europe and North America has increased rainwater pH by >0.5 (Vet et al., 2014). It is reasonable to assume that a similar change in cloud water pH will also have occurred and affected sulfate aerosol formation.

The treatment of in-cloud aqueous phase sulfate formation in global models varies from those using a fixed pH to those explicitly calculating the pH of different-sized cloud droplets (Ervens, 2015; Fahey, 2003; Gong et al., 2011). An accurate representation of aqueous phase oxidation and cloud water pH in models was previously found to be an important factor in reproducing measured SO_2 and sulfate (Barrie et al., 2001; Lohmann et al., 2001; Roelofs et al., 2001). Over the United Kingdom and Germany, increasing the fixed value of pH from 5 to 5.5–5.8 in two models improved the comparison of simulated sulfate mass with measurements (Banzhaf et al., 2012; Redington et al., 2009). The underestimation of in-cloud aqueous phase sulfate formation may contribute to the underestimation of sulfate mass and overestimation of SO_2 concentrations across polluted regions (Berglen, 2004; Feichter et al., 1996; Kasibhatla et al., 1997; Roelofs et al., 2001; Textor et al., 2006).

Different treatments of cloud water pH in models affects in-cloud sulfate formation, altering aerosol size distributions, cloud condensation nuclei (CCN) concentrations, and aerosol radiative effects (Kreidenweis et al., 2003; Roelofs et al., 2006). Cloud water pH is shown to be one of the main causes of uncertainty in calculating CCN concentrations in a global aerosol microphysics model (Lee et al., 2013). However, these studies have not considered how changes in cloud water pH affect aerosol formation, aerosol size distributions, and aerosol radiative effects over recent decades, especially for regions such as Europe and Asia where large changes in emissions (Granier et al., 2011; Hand et al., 2012; Vestreng et al., 2007), and consequently pH, have occurred.

Here we use a global composition-climate model to test the sensitivity of aqueous phase sulfate formation to different values of cloud water pH over a 40-year time period from 1970 to 2009. We show that changes in cloud water pH alter sulfate formation and the aerosol size distribution, resulting in large effects on aerosol radiative forcing over this period.

2. Methods

2.1. HadGEM3-UKCA Composition-Climate Model

The global composition-climate model HadGEM3-UKCA, as described in Turnock et al. (2015), is used to simulate aerosol processes and their impact on the radiative balance. HadGEM3-UKCA is a model with similar complexity to other composition climate models (Lamarque et al., 2013; Mann et al., 2014). Simulations have a horizontal resolution of 1.875 × 1.25 (~140 km at midlatitudes) with 63 levels in the vertical (~40 km). A "double-call" radiation configuration has been used to diagnose the top-of-atmosphere (ToA) radiative perturbation from all aerosol emissions, including both aerosol-radiation interactions (ari) and aerosol-cloud interactions (aci). The change in ToA radiative perturbation is calculated as the difference between two different pH simulations in the same time period. Aerosol radiative forcing is defined here as the difference between ToA radiative perturbations over the period 1970 to 2009. Further details on HadGEM3-UKCA are provided in the supporting information (Bellouin et al., 2013; Dee et al., 2011; Edwards & Slingo, 1996; Granier et al., 2011; Mann et al., 2010; O'Connor et al., 2014; Scott et al., 2014; Spracklen et al., 2006; Telford et al., 2008; Uppala et al., 2005; Woodward, 2001).

This model version has been shown to be able to reproduce observed long-term trends in European annual-mean sulfate aerosol mass over the period 1978 to 2009 (Turnock et al., 2015). However, the model consistently underestimated wintertime sulfate mass, particularly over northern Europe when oxidants (especially H_2O_2) are limited, suggesting that sulfate aerosol formation through in-cloud oxidation of SO_2 with O_3 was underrepresented. Here we further explore this issue by comparing simulations using different values of pH against observations of sulfate aerosol mass concentrations.

2.2. Sulfate Aerosol Formation in HadGEM3-UKCA

Sulfate aerosols are formed through the reaction of gas phase SO_2 with the hydroxyl radical (OH) to form sulfuric acid vapor (H_2SO_4):

$$SO_2 + OH + M \rightarrow HOSO_2 + M \tag{R1}$$

$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3 \tag{R2}$$

$$SO_3 + H_2O + M \rightarrow H_2SO_4 + M \tag{R3}$$

The aerosol processes of condensation and nucleation compete for the available H_2SO_4 to form secondary aerosol particles, increasing aerosol size and number.

