



# Global modeling of cloud water acidity, precipitation acidity, and acid inputs to ecosystems

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Received: 18 May 2020 – Discussion started: 22 June 2020

Revised: 27 August 2020 – Accepted: 7 September 2020 – Published: 28 October 2020

**Abstract.** Cloud water acidity affects the atmospheric chemistry of sulfate and organic aerosol formation, halogen radical cycling, and trace metal speciation. Precipitation acidity including post-depositional inputs adversely affects soil and freshwater ecosystems. Here, we use the GEOS-Chem model of atmospheric chemistry to simulate the global distributions of cloud water and precipitation acidity as well as the total acid inputs to ecosystems from wet deposition. The model accounts for strong acids (H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, and HCl), weak acids (HCOOH, CH<sub>3</sub>COOH, CO<sub>2</sub>, and SO<sub>2</sub>), and weak bases (NH<sub>3</sub> as well as dust and sea salt aerosol alkalinity). We compile a global data set of cloud water pH measurements for comparison with the model. The global mean observed cloud water pH is 5.2 ± 0.9, compared to 5.0 ± 0.8 in the model, with a range from 3 to 8 depending on the region. The lowest values are over East Asia, and the highest values are over deserts. Cloud water pH over East Asia is low because of large acid inputs (H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>), despite NH<sub>3</sub> and dust neutralizing 70 % of these inputs. Cloud water pH is typically 4–5 over the US and Europe. Carboxylic acids account for less than 25 % of cloud water H<sup>+</sup> in the Northern Hemisphere on an annual basis but 25 %–50 % in the Southern Hemisphere and over 50 % in the southern tropical continents, where they push the cloud water pH below 4.5. Anthropogenic emissions of SO<sub>2</sub> and NO<sub>x</sub> (precursors of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>) are decreasing at northern midlatitudes, but the effect on cloud water pH is strongly buffered by NH<sub>4</sub><sup>+</sup> and carboxylic acids. The global mean precipitation pH is 5.5 in GEOS-Chem, which is higher than the cloud water pH because of dilution and below-cloud scavenging of NH<sub>3</sub> and dust. GEOS-Chem successfully reproduces the an-

nual mean precipitation pH observations in North America, Europe, and eastern Asia. Carboxylic acids, which are undetected in routine observations due to biodegradation, lower the annual mean precipitation pH in these areas by 0.2 units. The acid wet deposition flux to terrestrial ecosystems taking into account the acidifying potential of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> in N-saturated ecosystems exceeds 50 meq m<sup>-2</sup> a<sup>-1</sup> in East Asia and the Americas, which would affect sensitive ecosystems. NH<sub>4</sub><sup>+</sup> is the dominant acidifying species in wet deposition, contributing 41 % of the global acid flux to continents under N-saturated conditions.

## 1 Introduction

Cloud water acidity (H<sup>+</sup> concentration) affects global atmospheric chemistry in a number of ways. It controls the rates of aqueous-phase reactions that (1) oxidize sulfur dioxide (SO<sub>2</sub>) to sulfate aerosols (Martin et al., 1981; Calvert et al., 1985), (2) oxidize dissolved organic compounds to less volatile forms leading to secondary organic aerosols (Ervens et al., 2011; Herrmann et al., 2015), and (3) convert halides into halogen radicals (von Glasow and Crutzen, 2003; Platt and Hönninger, 2003). It affects the solubility and bioavailability of iron in aerosol particles and, thus, the input of this micronutrient to marine ecosystems (Mahowald et al., 2005). Acidic deposition has a range of environmental effects on soil and freshwater ecosystems (Driscoll et al., 2001). Cloud water and precipitation acidity is affected in a complex way by natural and anthropogenic emissions, but there has been little effort so far to evaluate the ability of global models

to represent this. Here, we present such an evaluation using the GEOS-Chem atmospheric chemistry model and go on to discuss the factors controlling cloud water and precipitation acidity on a global scale.

Cloud water and precipitation  $H^+$  concentrations are determined by the balance between dissolved acids ( $H^+$  donors) and bases ( $H^+$  acceptors). Sulfuric acid ( $H_2SO_4$ ), nitric acid ( $HNO_3$ ), and hydrogen chloride ( $HCl$ ) are the major strong acids in the atmosphere, and they dissociate completely in cloud water and precipitation. The major weak acids are  $CO_2$ ,  $SO_2$ , and carboxylic acids including formic acid ( $HCOOH$ ) and acetic acid ( $CH_3COOH$ ). Ammonia ( $NH_3$ ) and alkaline dust particles are the major bases. Atmospheric acidity is commonly referenced to the  $CO_2$ – $H_2O$  system (pH 5.6 at current  $CO_2$  levels), with lower pH referred to as acidic conditions and higher pH as alkaline conditions. Cloud water pH generally varies between 3 and 7, with highly acidic cloud water typically found in industrialized areas with high  $SO_2$  and nitrogen oxides ( $NO_x$ ) emissions and alkaline cloud water found in agricultural and dusty areas (Warneck, 2000; Pye et al., 2020). Precipitation pH varies in a similar pattern (Dentener and Crutzen, 1994; Vet et al., 2014) but differs from cloud water pH because of dilution (Weathers et al., 1988; Bormann et al., 1989), riming (Collett et al., 1993), below-cloud scavenging (Castillo et al., 1983; Zinder et al., 1988; Ayers and Gillett, 1988), and oxidation chemistry within raindrops (Overton et al., 1979; Graedel and Goldberg, 1983).

The chemical and physical processes governing cloud water and precipitation acidity have been well-established since the 1980s (Morgan, 1982; NRC, 1983; Stumm et al., 1987). They have been incorporated in many regional models focused on acid deposition (Chang et al., 1987; Venkatram et al., 1988; Carmichael et al., 1991; Hass et al., 1993; Olen-drzynski et al., 2000; Langner et al., 2005) and global models focused on sulfur and nitrogen deposition (Dentener and Crutzen, 1994; Rodhe et al., 1995, 2002; Bouwman et al., 2002; Tost et al., 2007; Paulot et al., 2018). A few global modeling studies have focused on precipitation pH (Dentener and Crutzen, 1994; Rodhe et al., 1995, 2002; Tost et al., 2007). These models calculated precipitation  $[H^+]$  from the precipitation concentrations of  $SO_4^{2-}$ ,  $NO_3^-$ ,  $NH_4^+$ ,  $HCO_3^-$ , and  $CO_3^{2-}$  using ionic charge balance. Rodhe et al. (2002) also included dust alkalinity. None included carboxylic acids, which are known to be important but biodegrade rapidly after deposition (Keene et al., 1983; Keene and Galloway, 1984).

Cloud water pH has received less attention in models. Some current global atmospheric chemistry models assume a constant cloud water pH for aqueous reactions (Watanabe et al., 2011; Søvde et al., 2012), whereas others calculate it explicitly from the balance of acids and bases but again generally neglecting dust alkalinity and carboxylic acids (Tost et al., 2007; Huijnen et al., 2010; Myriokefalitakis et al., 2011; Alexander et al., 2012; Lamarque et al., 2012; Simpson et

al., 2012). Pye et al. (2020) presented the cloud water pH values simulated by five such models and included a limited comparison with observations. They found large differences among models particularly in dusty areas where pH estimates varied by 3–4 units. All models showed large systematic biases compared with observations. In light of these findings, Pye et al. (2020) highlighted the need for improvements in the cloud water simulations including further evaluation with observations.

Here, we present a global analysis of cloud water and precipitation pH in the GEOS-Chem model with an improved cloud water pH calculation, including in particular carboxylic acids and dust alkalinity, and an explicit precipitation pH calculation. We evaluate the simulation with extensive cloud water and precipitation measurements and determine the sources of acidity and alkalinity in different parts of the world. We examine the buffering effects of  $NH_3$  and carboxylic acids on cloud water pH as well as the changes in acid inputs to terrestrial ecosystems from post-depositional processes.

## 2 Model description

We use the GEOS-Chem atmospheric chemistry model (<http://www.geos-chem.org>, last access: 21 October 2020) version v11-02 with a number of modifications, some from more recent GEOS-Chem versions and some specifically from this work. The model is driven by assimilated meteorological fields from the NASA Global Modeling and Assimilation Office's Modern-Era Retrospective analysis for Research and Applications, version 2 (MERRA-2) system (Gelaro et al., 2017). These fields include in particular cloud water liquid and ice content, cloud volume fraction, and 3-D liquid and ice precipitation fluxes, updated every 3 h. GEOS-Chem includes detailed  $NO_x$ –hydrocarbon–aerosol–halogen chemistry (Mao et al., 2013; Kim et al., 2015; Travis et al., 2016; Sherwen et al., 2016), and here we have added recent halogen updates (X. Wang et al., 2019). The model distinguishes between fine and coarse aerosol but does not otherwise include aerosol microphysics. Wet deposition follows the algorithm of Liu et al. (2001) including rainout (in-cloud scavenging), washout (below-cloud scavenging), and scavenging in convective updrafts, with updates by Wang et al. (2011) and Amos et al. (2012). Dry deposition follows a standard resistance-in-series scheme (Wesely, 1989; Wang et al., 1998). We conduct the simulation on a global  $4^\circ$  latitude  $\times$   $5^\circ$  longitude grid for the year 2013 following an initialization period of 1 year.

### 2.1 Emissions and acid-producing chemistry

Here, we describe the GEOS-Chem emissions and chemistry most relevant to the simulation of cloud water and precipitation acidity. Emissions are calculated by the Harvard-NASA

Emissions Component (HEMCO; Keller et al., 2014). Default anthropogenic emissions of  $\text{SO}_2$ ,  $\text{NO}_x$ , and  $\text{NH}_3$  are from the global CEDS emissions inventory for 2013 (Hoesly et al., 2018). They are superseded by regional emission inventories including MIX over Asia for 2010 (M. Li et al., 2017), MEIC over China for 2013 (Zheng et al., 2018), NEI 2011 over the US scaled to 2013 (Travis et al., 2016; U.S. Environmental Protection Agency, 2018), APEI over Canada for 2013 (van Donkelaar et al., 2008), EMEP 2008 over Europe scaled to 2013 (EEA, 2019), and DICE over Africa for 2013 (Marais and Wiedinmyer, 2016). Ship  $\text{SO}_2$  emissions are from Eyring et al. (2005). Ship  $\text{NO}_x$  emissions are from the ICOADS inventory (Wang et al., 2008) and are pre-processed with the PARANOX ship plume model (Vinken et al., 2011; Holmes et al., 2014). Aircraft emissions are from the AEIC inventory (Stettler et al., 2011). Biomass burning emissions are from GFED v4 (van der Werf et al., 2017). Natural emissions include  $\text{NO}_x$  from lightning (Murray et al., 2012) and soil (Hudman et al., 2012), volcanic  $\text{SO}_2$  (Fisher et al., 2011), marine dimethyl sulfide (DMS; Breider et al., 2017), and  $\text{NH}_3$  from oceans, natural soils, and human population (Bouwman et al., 1997). Sea salt aerosol emissions in two size classes (fine and coarse) follow Jaeglé et al. (2011). Dust emissions include desert and semi-desert sources (Fairlie et al., 2007; Ridley et al., 2013) as well as combustion and industrial sources (Philip et al., 2017) in four size classes (one fine and three coarse). Biogenic volatile organic compound (VOC) emissions are from MEGAN (Guenther et al., 2012; Hu et al., 2015).

Sulfur chemistry in GEOS-Chem includes oxidation of DMS to  $\text{SO}_2$  and methanesulfonic acid (MSA), gas-phase oxidation of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$ , and aqueous-phase oxidation of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  in clouds, rain, and alkaline sea salt aerosols (Alexander et al., 2005, 2009; Q. Chen et al., 2017). Nitrogen chemistry includes oxidation of  $\text{NO}_x$  to  $\text{HNO}_3$  in the gas phase as well as in the aqueous phase of aerosols and clouds (McDuffie et al., 2018; Holmes et al., 2019). Tropospheric HCl is mainly from acid displacement reactions on sea salt aerosols (X. Wang et al., 2019).

$\text{HNO}_3$ , HCl, and  $\text{NH}_3$  are semi-volatile, and their gas-particle partitioning affects their scavenging efficiency in cloud water and precipitation (Amos et al., 2012). We calculate this partitioning at bulk thermodynamic equilibrium using ISORROPIA II for the  $\text{H}_2\text{SO}_4$ – $\text{HNO}_3$ –HCl– $\text{NH}_3$ –NVC metastable aqueous system, where NVC represents the non-volatile cations from fine-mode sea salt aerosol (X. Wang et al., 2019). The uptake of  $\text{HNO}_3$  and release of HCl (acid displacement) on coarse-mode sea salt aerosol is treated as a kinetic process (X. Wang et al., 2019).

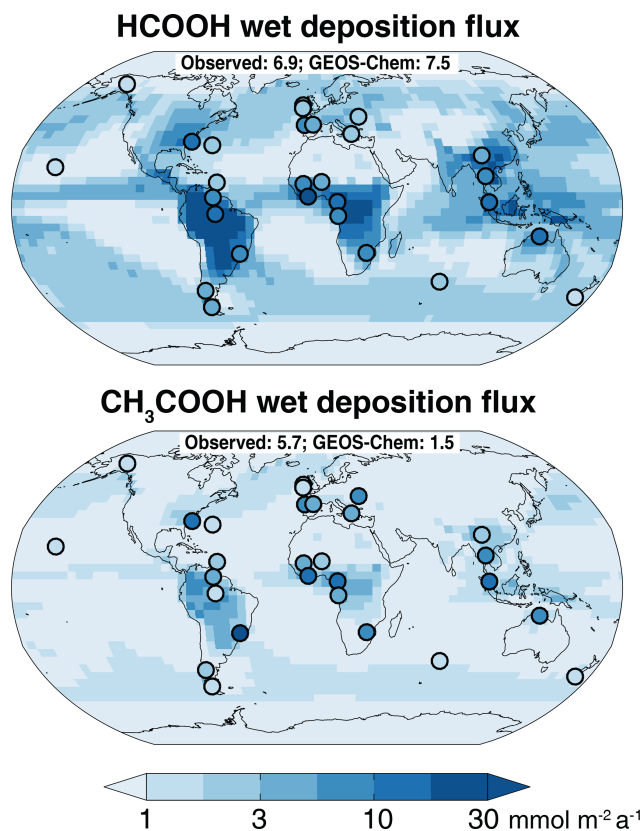
## 2.2 Simulation of HCOOH and $\text{CH}_3\text{COOH}$

The most important carboxylic acids for cloud water and precipitation acidity are HCOOH ( $\text{p}K_a = 3.8$  at 298 K) and  $\text{CH}_3\text{COOH}$  ( $\text{p}K_a = 4.8$  at 298 K) (Morgan, 1982; Keene et

al., 1983). ( $K_a$  is the acid dissociation constant and  $\text{p}K_a = -\log_{10} K_a$ .) HCOOH and  $\text{CH}_3\text{COOH}$  are present in the atmosphere at comparable concentrations (Talbot et al., 1997), but HCOOH is more important for contributing to acidity because of its higher Henry's law solubility and lower  $\text{p}K_a$ . Sources of these acids include secondary production from VOC oxidation and direct emissions from biomass burning, fossil fuels, soils, and vegetation (Khare et al., 1999), but these are poorly understood and models greatly underestimate atmospheric concentrations (Paulot et al., 2011; Stavrakou et al., 2012; Millet et al., 2015; Khan et al., 2018). Here, we use the previous GEOS-Chem HCOOH simulation by Millet et al. (2015) which scales up the biogenic emissions from the MEGAN inventory (Guenther et al., 2012) in order to fit atmospheric observations over the US. This yields a global HCOOH source of  $1900 \text{ Gmol a}^{-1}$ . Stavrakou et al. (2012) previously estimated a global HCOOH source of  $2200$ – $2600 \text{ Gmol a}^{-1}$  from the inversion of satellite data. In addition, we assume a minimum background mixing ratio of 100 pptv (50 pptv south of  $60^\circ \text{S}$ ), based on measurements in the marine boundary layer and the free troposphere (Arlander et al., 1990; Talbot et al., 1990, 1997; Legrand et al., 2004) and satellite-derived free troposphere HCOOH columns over marine areas of  $1$ – $2 \times 10^{15} \text{ molec. cm}^{-2}$  (Franco et al., 2020).

Our  $\text{CH}_3\text{COOH}$  simulation follows the standard GEOS-Chem mechanism (Mao et al., 2013; Travis et al., 2016) without further improvement, except that the minimum background  $\text{CH}_3\text{COOH}$  concentration is also taken to be 100 pptv (50 pptv south of  $60^\circ \text{S}$ ), based on observations in the marine boundary layer and the free troposphere (Arlander et al., 1990; Talbot et al., 1990, 1997; Helas et al., 1992; Franco et al., 2020). The global simulated  $\text{CH}_3\text{COOH}$  source is  $1000 \text{ Gmol a}^{-1}$ . Other modeling studies attempting to fit  $\text{CH}_3\text{COOH}$  observations have estimated a source in the range of  $1700$ – $3900 \text{ Gmol a}^{-1}$  (Baboukas et al., 2000; Khan et al., 2018).

Figure 1 compares annual mean GEOS-Chem wet deposition fluxes of HCOOH and  $\text{CH}_3\text{COOH}$  with observations from the compilations of Vet et al. (2014) and Keene et al. (2015). We find that the mean GEOS-Chem HCOOH flux ( $7.5 \text{ mmol m}^{-2} \text{ a}^{-1}$ ) is consistent with the mean of the observations ( $6.9 \text{ mmol m}^{-2} \text{ a}^{-1}$ ). The model captures the high fluxes observed in the tropical continents where there are large biogenic sources, and the low fluxes observed at marine sites. GEOS-Chem underestimates the  $\text{CH}_3\text{COOH}$  flux by a factor of 4. The observed patterns of HCOOH and  $\text{CH}_3\text{COOH}$  fluxes are similar, suggesting that model  $\text{CH}_3\text{COOH}$  could be corrected similarly to HCOOH in future work by scaling up biogenic emission; however, the effect is relatively small. In the model, we find that the global mean cloud water pH would decrease by 0.05 units if we increased  $\text{CH}_3\text{COOH}$  concentrations by a factor of 4.



**Figure 1.** Annual mean wet deposition fluxes of HCOOH and CH<sub>3</sub>COOH. The GEOS-Chem model values (contours) are for the year 2013, and the observations (circles) are for various years as compiled by Vet et al. (2014) and Keene et al. (2015). The compilations only include studies that used adequate methods to preserve HCOOH and CH<sub>3</sub>COOH in precipitation samples. We exclude studies with measurement periods of less than 1 year. For studies that reported only precipitation concentrations, we estimate the deposition fluxes using climatological rainfall data for the corresponding locations from the Global Precipitation Climatology Center (Meyer-Christoffer et al., 2018). The global mean observed fluxes and the corresponding GEOS-Chem fluxes are shown inset.

**Table 1.** Henry's law coefficients for the calculations of cloud water and precipitation pH\*.

Species	$H$ (M atm <sup>-1</sup> ) at 298 K	$\frac{d \ln H}{d(1/T)}$ (K)
HNO <sub>3</sub>	$2.1 \times 10^5$	0
HCl	$1.5 \times 10^3$	2300
NH <sub>3</sub>	60	4200
HCOOH	$8.8 \times 10^3$	6100
CH <sub>3</sub> COOH	$4.0 \times 10^3$	6300
SO <sub>2</sub>	1.2	3100
CO <sub>2</sub>	$3.4 \times 10^{-2}$	2400

\* From the compilation of Sander (2015).

### 2.3 Calculation of cloud water and precipitation composition and pH

Cloud water composition is computed locally in each grid cell containing liquid cloud water over 30 min time steps using the in-cloud liquid water content and cloud volume fraction from MERRA-2. Dissolution of gases in the cloud droplets follows the Henry's law constants of Table 1 and the acid–base dissociation constants of Table 2. We assume that 70 % of fine aerosol mass and 100 % of coarse aerosol mass are partitioned into cloud water (Hegg et al., 1984; Alexander et al., 2012). Sulfate–nitrate–ammonium and sea salt particles dissolve completely in cloud water, and the alkaline component of the dust particles also dissolves. Freshly emitted sea salt particles contain an alkalinity of 0.07 eq kg<sup>-1</sup> (Alexander et al., 2005), whereas freshly emitted dust particles contain an alkalinity of 4.5 eq kg<sup>-1</sup> based on the assumption of 7.1 % Ca<sup>2+</sup> and 1.1 % Mg<sup>2+</sup> by dry mass (Engelbrecht et al., 2016) with CO<sub>3</sub><sup>2-</sup> as the anion. Sea salt NVCs are expressed as Na<sup>+</sup> equivalents, whereas dust NVCs are expressed as Ca<sup>2+</sup> equivalents. The upper limit of the Ca<sup>2+</sup> concentration is set by the formation of CaCO<sub>3</sub>(s).

The calculation of cloud water composition in the cloudy fraction of each grid cell assumes a closed system where the summed concentrations of gas and cloud water species in Table 3 are conserved, and the partitioning is then computed following the equilibria of Tables 1 and 2. The calculation is done by solving the electroneutrality equation iteratively using Newton's method (Moch et al., 2020). This improves on the original calculation of the cloud water composition in GEOS-Chem (Alexander et al., 2012) through the inclusion of additional acidic and alkaline species (HCl, HCOOH, CH<sub>3</sub>COOH, and NVCs) and using a more stable numerical solver.