When low-level clouds are present, defined as when cloud liquid water content exceeds 0.2 g/m^3 (representative of marine stratocumulus clouds), aqueous phase oxidation of SO_2 is assumed to occur through reaction with H_2O_2 and O_3. SO_2 dissolves in cloud droplets, calculated using a Henry's law equilibrium approach, to form HSO_3^-, which can further dissociate to SO_3^{2-}. Both these species can lead to sulfate aerosol formation via the following oxidation reactions:

$$HSO_3^- + H_2O_2(aq) + H^+ \rightarrow SO_4^{2-} + 2H^+ + H_2O \tag{R4}$$

$$HSO_3^- + O_3(aq) \rightarrow SO_4^{2-} + H^+ + O_2 \tag{R5}$$

$$SO_3^{2-} + O_3(aq) \rightarrow SO_4^{2-} + O_2 \tag{R6}$$

The sulfate aerosol mass produced from in-cloud oxidation is partitioned into the soluble accumulation and coarse modes according to the ratio of their respective number concentrations to their sum. This process produces sulfate particles of larger size and mass but does not increase particle number.

2.3. Simulations

In a similar way to Turnock et al. (2015), simulations were conducted with HadGEM3-UKCA using cloud water pH values of 5.0 (default model value) and 6.5 to provide monthly output for each year over the period 1970 to 2009. Additional sensitivity simulations were undertaken using global cloud water pH values of 4.5, 5.5, and 6.0 over the 5-year periods of 1970–1974 and 2005–2009. The range of cloud water pH values was chosen based on the analysis by Lee et al. (2013) and observed values of cloud water pH. In all simulations a globally fixed value of pH is assumed to be representative of bulk cloud droplets, similar to other global climate models (see Table 1 in Ervens (2015)). Results have been analyzed for the regions defined in supporting information Figure S1.

3. Results and Discussions

3.1. Model Evaluation

Here we use measurements across Europe, North America, and East Asia from the European Monitoring and Evaluation Programme, the Interagency Monitoring of Protected Visual Environments, and the Acid Deposition Monitoring Network in East Asia over the period 2005–2009 to compare to simulated sulfate aerosol mass concentrations using different values of cloud water pH (Figure 1). A cloud water pH of <5.5 causes an underestimation of wintertime sulfate mass concentrations by a factor of >2, particularly over Europe when oxidation of SO_2 by O_3 dominates that by H_2O_2. An assumed cloud water pH of >5.5 reduces the model bias in simulated sulfate to less than a factor of 2. Smaller effects of pH on model bias are shown in spring and autumn with negligible effects in summertime.

To explore the effect of decadal changes in cloud water pH, we compared the model against European measurements over the periods 1980–1984 and 2005–2009 using a pH of 6.5 and 5.0. A pH of 5.0 causes a larger underestimate of wintertime concentrations in 2005–2009 compared to 1980–1984. In contrast, a pH of 6.5 causes a larger overestimate of wintertime sulfate in 1980–1984 compared to 2005–2009. Increasing cloud water pH from 5.0 to 6.5 improves the comparison of simulated and observed trends in wintertime sulfate concentrations over the period 1978 to 2009 at long-term European sites (Figure S2). This suggests that it is important to account for temporal changes in cloud water pH when calculating regional trends in sulfate aerosol.

3.2. Global Sulfate Formation

The global SO_4 column burden (Table S1) calculated here using a pH of 5.0 is within the range of values in other model studies (Berglen, 2004; Mann et al., 2010; Spracklen et al., 2005; Textor et al., 2006).

An increase in cloud water pH of 1.0 in both 1970–1974 and 2005–2009 causes a ~50% reduction in the annual mean global SO_2 column burden (Figure S3 and Table S1), as more SO_2 is oxidized in cloud droplets (R5) and (R6). The largest reductions in SO_2 occur over Europe, North America, and East Asia, the largest anthropogenic emission source regions. Increased cloud water pH causes small increases in the annual mean sulfate column burden (Figure S4) over polluted regions of Europe, North America, and East Asia (Figure 2), whereas it doubles in winter when oxidants (H_2O_2) tend to be more limited. Increased cloud water pH favors sulfate formation via in-cloud oxidation by O_3 (Table S2), with increases in sulfate mass restricted to the lower troposphere over the polluted Northern Hemisphere regions (Figures S5 and S6).