We will present the results as time averages (mainly annual) and spatial averages (vertical or zonal). The time- and space-averaged cloud water [H<sup>+</sup>] cannot be calculated directly from the [H<sup>+</sup>] computed at each model time step in each grid cell because [H<sup>+</sup>] is a nonconservative quantity controlled by the other acidic and basic species in cloud water (Liljestrand, 1985). Therefore, we calculate the average cloud water [H<sup>+</sup>] from the corresponding volume-weighted average (VWA) concentrations of the cloud water ions. We assume that all acids and bases except carbonates are conserved in the aqueous phase. For HCOOH and CH<sub>3</sub>COOH, the total (dissociated + undissociated) amounts are assumed to be conserved. Thus, the time- and space-averaged cloud water [H<sup>+</sup>] is given as follows:

$$\begin{aligned}
 \overline{[H^+]} = & 2\overline{[SO_4^{2-}]} + \overline{[NO_3^-]} + \overline{[Cl^-]} + \overline{[HSO_3^-]} \\
 & + 2\overline{[SO_3^{2-}]} + \overline{[HCOO^-]} + \overline{[CH_3COO^-]} \\
 & + \overline{[HCO_3^-]} - \overline{[NH_4^+]} - 2\overline{[Ca^{2+}]} - \overline{[Na^+]}, \quad (1)
 \end{aligned}$$

**Table 2.** Acid–base dissociation constants for the calculations of cloud water and precipitation pH\*.

Equilibrium reactions	$K$ (M or M <sup>2</sup> ) at 298 K	$\frac{d \ln K}{d(1/T)}$ (K)
$\text{HNO}_3(\text{aq}) \leftrightarrow \text{H}^+ + \text{NO}_3^-$	15	8700
$\text{HCl}(\text{aq}) \leftrightarrow \text{H}^+ + \text{Cl}^-$	$1.7 \times 10^6$	6900
$\text{NH}_4\text{OH}(\text{aq}) \leftrightarrow \text{NH}_4^+ + \text{OH}^-$	$1.7 \times 10^{-5}$	−450
$\text{HCOOH}(\text{aq}) \leftrightarrow \text{H}^+ + \text{HCOO}^-$	$1.8 \times 10^{-4}$	150
$\text{CH}_3\text{COOH}(\text{aq}) \leftrightarrow \text{H}^+ + \text{CH}_3\text{COO}^-$	$1.7 \times 10^{-5}$	50
$\text{SO}_2 \cdot \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HSO}_3^-$	$1.3 \times 10^{-2}$	2000
$\text{HSO}_3^- \leftrightarrow \text{H}^+ + \text{SO}_3^{2-}$	$6.6 \times 10^{-8}$	1500
$\text{CO}_2 \cdot \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HCO}_3^-$	$4.3 \times 10^{-7}$	−1000
$\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$	$4.7 \times 10^{-11}$	−1800
$\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$	$1 \times 10^{-14}$	−6700
$\text{CaCO}_3(\text{s}) \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$	$3.3 \times 10^{-9}$	−1200

\* From Pandis and Seinfeld (1989), except for  $\text{CaCO}_3(\text{s})$  (Nordstrom et al., 1990), and  $\text{HCOOH}(\text{aq})$  and  $\text{CH}_3\text{COOH}(\text{aq})$  (Khare et al., 1999).

**Table 3.** Species included in the cloud water pH calculation<sup>a</sup>.

Conserved totals $\equiv$ sum of partitioned species
$\text{H}_2\text{SO}_{4,T} \equiv \text{SO}_4^{2-}$ <sup>b</sup>
$\text{HNO}_{3,T} \equiv \text{HNO}_3(\text{g}) + \text{HNO}_3(\text{aq}) + \text{NO}_3^-$
$\text{HCl}_T \equiv \text{HCl}(\text{g}) + \text{HCl}(\text{aq}) + \text{Cl}^-$
$\text{NH}_{3,T} \equiv \text{NH}_3(\text{g}) + \text{NH}_4\text{OH}(\text{aq}) + \text{NH}_4^+$
$\text{HCOOH}_T \equiv \text{HCOOH}(\text{g}) + \text{HCOOH}(\text{aq}) + \text{HCOO}^-$
$\text{CH}_3\text{COOH}_T \equiv \text{CH}_3\text{COOH}(\text{g}) + \text{CH}_3\text{COOH}(\text{aq}) + \text{CH}_3\text{COO}^-$
$\text{SO}_{2,T} \equiv \text{SO}_2(\text{g}) + \text{SO}_2(\text{aq}) + \text{HSO}_3^- + \text{SO}_3^{2-}$
$\text{CO}_{2,T} \equiv \text{CO}_2(\text{g}) + \text{CO}_2(\text{aq}) + \text{HCO}_3^- + \text{CO}_3^{2-}$ <sup>c</sup>
$\text{Ca}_T \equiv \text{Ca}^{2+} + \text{CaCO}_3(\text{s})$
$\text{Na}_T \equiv \text{Na}^+$

<sup>a</sup> The calculation assumes a closed system for the cloudy fraction of the model grid cell where concentration totals ( $T$ ) are conserved and are partitioned between species using the Henry's law and the acid–base dissociation equilibria of Tables 1 and 2 as well as the local cloud water liquid water content and temperature.

<sup>b</sup>  $\text{H}_2\text{SO}_4$  has sufficiently low vapor pressure to be completely in the cloud water phase, and  $\text{H}_2\text{SO}_4(\text{aq})$  and  $\text{HSO}_4^-$  concentrations are negligible at typical cloud water pH (> 3).

<sup>c</sup> The  $\text{CO}_2(\text{g})$  mixing ratio is taken to be 390 ppm as representative of 2013.

where  $\overline{[A]}$  represents the VWA molar concentration in cloud water of species  $A$  over the time period and spatial domain of interest. We calculate  $\overline{[A]}$  from the concentration of the species,  $[A]_{i,j}$ , and the cloud liquid water content,  $L_{i,j}$ , at each model time step  $i$  and grid cell  $j$ :

$$\overline{[A]} = \frac{\sum_{j=1}^m \sum_{i=1}^t L_{i,j} [A]_{i,j}}{\sum_{j=1}^m \sum_{i=1}^t L_{i,j}}, \quad (2)$$

where  $[1, t]$  is the averaging time period, and  $[1, m]$  is the ensemble of grid cells included in the average.  $\overline{[\text{HCOO}^-]}$  is calculated from the total aqueous concentra-

tion,  $\overline{[\text{HCOOH}]_{\text{aq},T}} = \overline{[\text{HCOOH}]_{\text{aq}}} + \overline{[\text{HCOO}^-]}$ , as follows:

$$\overline{[\text{HCOO}^-]} = \left( \frac{K_a}{K_a + \overline{[\text{H}^+]}} \right) \overline{[\text{HCOOH}]_{\text{aq},T}}, \quad (3)$$

where  $K_a$  is the  $\text{HCOOH}(\text{aq})/\text{HCOO}^-$  acid dissociation constant from Table 2 computed at the average cloud water temperature for the time period and spatial domain. The same procedure is used for  $\overline{[\text{CH}_3\text{COO}^-]}$ .  $\overline{[\text{HCO}_3^-]}$  is calculated from equilibrium with atmospheric  $\text{CO}_2$  as follows:

$$\overline{[\text{HCO}_3^-]} = \frac{H_{\text{CO}_2} K_{c1} P_{\text{CO}_2}}{\overline{[\text{H}^+]}} \quad (4)$$

where  $H_{\text{CO}_2}$  and  $K_{c1}$  are the Henry's law coefficient for  $\text{CO}_2$  and the  $\text{CO}_2(\text{aq})/\text{HCO}_3^-$  acid dissociation constant, respectively, at the average cloud water temperature for the period and domain (Tables 1 and 2);  $P_{\text{CO}_2}$  is the  $\text{CO}_2$  partial pressure, taken to be 390 ppm as representative of 2013. Substituting these values in Eq. (4),  $\overline{[\text{HCO}_3^-]} \approx 10^{-11.3}/\overline{[\text{H}^+]}$ . Over the range of cloud water pH values (3–8.5),  $\overline{[\text{CO}_3^{2-}]}$  ( $\approx 10^{-21.6}/\overline{[\text{H}^+]^2}$ ) and  $\overline{[\text{OH}^-]}$  ( $\approx 10^{-14}/\overline{[\text{H}^+]}$ ) are negligible compared with  $\overline{[\text{HCO}_3^-]}$  and are omitted from Eq. (1) (Stumm et al., 1987). As  $\overline{[\text{HCOO}^-]}$ ,  $\overline{[\text{CH}_3\text{COO}^-]}$ , and  $\overline{[\text{HCO}_3^-]}$  calculated in this way depend on  $\overline{[\text{H}^+]}$ , Eq. (1) is cubic in  $\overline{[\text{H}^+]}$ . The time- and space-averaged pH ( $\overline{\text{pH}}$ ) is calculated from  $\overline{[\text{H}^+]}$ :

$$\overline{\text{pH}} = -\log_{10} \left( \overline{[\text{H}^+]} \right) \quad (5)$$

There is some arbitrariness in assuming that  $\text{NH}_3$ ,  $\text{SO}_2$ , and carboxylic acids do not equilibrate with the gas phase during averaging. We examined the sensitivity to this assumption by

assuming alternatively that  $\text{NH}_{3,T}$ ,  $\text{SO}_{2,T}$ ,  $\text{HCOOH}_T$ , and  $\text{CH}_3\text{COOH}_T$  as defined in Table 3 (sum of gas-phase and aqueous-phase concentrations) are conserved and recalculating the gas–cloud water equilibrium for the time-averaged conditions. We find no significant difference in the computed  $[\text{H}^+]$ .

Calculation of precipitation VWA composition including  $[\text{H}^+]$  follows the same approach as for cloud water. In that case, we use the model-archived wet deposition fluxes including contributions from in-cloud and below-cloud scavenging. We assume that  $\text{SO}_2$  is instantly oxidized by  $\text{H}_2\text{O}_2$  (as available) in precipitation and is scavenged as  $\text{SO}_4^{2-}$ . As with cloud water, the maximum  $[\text{Ca}^{2+}]$  is set by the formation of  $\text{CaCO}_3(\text{s})$ . Precipitation pH measurements are generally reported as monthly means and do not account for  $\text{HCOOH}$  and  $\text{CH}_3\text{COOH}$ , which biodegrade rapidly. To compare with measurements, we calculate a monthly  $[\text{H}^+]$  for each grid cell by removing  $[\text{HCOO}^-]$  and  $[\text{CH}_3\text{COO}^-]$  from the charge balance in Eq. (1). From there, we calculate the annual precipitation VWA pH:

$$\overline{\text{pH}}_{\text{VW}} = -\log_{10} \left( \frac{\sum_{k=1}^{12} P_k [\text{H}^+]_k}{\sum_{k=1}^{12} P_k} \right), \quad (6)$$

where  $[\text{H}^+]_k$  is the mean precipitation  $[\text{H}^+]$ , and  $P_k$  is the precipitation depth for month  $k$ .

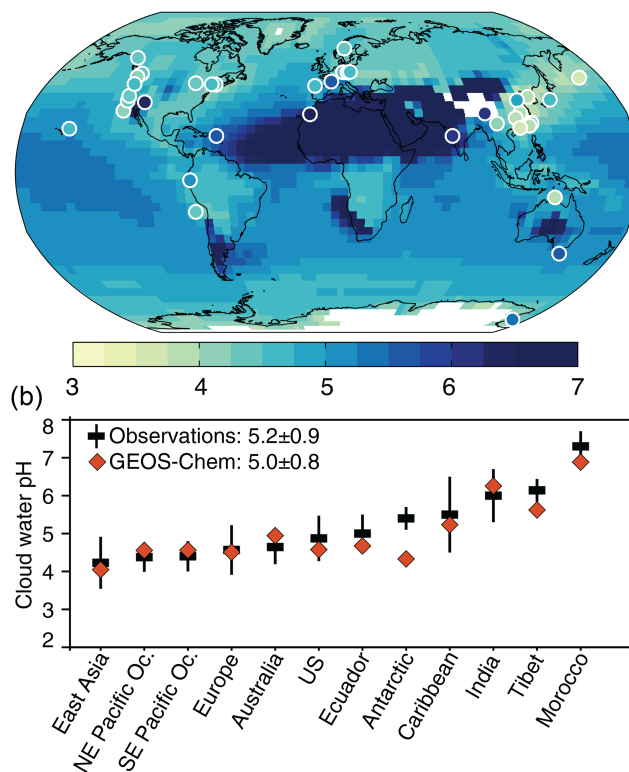
### 3 Results and discussion

#### 3.1 Global distribution of cloud water pH and composition

Figure 2 shows the global distribution of cloud water pH as simulated by GEOS-Chem and as measured at mountain sites, coastal sites (marine fog), and from aircraft campaigns (Table A1). We exclude continental fog water measurements because of their sensitivity to local emissions. The measurements span the period from 1980 to 2018, but we generally exclude observations made before 2005 in East Asia, Europe, and the US because of the strong emission trends in these areas. We include some older measurements in the western US and northern Europe when there are no recent measurements in a particular region and the sites are relatively remote. Some of the observations are taken from the Pye et al. (2020) compilation.

Figure 2a shows the mean observed and simulated pH values. The observed values are as reported in the literature, where the computation of the mean is generally based on VWA  $[\text{H}^+]$ . The model values are annual means below 700 hPa ( $\approx 3$  km above sea level) for the year 2013. Figure 2b shows the observations aggregated by region and arranged in ascending pH order, along with the corresponding

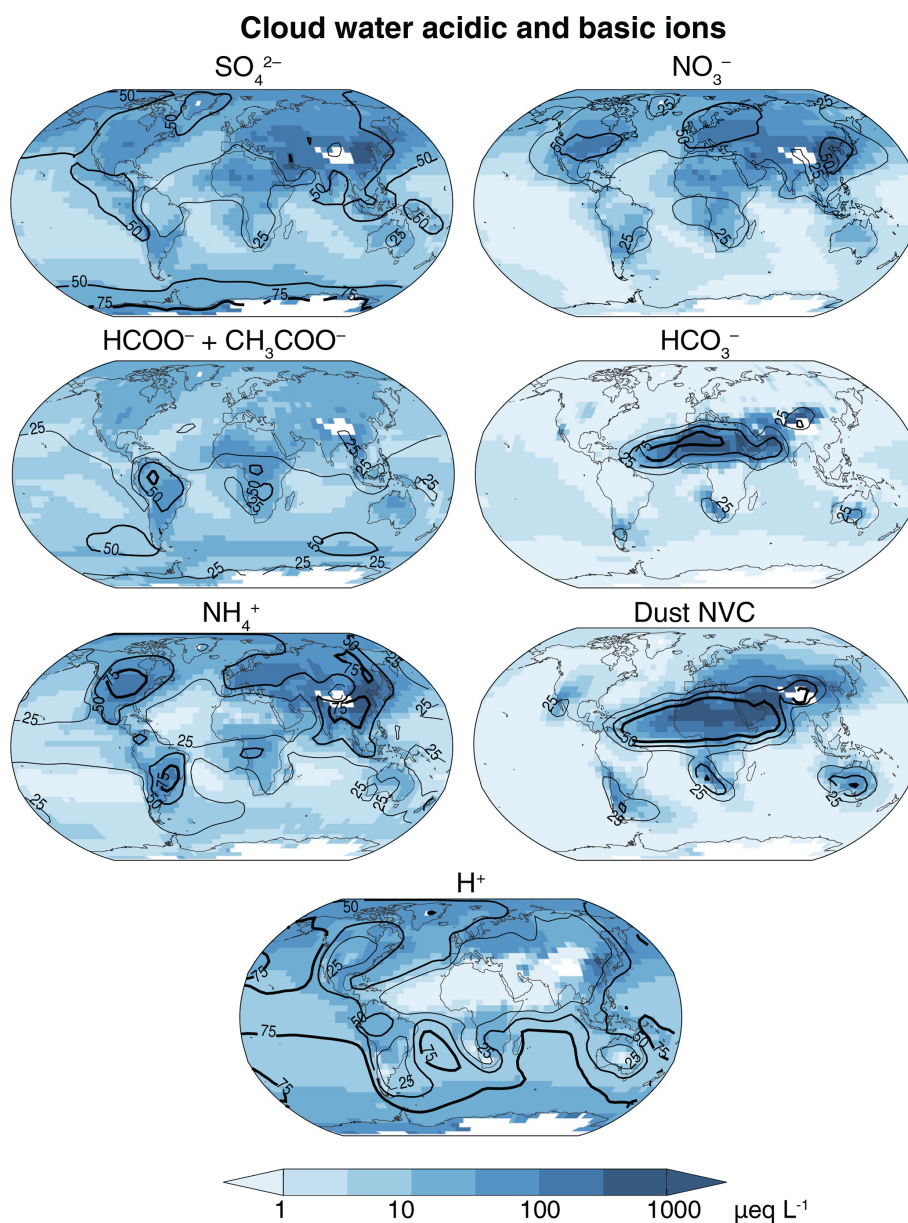
#### (a) Global distribution of cloud water pH



**Figure 2.** Observed and simulated cloud water pH. Panel (a) shows the GEOS-Chem annual mean cloud water pH below 700 hPa for the year 2013 along with cloud water pH observations (filled circles) collected since 1980 (Table A1). See Sect. 2.3 for the procedure to compute average pH in the model. White color denotes areas where the topographic elevation is higher than 700 hPa. The maximum modeled and observed pH values are 8.2 and 7.3, respectively. Panel (b) shows the observations grouped by region (Table A1), with means  $\pm$  standard deviations calculated from the ensemble of data sets for the region, and the corresponding GEOS-Chem mean values sampled at the location and month of the measurements. The global mean  $\pm$  standard deviation pH values computed from the regional mean observed and modeled values are inset in panel (b).

GEOS-Chem values. For comparison with the observations, the model is sampled at the locations and months of the measurements.

The global mean cloud water pH in the observations is  $5.2 \pm 0.9$ , compared to  $5.0 \pm 0.8$  in the model. Annual mean values in Fig. 2 range from 3 to 8, showing distinct spatial patterns. The spatial patterns can be understood from the distributions of acidic and basic ions shown in Fig. 3.  $\text{Na}^+$  and  $\text{Cl}^-$  are major constituents of cloud water in marine and coastal areas, but they are not shown in the Fig. 3 because they are largely in balance and have little net effect on pH. Figure 3 also shows the percent contribution of each ion to the total anion or cation concentrations (contour lines).



**Figure 3.** GEOS-Chem cloud water equivalent concentrations of major acidic and basic ions. Values are annual volume-weighted averages below 700 hPa for the year 2013. The contour lines (25 %, 50 %, 75 %) show the percent contribution of each ion to the total anion or cation equivalents.  $\text{Na}^+$  and  $\text{Cl}^-$  are not included in this total because they are largely in balance and make little net contribution to acidity. White color denotes areas where the topographic elevation is higher than 700 hPa.

The lowest pH values are generally over East Asia, both in the observations and in the model, with values mostly below 4.3 in eastern and southern China and Japan. In GEOS-Chem, this is due to extremely high  $[\text{SO}_4^{2-}]$  and  $[\text{NO}_3^-]$ , and despite 70 % of these anions being balanced by  $\text{NH}_4^+$  and dust cations. pH values remain low over the North Pacific ( $\sim 4.5$ ), despite much lower acid inputs, because less than half of the acidic anions are balanced by bases.

Over the US and Europe, average pH values are in the range from 4 to 5 both in the observations and in the model,

with most of the acidity as  $\text{NO}_3^-$  and with  $\text{NH}_4^+$  balancing over 50 % of the acidic anions. The model shows higher values in the central US ( $\sim 5.5$ ) because of  $\text{NH}_3$  and dust emissions. Summertime observations in the southwest US by Hutchings et al. (2009) show a pH of 6.3 due to the large dust influence, but this seasonal dust emission is underestimated in GEOS-Chem (Fairlie et al., 2007). Over southern Europe, about 25 % of the base cations are from Saharan dust.  $\text{NH}_4^+$  is the main cation elsewhere in Europe.  $\text{SO}_4^{2-}$  is the dominant acidic component over the northern midlatitude oceans

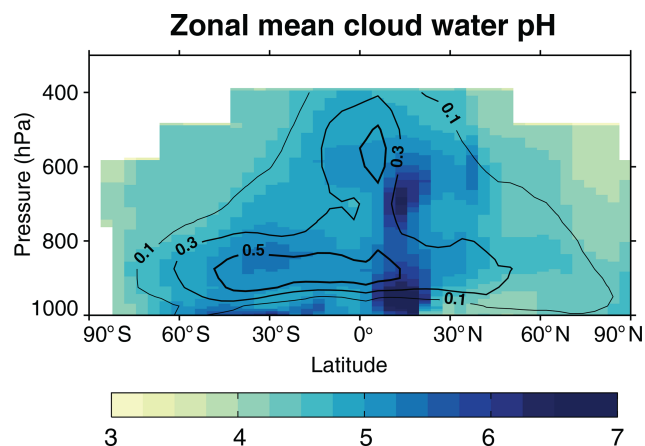
because of the oceanic source of  $\text{SO}_4^{2-}$  from the oxidation of DMS and because the continental influence extends further for  $\text{SO}_4^{2-}$  than for  $\text{NO}_3^-$  (Heald et al., 2006). Over the Arctic, the simulated pH is much lower (4–4.5) because of the long-range transport of acidic species and less than 50 % neutralization (Fisher et al., 2011).

The carboxylate ions  $\text{HCOO}^-$  and  $\text{CH}_3\text{COO}^-$  account for less than 25 % of  $\text{H}^+$  throughout the extra-tropical Northern Hemisphere (Fig. 3). The carboxylic acids are more important relative contributors to  $\text{H}^+$  in the tropics and in the Southern Hemisphere, exceeding 50 % in some areas of the tropical continents and southern midlatitudes. Ayers and Gillett (1988) found that carboxylic acids were responsible for an observed cloud water pH below 4 over tropical Australia, but GEOS-Chem underestimates carboxylic acids in that region (Fig. 1). Carboxylates were not measured in the Ecuadorian cloud water measurements (Makowski Giannoni et al., 2016), but we find from the model that the carboxylic acids contribute about 50 % of the  $\text{H}^+$ . GEOS-Chem shows similar pH values to those observed at Cape Grim (mean of 5.5), reflecting the low concentrations of acidic and basic species from continental sources. Cloud water pH sampled on the Antarctic coast also has a mean pH of 5.5 (Saxena and Lin, 1990), but the model is much lower over the Antarctic coast because of  $\text{SO}_4^{2-}$  from the oxidation of DMS. This may be because of sea salt alkalinity from blowing snow that is not accounted for in the model (Huang et al., 2018).