Across the rest of the globe, outside of polluted regions and in the free troposphere, an increase in cloud water pH reduces the sulfate column burden (Figure 2), by 10% to 40% globally (Table S1). Enhanced in-cloud sulfate formation depletes SO_2, reduces SO_2 transport, and reduces sulfate formation via gas phase oxidation (R1), as indicated by the reduction in gas phase H_2SO_4 (Figure S7) and the nucleation and condensation fluxes (Table S2). Additionally, an increase in cloud water pH reduces the global sulfate lifetime due to enhanced wet and dry sulfate deposition rates (Table S2) because in-cloud formation results in larger sulfate particles within the accumulation and coarse modes that are more efficiently removed from the atmosphere.

The impact of cloud water pH on SO_2 and sulfate mass column burdens differs between the 1970–1974 and 2005–2009 time periods (Figures 2, S3, and S4). Over Europe and the northeastern United States the increase in wintertime sulfate column burden is greatest in the 1970s, while over China the increase is greatest in the 2000s. These regional differences in the temporal response of the sulfate mass burden reflect the relative changes in anthropogenic emissions of SO_2: decreases in emissions over Europe and United States but an increase over China. However, temporal changes in other emissions (e.g., NH_3) could also have an important effect on pH and aerosols (Li et al., 2017; Weber et al., 2016). Aqueous phase sulfate formation across polluted continental regions is sensitive to changes in cloud water pH, particularly in winter, due to larger SO_2 concentrations and strong seasonal limitation in oxidants at higher latitudes (Manktelow et al., 2007).

3.3. Implications for Aerosol Radiative Forcing

Changes in the aerosol size distribution alter the climate-relevant properties of aerosols and are critical in determining the magnitude of aerosol radiative forcing. Increasing cloud water pH by 0.5–1.5 causes the simulated global surface number concentration of particles larger than 3 nm diameter (N_{total}) to decrease by 15–50% (Figures 3 and S8). For particles larger than 50 nm diameter (N_{50}) the reduction is 20–60%.

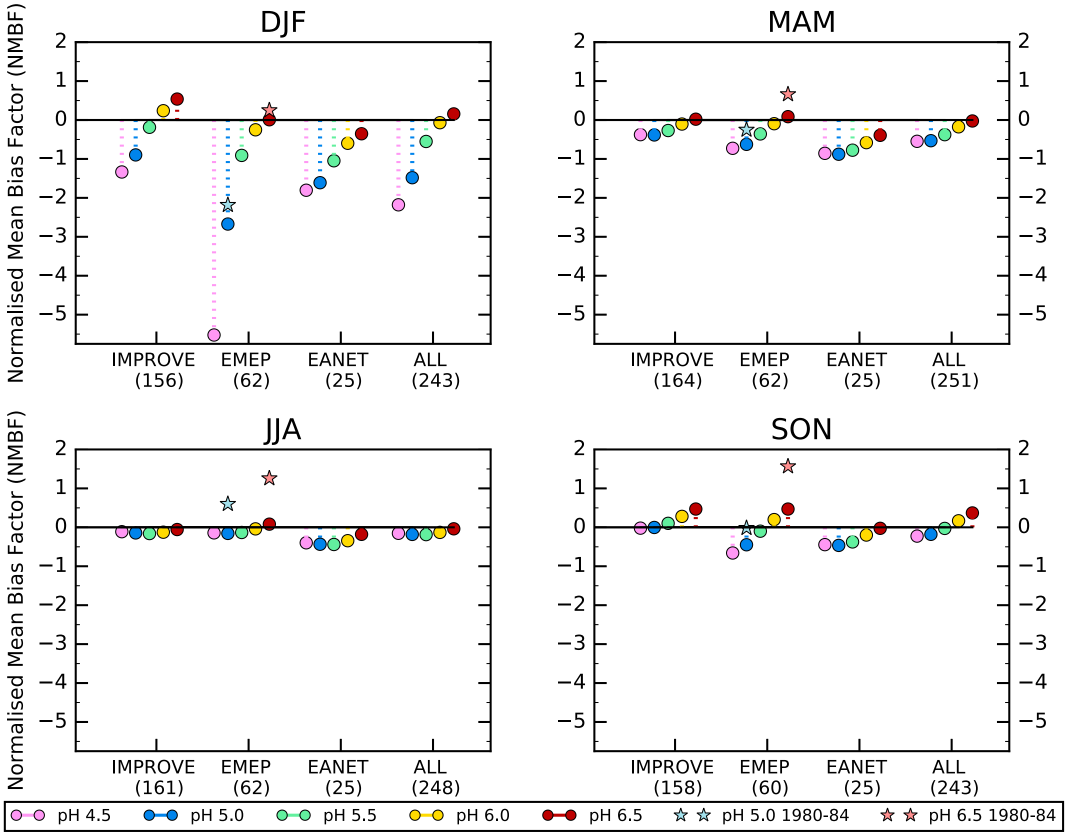

Figure 1. Normalized mean bias factor over the period 2005–2009 between observed and modeled sulfate aerosol mass concentrations across North America (IMPROVE), Europe (EMEP), and East Asia (EANET) monitoring locations for DJF (December-January-February), MAM (March-April-May), JJA (June-July-August), and SON (September-October-November). The NMBF are colored by the different values of cloud water pH used in the model simulations. Number of observations used is shown in parenthesis. NMBFs calculated for the 1980–1984 period are shown for pH 5.0 and pH 6.5 simulations (star). IMPROVE = Interagency Monitoring of Protected Visual Environments; EMEP = European Monitoring and Evaluation Programme; EANET = Acid Deposition Monitoring Network in East Asia; NMBF = normalized mean bias factor.

The increase in cloud water pH alters the aerosol size distribution by reducing the number of particles smaller than 50 nm diameter and increasing the number larger than 100 nm diameter (Figure S9). These changes occur because increased in-cloud oxidation increases the amount of sulfate mass in the accumulation and coarse modes (which formed the cloud droplets) while causing a reduction in the availability of gas phase H_2SO_4 for aerosol nucleation and condensational growth of all particles (Table S3). This shift in the aerosol size distribution reduces the number of particles able to act as CCN (defined as particles greater than 50 nm diameter at 850 hPa in the atmosphere) by more than 50% (Figure 3).

Changes in cloud water pH that alter the aerosol size distribution affect how aerosols interact with climate, in terms of the aerosol radiative forcing. The impact of cloud water pH on aerosol radiative forcing depends on how it affects the radiative perturbation in different time periods. In a single time period and under all-sky conditions an increase in cloud water pH of 0.5 units increases the global ToA radiative flux perturbation by 1.0 W m^{-2} (Figure S10 and Table S3). Increasing the pH by 1.5 units in a single time period increases the global ToA radiative perturbation by 4 W m^{-2} (Figure S10 and Table S3). The increase in global ToA radiative perturbation is largely caused by decreased aci (cloud albedo effect) as the increase in pH means fewer particles are able to act as CCN (Figure 3). The largest increase in the all-sky ToA radiative perturbation (up to 8.4 W m^{-2}) occurs over the North Atlantic, where low absolute CCN concentrations mean that changes in cloud water pH lead to large relative changes in CCN concentrations (Figure 3), which combined with high cloud fraction result in a large change in the cloud albedo radiative effect.