Alkaline cloud water ( $\text{pH} > 5.6$ ) is found in the observations over western India, Tibet, and Morocco, which is consistent with the model where the alkalinity is mainly from dust. GEOS-Chem simulates pH values of 6–8 over the area extending from the Sahara to the Gobi Desert. The transport of dust alkalinity from North Africa raises the cloud water pH in the Caribbean to above 5.5, both in the observations (Gioda et al., 2011) and in the model.

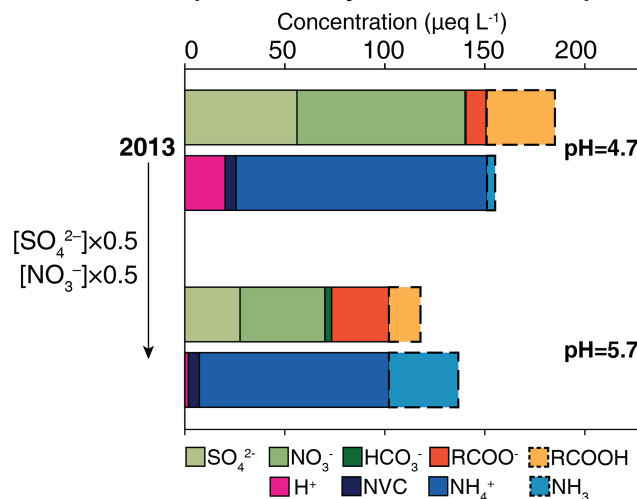
Figure 4 shows the zonal mean distributions of cloud water pH and cloud liquid water content (contour lines). In addition to the latitudinal variations described previously, cloud water pH increases as the cloud liquid water content increases because of the effect of dilution. Liquid water content peaks at about 900 hPa and decreases at higher altitudes, and this largely explains the mean variation of pH with altitude.

In their review, Pye et al. (2020) showed the annual mean tropospheric-column cloud water pH from three models: CMAQ (Community Multiscale Air Quality Modeling System; Northern Hemisphere only), TM4-ECPL (Tracer Model 4 of the Environmental Chemical Processes Laboratory), and GEOS-Chem. They calculated the annual mean pH using VWA  $[\text{H}^+]$  rather than Eq. (1). We find that their calculation method underestimates the pH over alkaline regions by 1–3 units but has little error for acidic regions. The GEOS-Chem results shown in Pye et al. (2020) follow the previous cloud water  $[\text{H}^+]$  calculation from Alexander et al. (2012), which is different from our calculation (Sect. 2). The resulting pH values are comparable over industrialized regions but



**Figure 4.** Zonal mean cloud water pH simulated by GEOS-Chem. Values are annual volume-weighted averages for the year 2013. The contour lines show the annual mean MERRA-2 cloud liquid water content in grams per cubic meter ( $\text{g m}^{-3}$ ) for the cloudy fraction of grid cells where a liquid cloud is present. White color denotes areas where the cloud liquid water content is below  $0.01 \text{ g m}^{-3}$ .

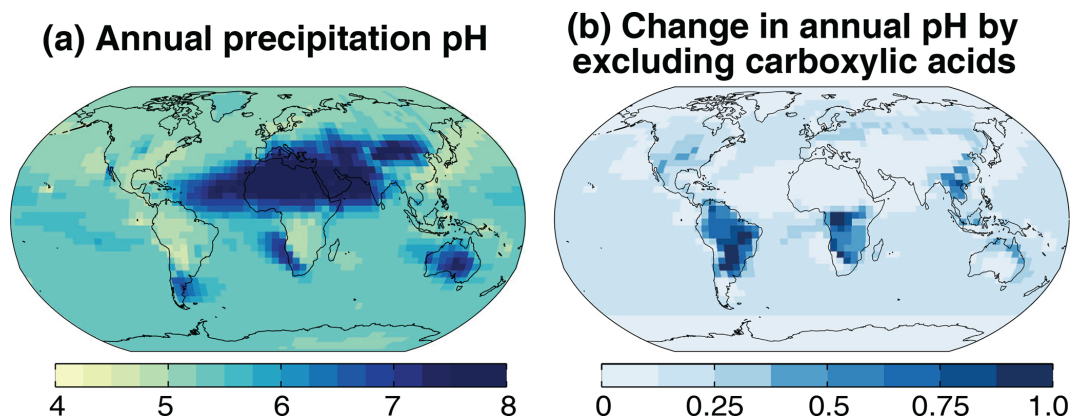
#### Cloud water pH sensitivity to reduced acid inputs



**Figure 5.** Sensitivity of cloud water pH to decreasing acid inputs over the contiguous US. The upper bars show the volume-weighted average concentrations of acidic and basic ions for 2013, with additional dashed lines showing the undissociated concentrations of carboxylic acids (RCOOH) and the gas-phase concentration of ammonia ( $\text{NH}_3$ ). The lower bars show the effect of decreasing  $[\text{SO}_4^{2-}]$  and  $[\text{NO}_3^-]$  by half relative to 2013 levels. All concentrations are expressed as cloud water equivalents. The corresponding pH values are indicated.

differ by up to 2 units over tropical forests and deserts because carboxylic acids and dust alkalinity were not included. They are also generally higher than 6 over the oceans because of an error in the numerical solver. The pH values shown by Pye et al. (2020) for TM4-ECPL are lower than our simulation by 1–2 units over most areas, and they would be incon-





**Figure 6.** (a) Annual mean precipitation pH simulated by GEOS-Chem for 2013. Panel (b) shows the change in precipitation pH when  $[\text{HCOO}^-]$  and  $[\text{CH}_3\text{COO}^-]$  are excluded from the ionic charge balance. See Sect. 2.3 for the procedure to compute average pH in the model.

sistent with the observations shown in Fig. 2. Our pH estimates are closest to those from CMAQ, which was the only model in Pye et al. (2020) that included dust alkalinity and  $\text{HCOOH}$  in the cloud water pH calculation. The zonal mean cloud water pH values from the ECHAM5/MESSy1 (European Centre for Medium-Range Weather Forecasts Hamburg – Modular Earth Submodel System) model presented by Tost et al. (2007) are 0.2–0.3 units higher than our values, likely because of their omission of carboxylic acids.

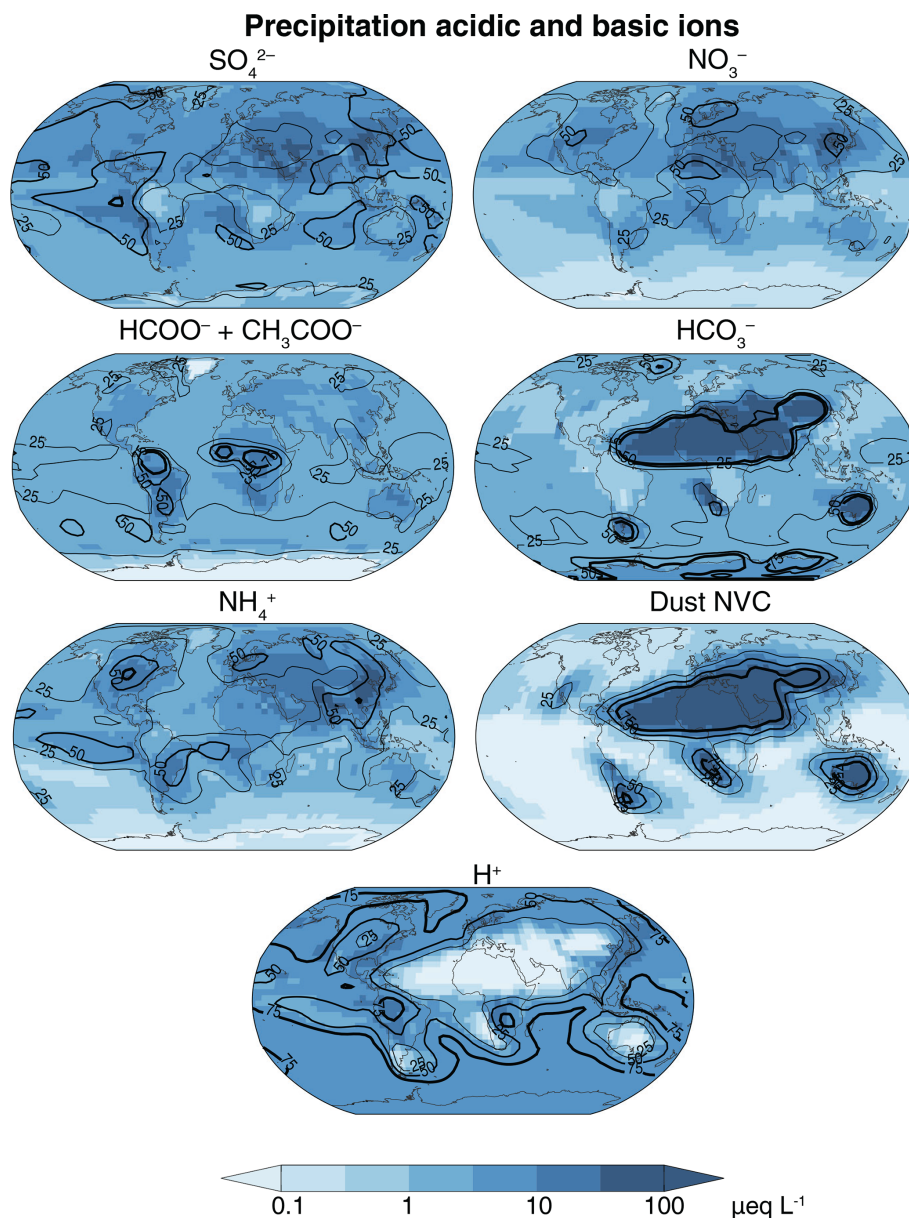
Emissions of  $\text{SO}_2$  and  $\text{NO}_x$  in the northern midlatitude continents are decreasing rapidly because of air quality concerns (Hoesly et al., 2018; Zheng et al., 2018). Considering that  $\text{NH}_3$  and dust cations presently balance over 50% of the acidic anions over these continents (Fig. 3), one might expect large increases in the cloud water pH as  $\text{SO}_2$  and  $\text{NO}_x$  emissions decrease. There is, however, a large buffering effect from the semi-volatile carboxylic acids and  $\text{NH}_3$ . Consider the case of the US. Figure 5 shows the mean simulated cloud water composition for 2013 over the continental US as well as the change in composition resulting from a factor of 2 decrease in strong acidity ( $\text{SO}_4^{2-} + \text{NO}_3^-$ ). The total concentrations of carboxylic acids ( $\text{RCOOH}_T \equiv \text{HCOOH}_T + \text{CH}_3\text{COOH}_T$ ) and ammonia ( $\text{NH}_{3,T}$ ) are held at 2013 levels and the gas–cloud water equilibrium is recalculated. For 2013, the mean cloud water pH is 4.7, a level at which only one-fourth of  $\text{RCOOH}_T$  is present as carboxylate ions and most of the  $\text{NH}_{3,T}$  is present as  $\text{NH}_4^+$ . Decreasing the strong acidity by half triples the dissociated fraction of  $\text{RCOOH}_T$  and volatilizes a significant fraction of  $\text{NH}_4^+$ ; this limits the increase in the cloud water pH to 5.7. Without this buffering effect, the pH would have increased by 2.1 units to 6.8.  $\text{NH}_4^+$  volatilization exerts a stronger buffering effect than carboxylic acid dissolution because  $\text{NH}_{3,T}$  concentrations are much larger. Buffering by  $\text{CO}_2$  and  $\text{SO}_2$  becomes important at pH values above 6 (Liljestrand, 1985),

and buffering by higher organic acids is important in highly polluted areas (Collett et al., 1999).