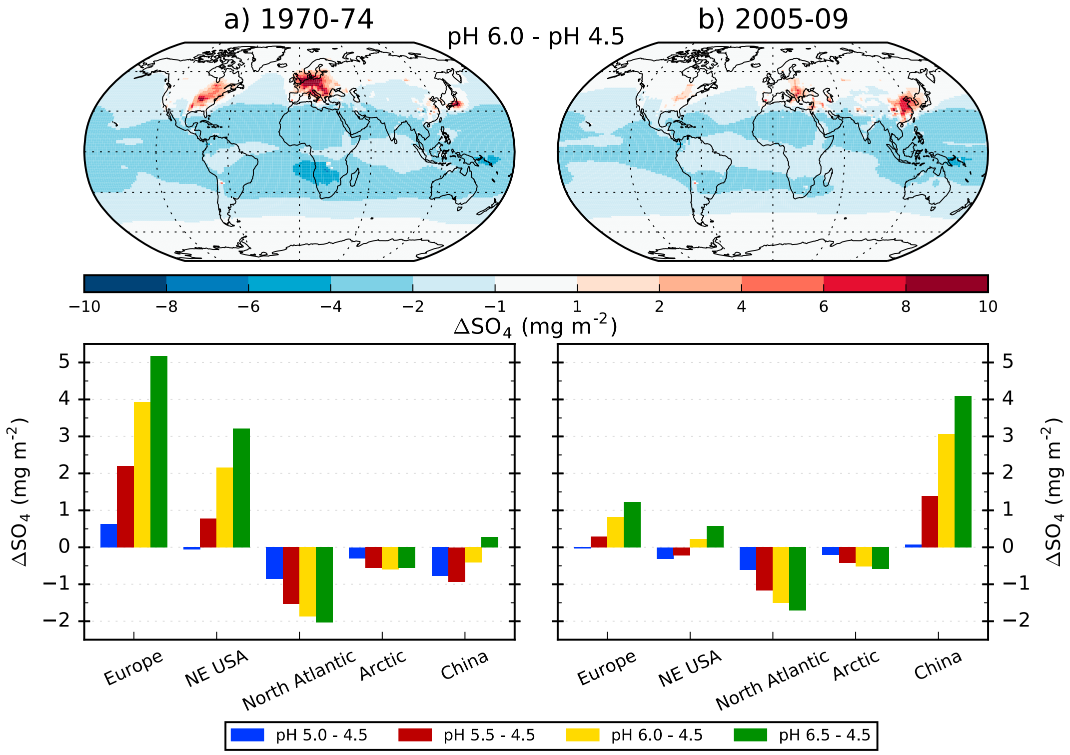

Figure 2. Global and regional impact of cloud water pH on the December-January-February mean sulfate column burden for the 5-year mean periods of 1970–1974 (a) and 2005–2009 (b). All changes are calculated relative to the pH 4.5 model simulation.

Increases in cloud water pH over polluted regions results in a larger sulfate mass burden and increases the magnitude of the negative clear-sky ToA radiative perturbation, from enhanced aerosol-radiation interactions. In other areas of the world the slight reduction in sulfate aerosol mass causes a small increase in the clear-sky ToA radiative perturbation (Figure S11 and Table S3).

The aerosol radiative forcing (calculated as the difference in ToA radiative flux perturbations between 1970 and 2009 for all-sky and clear-sky conditions; Figures 4 and S12) is found to be relatively insensitive to cloud water pH, provided that the value of pH remains constant over time, consistent with Regayre et al. (2018). Using the same cloud water pH in both time periods results in a global radiative forcing of up to +0.2 W m^{-2}, with similar insensitivities exhibited at the regional scale.

Calculated aerosol radiative forcing is much more sensitive to pH if a temporal change in cloud water pH is assumed to have occurred between 1970 and 2009 (Figure 4). On a regional scale pH has been observed to have changed by 1.0 unit (e.g., United States and Europe; Aleksic et al. (2009); Murray et al. (2013); Vet et al. (2014); Schwab et al. (2016)). We assess the impact of such temporal changes in pH by comparing the results from simulations using different global cloud water pH values over the period 1970 to 2009. Over Europe, the regional all-sky radiative forcing is +4.0 W m^{-2} when using a temporally constant value of pH 5.0. However, assuming pH has increased by 0.5 units (from pH 5.0) since 1970 over Europe results in a radiative forcing of +5.2 W m^{-2}. The regional radiative forcing over Europe is +6.3 W m^{-2} when pH is assumed to have increased by 1.0 unit. Over China, assuming a temporally constant pH of 5.5 results in an all-sky regional radiative forcing of −6.7 W m^{-2}. However, if pH is assumed to have decreased by 1.0 over China since 1970 (from 5.5) then regional radiative forcing is −9.5 W m^{-2}. The sign of the pH change is particularly important over the North Atlantic due to the large susceptibility to changes in cloud albedo. If pH is assumed to have increased by 1.0 since 1970 (from pH 5.0) then the radiative forcing over the North Atlantic is +5.2 W m^{-2}, whereas for a decrease in pH of 1.0 (from pH 6.0) the radiative forcing is −3.7 W m^{-2}.

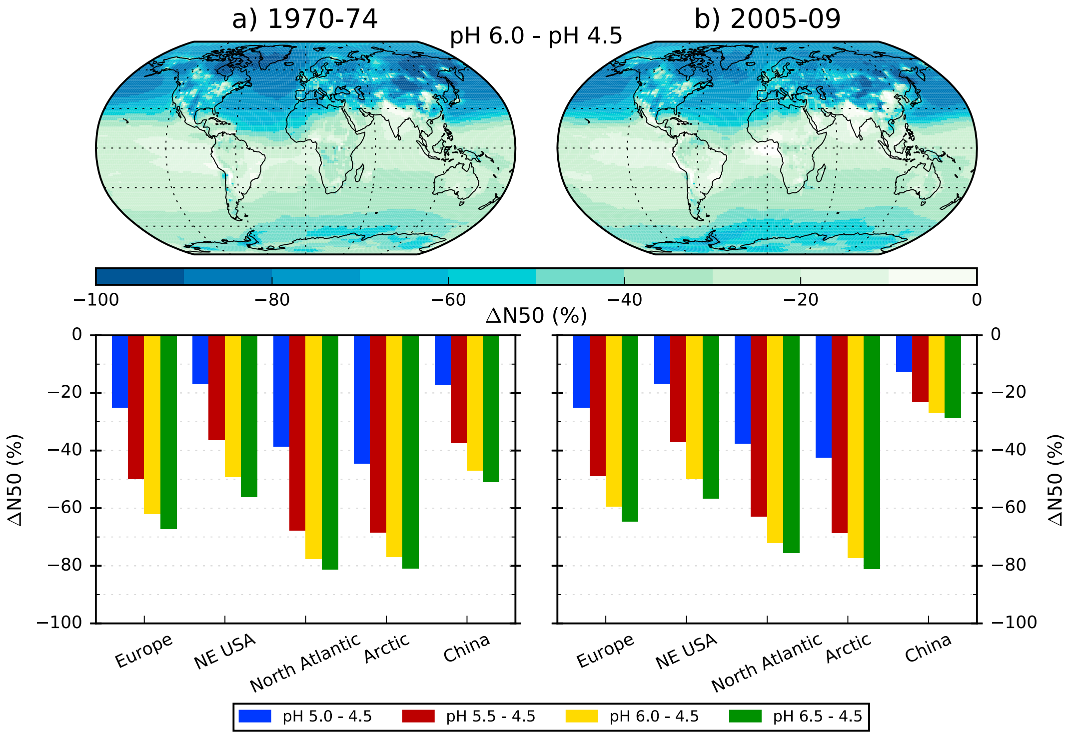

Figure 3. Global and regional impact of cloud water pH on annual mean N50 (particles greater than 50 nm diameter) aerosol number concentrations at 850 hPa in the atmosphere for the 5-year mean periods of 1970–1974 (a) and 2005–2009 (b). All changes are calculated relative to the pH 4.5 model simulation.