The low sensitivity of cloud water pH to strong acidity is seen in the long-term measurements of summertime cloud water ions at Whiteface Mountain, NY ( $44^\circ 22' \text{N}$ ,  $73^\circ 54' \text{W}$ ). Between 1994 and 2013, strong acidity at the site decreased by about 60%, but cloud water pH increased by only 0.8 units (Schwab et al., 2016). At the same time,  $[\text{NH}_4^+]$  decreased by 45% but co-located precipitation measurements showed no trend in  $\text{NH}_{3,T}$  (Schwab et al., 2016), which suggests cloud water pH buffering by  $\text{NH}_4^+$  volatilization. Carboxylate ions were not measured.

### 3.2 Global distribution of precipitation pH and composition

Figure 6a shows the global distribution of the annual mean precipitation pH for the year 2013. The pH averaging procedure is as described in Sect. 2.3. The global mean precipitation pH is 5.5 and varies from 4.5 over industrialized areas and the tropical forests to 8 over deserts, showing the same spatial patterns as cloud water pH but with lower acidity because of dilution. Figure 7 shows the simulated concentrations of precipitation ions, except for  $\text{Na}^+$  and  $\text{Cl}^-$  which again do not contribute significantly to net acidity. Precipitation ion concentrations are on average 4 times more dilute than cloud water concentrations (Fig. 3). The relative contribution of  $\text{SO}_4^{2-}$  in industrialized regions is higher than for cloud water because of additional  $\text{SO}_4^{2-}$  from below-cloud scavenging of  $\text{SO}_2$ . The  $\text{NO}_3^-$  contribution in central Africa is higher than for cloud water because of high-altitude convective scavenging of  $\text{HNO}_3$  produced from lightning  $\text{NO}_x$ . In Amazonia and tropical Africa,  $\text{HCOO}^-$  and  $\text{CH}_3\text{COO}^-$  contribute a larger fraction of precipitation acidity compared with cloud water because of below-cloud scavenging, and as a result the precipitation pH is similar to that of cloud water. Similarly, below-cloud scavenging of desert-generated dust



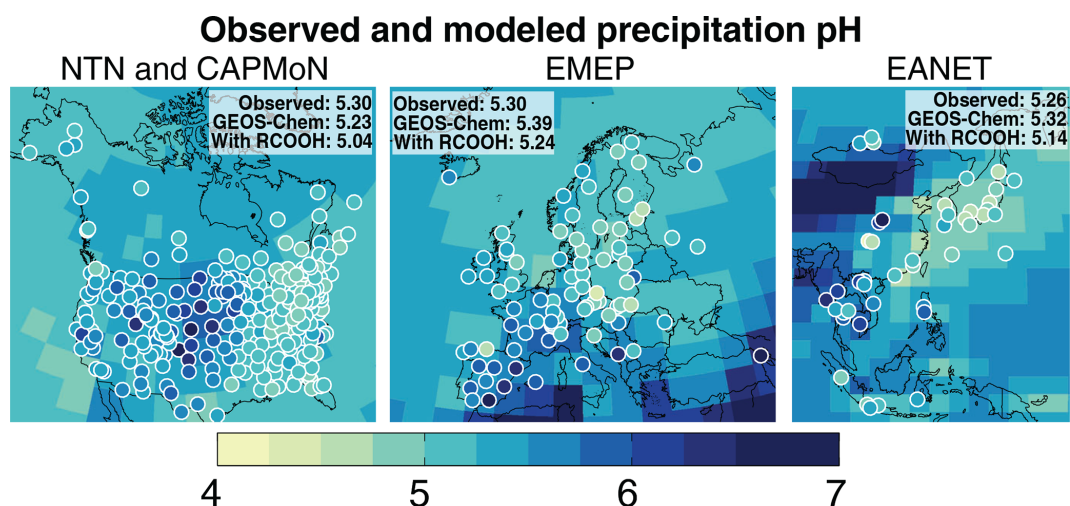
**Figure 7.** GEOS-Chem precipitation equivalent concentrations of major acidic and basic ions for the year 2013. The contour lines (25 %, 50 %, and 75 %) show the percent contribution of each ion to the total anion or cation equivalents.  $\text{Na}^+$  and  $\text{Cl}^-$  are not included in this total because they are largely in balance and make little net contribution to acidity.

results in alkaline precipitation over a much larger area compared with cloud water.

Figure 6b shows the change in precipitation pH when the contribution from carboxylic acids is excluded. These acids biodegrade quickly; thus, their acidity is not generally captured by precipitation pH measurements. We find that precipitation pH increases by 0.4–1 unit in the Amazon, tropical Africa, and southeast Asia, which is consistent with observations (Andreae et al., 1990; Sanhueza et al., 1992; Sigha-Nkamdjou et al., 2003; Yoboué et al., 2005). Over the US, Europe, and eastern China the increase in pH is 0.1–0.4 units,

which is similar to the observed contribution of carboxylic acids to precipitation  $\text{H}^+$  (10 %–60 %) in these areas (Keene and Galloway, 1984; Kawamura et al., 1996; Peña et al., 2002; Xu et al., 2010; Niu et al., 2018). Over the oceans, the change in pH from  $\text{HCOOH}$  and  $\text{CH}_3\text{COOH}$  is small ( $\sim 0.15$  units) and is in agreement with marine observations (Keene et al., 2015).

Figure 8 compares the simulated annual VWA precipitation pH ( $\overline{\text{pH}}_{\text{VW}}$ , Eq. 6) with observations from monitoring networks for the year 2013. Precipitation (rain and snow) pH observations are from the US National Trends Net-



**Figure 8.** Annual volume-weighted average (VWA) precipitation pH over North America, Europe, and East Asia for the year 2013. Values are the precipitation volume-weighted averages of the monthly means (Eq. 6). The GEOS-Chem model values (solid background) exclude RCOOH (HCOOH and CH<sub>3</sub>COOH) from the pH calculation for the comparison to observations. Observations (circles) are from the US National Trends Network (NTN), the Canadian Air and Precipitation Monitoring Network (CAPMoN), the European Monitoring and Evaluation Programme (EMEP), and the Acid Deposition Monitoring Network in East Asia (EANET). The EANET sites in Malaysia are not shown because of their different sampling procedure (see text). The insets in each panel show the spatial means of the observations for the corresponding region as well as the corresponding GEOS-Chem means at the measurement locations. The mean GEOS-Chem pH values with RCOOH included in the pH calculations are also shown.

work (NTN; NADP, 2019), the Canadian Air and Precipitation Monitoring Network (CAPMoN; ECCC, 2018), the European Monitoring and Evaluation Programme (EMEP; EMEP, 2015), and the Acid Deposition Monitoring Network in East Asia (EANET; EANET, 2019). We use monthly mean measurements from NTN (249 sites), EMEP (83 sites), and EANET (45 sites) and daily measurements from CAPMoN (30 sites), which we average to a monthly VWA [H<sup>+</sup>]. The monthly [H<sup>+</sup>] values are used to calculate  $\overline{\text{pH}}_{\text{VW}}$  following Eq. (6). The acidity from HCOO<sup>-</sup> and CH<sub>3</sub>COO<sup>-</sup> is not considered in the network measurements unless treated with biocide, which is only done in Malaysia. Thus, for comparison with observations, we use the simulated  $\overline{\text{pH}}_{\text{VW}}$  calculated without HCOO<sup>-</sup> and CH<sub>3</sub>COO<sup>-</sup>.

GEOS-Chem precipitation pH values are largely consistent with the observations, reproducing the observed regional means to within 0.1 pH unit (observed: 5.26–5.30; GEOS-Chem: 5.23–5.39). Carboxylic acids lower the mean GEOS-Chem pH by 0.15–0.2 units. The model also generally reproduces the observed spatial variations within the regions. Observations and model values show a higher pH in the Midwest than in the rest of the US because of neutralization by agricultural NH<sub>3</sub>. Precipitation pH in southern Europe is also relatively high because of the Saharan dust influence. Model values there are lower than in Fig. 6 due to the different forms used to calculate the annual mean pH (Eq. 6 here instead of Eq. 1). High [SO<sub>4</sub><sup>2-</sup>] and [NO<sub>3</sub><sup>-</sup>] lower the precipitation pH to below 4.5 in eastern China, Korea, and Japan. The high pH value observed in Xi'an (central China) is due to alkalinity

from dust sources (EANET, 2016), but the corresponding dust influence in the model is shifted slightly to the northwest. The low pH observed over Chongqing (central China) is because of high SO<sub>2</sub> and NO<sub>x</sub> emissions that are trapped locally by the surrounding terrain (Y. Chen et al., 2017).

Our global distribution of precipitation pH can be compared to previous model simulations by Rodhe et al. (2002) and Tost et al. (2007). Neither included carboxylic acids; thus, they overestimated pH values over tropical continents. Tost et al. (2007) did not include dust alkalinity either, resulting in large pH underestimates over desert regions. The pH values over eastern North America and Europe in these previous studies are about 0.5 units lower than in our simulation, reflecting the more recent decreases in SO<sub>2</sub> and NO<sub>x</sub> emissions (Hoesly et al., 2018).