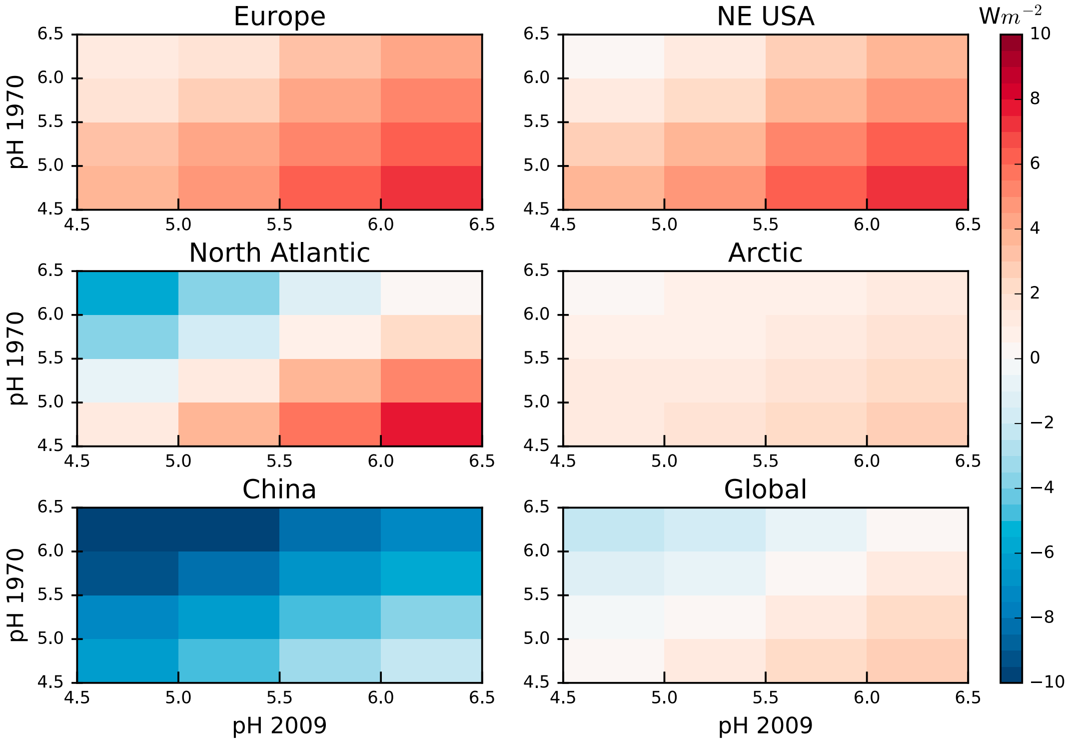

Figure 4. Global and regional all-sky shortwave top-of-atmosphere aerosol radiative forcing, calculated as the mean difference between the 1970–1974 to 2005–2009 periods for different values of cloud water pH assumed during the two time periods.

4. Conclusions

Large changes in anthropogenic SO_2 emissions over recent decades have altered regional cloud water pH values, but the impacts on sulfate aerosol formation and aerosol radiative effects are not well understood. Changes in other emissions, for example, NH_3, could also have important consequences for pH and aerosols. We used a global composition-climate model to estimate how changes in cloud water pH over recent decades may have affected aerosol radiative forcing from changes in all aerosol emissions.

Over Europe and the United States, measured cloud water pH has increased by >0.5 units since the 1980s (Schwab et al., 2016; Vet et al., 2014). A change in cloud water pH alters sulfate formation by changing the rate of aqueous phase oxidation of SO_2 by ozone. We evaluated the model against observed sulfate mass concentrations across sites in the Northern Hemisphere for 2005–2009 and across Europe over the last 30 years. For Europe, a cloud water pH of 5.0 gave better agreement with observations during the 1980s, whereas in the 2000s better agreement occurred using a pH of 6.5. This evaluation is consistent with the observed increase in cloud water pH across Europe over recent decades and suggests it may be an important consideration in reconciling the long-standing model overestimation of SO_2 and underestimation of sulfate (Berglen, 2004; Feichter et al., 1996; Kasibhatla et al., 1997; Roelofs et al., 2001; Textor et al., 2006).

We found that regional aerosol radiative forcings over the period 1970 to 2009 are particularly sensitive to changes in cloud water pH. Global aerosol radiative forcings varied by as much as 4 $W\ m^{-2}$, with larger regional changes, depending on whether an increase or decrease in cloud water pH was assumed over recent decades. Taking account of temporal changes in cloud water pH could increase the uncertainty in aerosol radiative forcing by contributing more to the variance than the 10% reported in Regayre et al. (2018). The change in pH is particularly important over oceanic regions that are highly susceptible to aci. Over the North Atlantic, the all-sky aerosol radiative forcing was +5.2 $W\ m^{-2}$ if a 1.0 unit increase in pH (from pH 5.0) is assumed between 1970 and 2009, whereas a value of −3.7 $W\ m^{-2}$ was calculated for a 1.0 unit decrease in pH (from pH 6.0). Recent studies examining the uncertainty in radiative forcing from aci identified cloud water pH as one of the largest contributors to the overall uncertainty, although these studies did not account for effect of temporal changes in pH across different regions (Carslaw et al., 2013; Regayre et al., 2018).

Accounting for changes in cloud water pH over recent decades and in the next few decades is important to accurately simulate sulfate aerosol formation and aerosol radiative effects. We recommend that global composition climate models need to include a representation of spatially and temporally variable cloud water pH that takes into account realistic aerosol composition and chemistry to improve the simulation of aerosols and their radiative impacts.

Acknowledgments
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