### 3.3 Soil and freshwater acidification by wet deposition

Acidification of soil and freshwater is one of the major adverse effects of wet deposition fluxes on ecosystems because it causes the leaching of nutrients, mobilizes toxic metals, and directly damages biota (Driscoll et al., 2001). Quantifying this effect requires accounting for post-depositional processes. The H<sup>+</sup> flux associated with carboxylates and HCO<sub>3</sub><sup>-</sup> is not relevant because carboxylic acids are readily consumed by bacteria, and the amount of HCO<sub>3</sub><sup>-</sup> in ecosystems is controlled by the ambient CO<sub>2</sub> concentrations (Reuss and Johnson, 1986). The acidifying effects of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> depend on the biotic demand for nitrogen (N) (Reuss and John-

son, 1986). In ecosystems with high N demand (so-called N-limited ecosystems),  $\text{NO}_3^-$  and  $\text{NH}_4^+$  are readily assimilated by plants and microbes. Uptake of  $\text{NO}_3^-$  is accompanied by the uptake of  $\text{H}^+$  (or release of  $\text{OH}^-$ ), canceling the acidic effect of  $\text{NO}_3^-$  deposition.  $\text{NH}_4^+$  uptake is accompanied by the release of  $\text{H}^+$ , reversing the neutralizing effect of  $\text{NH}_4^+$ . Therefore, in N-limited ecosystems the acidic flux is calculated as follows (Rodhe et al., 2002):

$$F_{\text{H}^+(\text{N-lim})} = F_{\text{SO}_4^{2-}} - F_{\text{dustNVC}}, \quad (7)$$

where  $F$  denotes the wet deposition flux in equivalents. However, in many industrialized regions, N deposition greatly exceeds the biotic demand and results in N-saturated conditions (Aber et al., 1989; Watmough et al., 2005; Gundersen et al., 2006; Duan et al., 2016). Under such conditions, only a small fraction of the deposited  $\text{NO}_3^-$  and  $\text{NH}_4^+$  is assimilated. The excess  $\text{NO}_3^-$  causes  $\text{H}^+$  accumulation, whereas the excess  $\text{NH}_4^+$  can be converted by microbes to  $\text{NO}_3^-$  (nitrification), which releases  $2\text{H}^+$  for every  $\text{NH}_4^+$  converted and also results in net  $\text{H}^+$  formation. Considering the full acidifying potential of  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , we calculate the acidic flux under N-saturated conditions as follows (Galloway, 1995; Rodhe et al., 2002):

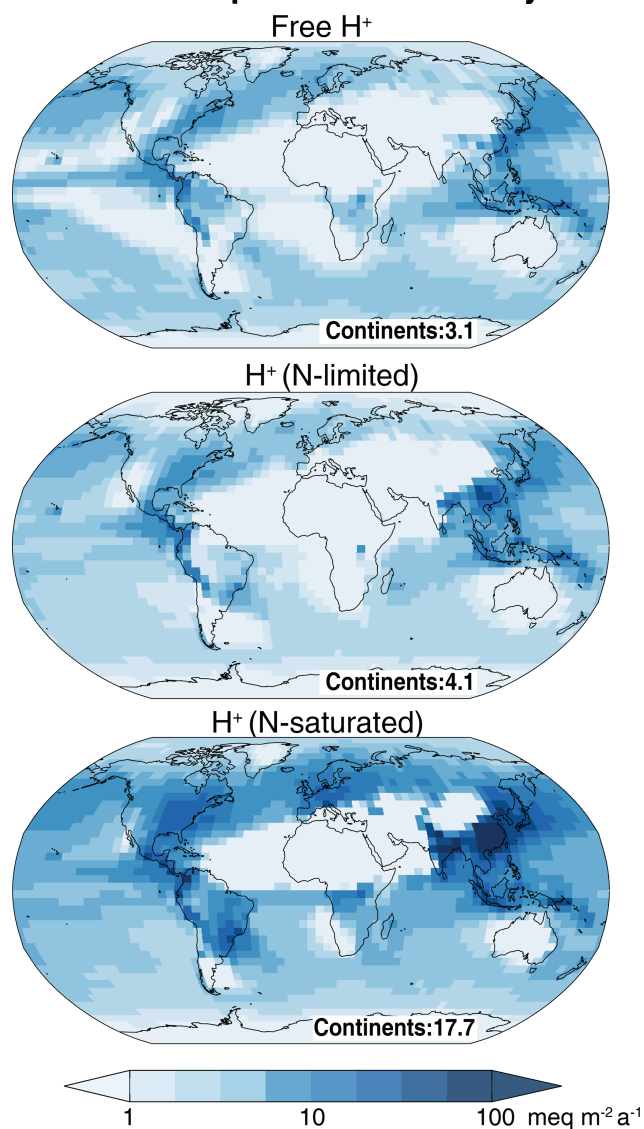
$$F_{\text{H}^+(\text{N-sat})} = F_{\text{SO}_4^{2-}} + F_{\text{NO}_3^-} + F_{\text{NH}_4^+} - F_{\text{dustNVC}} \quad (8)$$

$F_{\text{H}^+(\text{N-sat})}$  can be viewed as the upper limit of acidic inputs through wet deposition as some of the accumulated  $\text{NO}_3^-$  can denitrify to  $\text{N}_2$ .

Figure 9 shows  $F_{\text{H}^+(\text{N-lim})}$  and  $F_{\text{H}^+(\text{N-sat})}$ , along with the free  $\text{H}^+$  flux which represents the direct acid input to ecosystems excluding carboxylic acids. The global mean  $F_{\text{H}^+(\text{N-lim})}$  over continents ( $4.1 \text{ meq m}^{-2} \text{ a}^{-1}$ ) is higher than the mean free  $\text{H}^+$  flux ( $3.1 \text{ meq m}^{-2} \text{ a}^{-1}$ ). The free  $\text{H}^+$  flux is higher than  $F_{\text{H}^+(\text{N-lim})}$  over central Africa and Amazonia because of  $\text{H}^+$  associated with  $\text{NO}_3^-$  and  $\text{HCO}_3^-$ , respectively.  $F_{\text{H}^+(\text{N-lim})}$  is highest over the eastern US, Central and South America, and East Asia, reflecting high  $\text{SO}_4^{2-}$  fluxes. The global mean  $F_{\text{H}^+(\text{N-sat})}$  over continents ( $17.7 \text{ meq m}^{-2} \text{ a}^{-1}$ ) is much larger than  $F_{\text{H}^+(\text{N-lim})}$  and the free  $\text{H}^+$  flux because of acidity generated from  $\text{NH}_4^+$  nitrification. Over eastern India, East and Southeast Asia, the eastern US, and Central and South America,  $F_{\text{H}^+(\text{N-sat})}$  is more than  $50 \text{ meq m}^{-2} \text{ a}^{-1}$ , which exceeds the critical load for the acidification of highly sensitive ecosystems with a low acid buffering capacity (Kuylenstierna et al., 2001; Bouwman et al., 2002).

The total wet deposition of individual ions over the continents is largest for  $\text{NH}_4^+$  ( $1.3 \times 10^{12} \text{ eq a}^{-1}$ ) followed by  $\text{SO}_4^{2-}$  ( $1.0 \times 10^{12} \text{ eq a}^{-1}$ ) and  $\text{NO}_3^-$  ( $0.85 \times 10^{12} \text{ eq a}^{-1}$ ). For the year 2000, Lamarque et al. (2013) reported that the multimodel mean ( $\pm$  standard deviation) of the wet deposition flux over continents was higher for  $\text{SO}_4^{2-}$  ( $1.5 \pm 0.3 \times 10^{12} \text{ eq a}^{-1}$ ) than for  $\text{NH}_4^+$  ( $1.2 \pm 0.3 \times 10^{12} \text{ eq a}^{-1}$ ) and  $\text{NO}_3^-$  ( $1.1 \pm 0.2 \times$

## Acidic wet deposition flux to ecosystems



**Figure 9.** Acid wet deposition fluxes including post-depositional effects. Values are annual means for 2013 as simulated by GEOS-Chem.  $\text{H}^+$  associated with carboxylic acids is excluded, as these acids are rapidly consumed by bacteria. The free  $\text{H}^+$  flux represents the direct  $\text{H}^+$  input to ecosystems not accounting for any post-deposition nitrogen (N) transformation. The  $\text{H}^+$  flux for N-limited conditions is computed using Eq. (7) and assumes complete assimilation of  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , whereas the  $\text{H}^+$  flux for N-saturated conditions is computed using Eq. (8) and assumes complete nitrification of  $\text{NH}_4^+$  and no assimilation of  $\text{NO}_3^-$ . The global mean flux over continents in units of milliequivalents per square meter per annum ( $\text{meq m}^{-2} \text{ a}^{-1}$ ) is indicated.

$10^{12} \text{ eq a}^{-1}$ ). The decrease in the  $\text{SO}_4^{2-}$  wet deposition flux between 2000 and 2013 reflects the global decrease in anthropogenic  $\text{SO}_2$  emissions (Hoesly et al., 2018). We find that  $\text{NH}_4^+$  is now the largest source of acidifying wet deposition, contributing 41 % of  $F_{\text{H}^+ (N\text{-sat})}$  over continents globally, and it will contribute even more in the future as global  $\text{NH}_3$  emissions continue to grow (Hoesly et al., 2018).

#### 4 Conclusions

We used the GEOS-Chem global model of atmospheric chemistry to simulate the global distributions of cloud water and precipitation acidity as well as the total acid inputs from wet deposition to terrestrial ecosystems. This involved an improved pH calculation in GEOS-Chem including contributions from dust alkalinity, sea salt aerosol alkalinity, and carboxylic acids ( $\text{HCOOH}$  and  $\text{CH}_3\text{COOH}$ ). Our prime motivation was to better understand and evaluate the global cloud water pH distribution in the model for future simulations of sulfate, organic, and halogen chemistry. Extending the analysis to precipitation pH provided further opportunity for model evaluation and allowed us to quantify post-depositional effects in acid inputs to ecosystems on a global scale.

We compiled cloud water pH measurements worldwide from the literature and compared them to the GEOS-Chem simulation. The global mean cloud water pH is  $5.2 \pm 0.9$  in the observations and  $5.0 \pm 0.8$  in GEOS-Chem sampled at the same locations. The lowest pH values of 3–4 are over East Asia due to high acid inputs and despite an average 70 % neutralization by  $\text{NH}_3$  and dust cations. Low pH values extend across the North Pacific because of weak neutralization. Cloud water pH is 4–5 over the US and Europe with dominant acid input from  $\text{HNO}_3$  and over 50 % neutralization from  $\text{NH}_3$ . Alkaline cloud water with a pH as high as 8 is found over the northern subtropical desert belt extending from the Atlantic Ocean to Mongolia, including western India. Carboxylic acids account for less than 25 % of the cloud water  $\text{H}^+$  in the Northern Hemisphere but 25 %–50 % in the Southern Hemisphere and over 50 % in the southern tropical continents, where they drive the pH to below 4.5. We find little dependence of cloud water pH on altitude other than dilution from changes in the liquid water content.

Anthropogenic emissions of  $\text{SO}_2$  and  $\text{NO}_x$  are decreasing rapidly in the developed world, and this in combination with the large fraction of neutralized acidity might be expected to lead to large increases in the cloud water pH. However, there is a strong buffering effect because of the semi-volatility of  $\text{NH}_4^+$  and carboxylates. We find that a factor of 2 decrease in  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  inputs over the US increases the cloud water pH by 1 unit, compared with an increase of 2.1 units in the absence of buffering.

The global mean precipitation pH in GEOS-Chem is 5.5, which is higher than the cloud water pH because of dilution and below-cloud scavenging of bases ( $\text{NH}_3$  and dust). The precipitation pH shows spatial patterns similar to the cloud water pH but is influenced more strongly by carboxylic acids and dust near source regions because of below-cloud scavenging. GEOS-Chem is consistent with the annual mean precipitation pH observed at monitoring networks in North America, Europe, and East Asia. We find that the carboxylic acids lower the precipitation pH by up to 1 unit in the Amazon, tropical Africa, and southeast Asia, and by about 0.2 units in the US, Europe, and East Asia. This pH depression would not be seen in the observations because of the fast biological consumption of the carboxylic acids after deposition.

Carboxylic acids affect cloud water and precipitation pH globally, but their sources are uncertain. Our simulation could reproduce the observed  $\text{HCOOH}$  wet deposition flux by using scaled-up biogenic emissions, but it underestimated  $\text{CH}_3\text{COOH}$  flux by a factor of 4, indicating that a better understanding of their sources is needed. Dicarboxylic acids, such as oxalic, succinic, and malonic acids, are also present in cloud water and precipitation and their effect on pH needs to be evaluated.

Lastly, we examined the total acid inputs to soil and freshwater from wet deposition, including the post-depositional effects from  $\text{NH}_4^+$  and  $\text{NO}_3^-$  utilization by the biosphere. We find that total acid inputs under N-saturated conditions exceed  $50 \text{ meq m}^{-2} \text{ a}^{-1}$  in many parts of East Asia and the Americas, a level that can damage sensitive ecosystems.  $\text{NH}_4^+$  contributes 41 % of the acid input under N-saturated conditions globally.

## Appendix A

**Table A1.** Cloud water pH observations grouped by region and listed from west to east and north to south.

Location	Altitude (km)	Period	Mean $\pm$ SD	Median	Range	Reference
NE Pacific Ocean						
California coast (29–33° N, 121–123° W)	0–1	Jul 2001	4 $\pm$ 0.4 <sup>a,b</sup>	4	3.3–4.8	Straub et al. (2007)
California coast (35–37° N, 122–123° W <sup>a</sup> )	0.12–0.8	Jul–Aug 2011	4.5 $\pm$ 0.7	–	–	Z. Wang et al. (2014)
California coast (34–43° N, 119–126° W)	0.12–1	Jul–Aug 2013	4.3 $\pm$ 0.5	–	–	Prabhakar et al. (2014)
Hawaii (22° N, 152° W)	0–1	Jun 1980	4.5 $\pm$ 0.1 <sup>a,c</sup>	–	4.2–4.7	Parungo et al. (1982)
Alaska, US (58° N, 135° W)	0.8	Aug–Sep 1984; Jul–Aug 1985	4.5 $\pm$ 0.4	4.8	–	Bormann et al. (1989)
Whistler Mountain, Canada (50° N, 123° N)	1.7	Jun–Jul 2010	4.4 <sup>b</sup>	4.4	–	Ervens et al. (2013)
Cheeka Peak, US (48° N, 125° W)	1	May 1993	4.2 $\pm$ 0.2	–	–	Vong et al. (1997)
Mary’s Peak, US (45° N, 124° W)	1.3	Jul–Nov 1985	4.7 $\pm$ 0.3 <sup>a</sup>	5.2	4.4–4.9	Bormann et al. (1989)
Continental US						
Mt Washington (44° N, 71° W)	1.9	Jun–Aug 2008–2010	4.3	–	–	G. L. D. Murray et al. (2013)
Whiteface Mountain (44° N, 74° W)	1.5	Jun–Sep 2010–2013	4.5 $\pm$ 0.8 <sup>a</sup>	–	3.4–6.6	Schwab et al. (2016)
Michigan (44–46° N, 83–85° W)	1.4–3.1	Jul–Aug 2005	4.4 $\pm$ 0.8 <sup>a</sup>	–	2.2–5.2	Hill et al. (2007); Pye et al. (2020)
Mt Elders (35° N, 112° W)	2.8	Jun–Sep 2005–2007	6.3 $\pm$ 0.4 <sup>a</sup>	–	5.1–6.6	Hutchings et al. (2009)
Caribbean						
Puerto Rico (18° N, 65° W)	1.1	2004–2007	5.5 $\pm$ 1.0	–	–	Gioda et al. (2011)
Southeast Pacific Ocean						
Peru/Chile coast (16–24° S, 72–82° W)	0–1	Oct–Nov 2008	4.4 $\pm$ 0.4 <sup>a</sup>	–	3.5–6	Benedict et al. (2012)
Ecuador						
Andes (79° W, 4° S)	1.9–3.2	2004–2009	5.0 $\pm$ 0.5 <sup>a</sup>	–	–	Makowski Giannoni et al. (2013, 2016); Pye et al. (2020)
Europe						
Åreskutan, Sweden (63° N, 13° E)	1.3	Jul–Aug 1983; Jul–Aug 1984	4.4	–	–	Ogren and Rodhe (1986)
Mt Schmücke, Germany (51° N, 11° E)	0.9	Sep–Oct 2010	4.3 $\pm$ 0.4 <sup>a</sup>	4.6	3.6–5.3	van Pinxteren et al. (2016)
Mt Milešovka, Czech Republic (51° N, 14° E)	0.8	May–Jun 2006	4.1 $\pm$ 0.2 <sup>a</sup>	–	3.8–4.7	Fisak et al. (2009)
Mt Szrenica, Poland (51° N, 16° E)	1.3	Dec 2005–Dec 2006	4.6 $\pm$ 1.0 <sup>a</sup>	–	3.5–7.4	Błaś et al. (2010)
Niesen, Switzerland (47° N, 7–8° E)	1.6–2.3	Apr–Oct 2006; Apr–Oct 2007	6.5 $\pm$ 0.5 <sup>a</sup>	–	5.8–7.7	Michna et al. (2015)
Puy de Dôme, France (46° N, 3° E)	1.5	2001–2006; 2009–2011	5.5 $\pm$ 1.1 <sup>a</sup>	5.6	3.1–7.6	Deguille et al. (2014)
Xistral mountains, Spain (44° N, 8° W)	0.9	Sep 2011–Apr 2012	4.5 $\pm$ 0.4 <sup>a</sup>	–	3.8–5.2	Fernández-González et al. (2014)
Morocco						
Mt Boutmezguida (29° N, 10° W)	1.2	Nov–Jun 2013–2015	7.3 $\pm$ 0.4 <sup>a</sup>	–	7–8.5	Schunk et al. (2018); Pye et al. (2020)
India						
Sinhagad (18° N, 74° E)	1.5	2007–2010	6.0 $\pm$ 0.7 <sup>a</sup>	–	4.7–7.4	Budhavant et al. (2014)
Tibet						
Sejila Mountain (30° N, 95° E)	4	Jul 2017–Sep 2018	6.1 $\pm$ 0.3	–	–	W. Wang et al. (2019)

Table A1. Continued.

Location	Altitude (km)	Period	Mean $\pm$ SD	Median	Range	Reference
East Asia						
North Pacific Ocean (45–51° N, 159–171° E)	0.1	Jul 2012	3.6 $\pm$ 0.2	–	–	H. J. Kim et al. (2019)
Yellow Sea (38° N, 125° E)	0.1	Jul 2014	3.9 $\pm$ 0.4 <sup>a</sup>	–	3.5–5	Boris et al. (2016); Pye et al. (2020)
Tateyama, Japan (37° N, 138° E)	2.5	Sep–Oct 2007–2009	4.5 $\pm$ 0.7 <sup>a</sup>	–	3.5–6.3	Watanabe et al. (2010)
Mt Tai, China (36° N, 117° E)	1.6	Jul–Oct 2014	5.9 $\pm$ 0.8 <sup>a</sup>	–	3.8–7.0	J. Li et al. (2017)
		Mar–Apr, Jun–Jul, Oct–Nov 2007; Mar–Apr, Jun–Jul 2008	4.3 $\pm$ 1.3 <sup>a</sup>	–	2.6–7.6	Guo et al. (2012)
		Jun–Aug 2015	4.9 $\pm$ 0.6 <sup>a</sup>	–	3.8–6.3	Zhu et al. (2018)
Mt Lu, China (30° N, 116° E)	1.2	Aug–Sep 2011; Mar–May 2012	3.8 $\pm$ 0.7 <sup>a</sup>	–	2.8–5.6	Sun et al. (2015)
Mt Heng, China (27° N, 113° E)	1.3	Mar–May 2009	3.8 $\pm$ 1.0 <sup>a</sup>	–	2.9–6.9	Sun et al. (2010)
Ailaoshan, China (25° N, 101° E)	2.5	Dec 2015–Mar 2016	4.1 $\pm$ 0.4 <sup>a</sup>	–	3.5–4.9	Nieberding et al. (2018)
Mt Bamboo, Taiwan (25° N, 122° E)	1.1	Jan–Mar 2009	4.1 $\pm$ 0.6 <sup>a</sup>	–	3.1–5.6	Sheu and Lin (2013)
Chilan Mountain, Taiwan (25° N, 122° E)	1.7	Apr–May 2011	4.5 $\pm$ 0.4 <sup>a</sup>	–	3.7–5.2	Simon et al. (2016)
Lulin Station, Taiwan (23° N, 121° E)	2.9	Apr–May 2011	3.9 $\pm$ 0.3 <sup>a</sup>	–	3.4–4.5	Simon et al. (2016)
Mt TaiMoSha, Hong Kong (22° N, 114° E)	1	Oct–Nov 2016	3.6 $\pm$ 0.7 <sup>a</sup>	–	3.0–6.0	Li et al. (2020)
Australia						
Cape Grim (40–42° S, 144–149° E)	0.6–1.5	Jun 1981; Mar 1983	5.5 $\pm$ 0.5	–	–	Gillett and Ayers (1989)
Jabiru (133° E, 13° S)	2.7–3.7	Nov 1985	3.8 $\pm$ 0.4 <sup>a</sup>	–	3.5–5.2	Ayers and Gillett (1988)
Antarctic						
Antarctica coast (78° S, 167° E)	0.6–1.5	Dec 1982	5.4 $\pm$ 0.3 <sup>a</sup>	–	4.9–6.2	Saxena and Lin (1990)

<sup>a</sup> Standard deviation estimated as range / 4.

<sup>b</sup> Median value used as the mean.

<sup>c</sup> Mean estimated as (max + min)/2.

**Data availability.** The NTN data are available at <http://nadp.slh.wisc.edu/data/NTN/ntnAllsites.aspx> (last access: 11 October 2019; NADP, 2019), the CAP-MoN data at <http://donnees.ec.gc.ca/data/air/monitor/monitoring-of-atmospheric-precipitationchemistry/?lang=en> (last access: 18 October 2019; ECCO, 2018), the EMEP data at <https://projects.nilu.no/ccc/emepdata.html> (last access: 1 April 2020; EMEP, 2015), and the EANET data at <https://monitoring.eanet.asia/document/public/index> (last access: 9 October 2019; EANET, 2019). The model results are available on request from the corresponding author.

**Author contributions.** VS and DJJ designed the study. VS carried out the modeling and analysis. JMM, XW, and SZ contributed model updates. VS and DJJ wrote the paper with input from all authors.

**Competing interests.** The authors declare that they have no conflict of interest.

**Acknowledgements.** We thank the US National Trends Network, the Canadian Air and Precipitation Monitoring Network, the European Monitoring and Evaluation Programme, and the Acid Deposition Monitoring Network in East Asia for the precipitation pH measurements. Viral Shah thanks Becky Alexander (UW), Dylan Millet, and Xin Chen (UMN) for helpful discussions.

**Financial support.** This research has been supported by the National Science Foundation (grant no. AGS-1643217) and the U.S. Environmental Protection Agency (grant no. R840014).

**Review statement.** This paper was edited by Eliza Harris and reviewed by two anonymous referees.

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