

**Effect of nitric acid  
on cloud forcing**

R. Makkonen et al.

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# Brightening of the global cloud field by nitric acid and the associated radiative forcing

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Title Page	
Abstract	Introduction
Conclusions	References
Tables	Figures
◀	▶
◀	▶
Back	Close
Full Screen / Esc	
Printer-friendly Version	
Interactive Discussion	



## Abstract

Clouds cool Earth's climate by reflecting 20 % of the incoming solar energy, while also trapping part of the outgoing radiation. The effect of human activities on clouds is poorly understood, but the present-day anthropogenic cooling via changes of cloud albedo and lifetime could be of the same order as warming from anthropogenic addition in CO<sub>2</sub>. Soluble trace gases can increase water condensation to particles, possibly leading to activation of smaller aerosols and more numerous cloud droplets. We have studied the effect of nitric acid on the aerosol indirect effect with a global climate model. The nitric acid contribution to the present-day cloud albedo effect was found to be  $-0.32 \text{ W m}^{-2}$  and the total indirect effect  $-0.46 \text{ W m}^{-2}$ . The contribution to the cloud albedo effect is shown to increase to  $-0.37 \text{ W m}^{-2}$  by 2100, if considering only the reductions in available cloud condensation nuclei. Overall, the effect of nitric acid can play a large part in aerosol cooling during the following decades with decreasing SO<sub>2</sub> emissions and increasing NO<sub>x</sub> and greenhouse gases.

## 1 Introduction

Throughout industrialization humankind has injected increasing amounts of greenhouse gases (GHGs) into the atmosphere and thereby induced anthropogenic global warming. However, there has been a simultaneous increase in emissions of counter-acting agents: aerosols and their precursors (e.g. SO<sub>2</sub>). Aerosols alter radiative fluxes directly by scattering and absorbing radiation, and indirectly by acting as cloud condensation nuclei (CCN) and altering cloud properties (Twomey, 1977; Albrecht, 1989; Small et al., 2009). The present-day anthropogenic aerosol forcing (direct and cloud albedo effect) ranging from  $-0.5$  to  $-2.2 \text{ W m}^{-2}$  (Forster et al., 2007) acts to cool Earth's climate, partly masking the warming from e.g. increased CO<sub>2</sub> concentration. The indirect aerosol effects ( $-0.5$  to  $-1.9 \text{ W m}^{-2}$  for the cloud albedo effect,  $-0.3$  to  $-1.4 \text{ W m}^{-2}$  for the cloud lifetime effect, Lohmann and Feichter, 2005) are dominating

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12, 5225–5245, 2012

## Effect of nitric acid on cloud forcing

R. Makkonen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



the anthropogenic aerosol forcing over the direct effect ( $-0.50 \pm 0.40 \text{ W m}^{-2}$ , Forster et al., 2007).

Anthropogenic  $\text{SO}_2$  emissions increased from  $2 \text{ Tg}(\text{SO}_2)$  in year 1850 to  $130 \text{ Tg}(\text{SO}_2)$  in 1970's, but have already decreased about 20 % from the peak value due to emission regulations (Smith et al., 2011). In China,  $\text{SO}_2$  emissions increased between 2000 and 2006 by 53 %, but have already shown a decreasing trend since 2006 (Lu et al., 2010). The reductions of  $\text{SO}_2$  emissions due to air pollution control measures can cut global emissions even by 90 % until 2100 (van Vuuren et al., 2007) which, together with reductions in primary particle emissions, would lead to a substantially weaker aerosol cooling in the future (Andreae et al., 2005; Arneth et al., 2009; Makkonen et al., 2012). This decline in cooling could be offset by an increase in nitrate aerosols (Adams et al., 2001). Moreover, it has been suggested that the effects of nitrogen oxides on clouds could be increasingly important with declining  $\text{SO}_2$  emissions (Kulmala et al., 1995).

Nitrogen oxides are precursors of nitric acid, which as a semivolatile compound can condense on aqueous aerosols at relative humidities (RH) close to and exceeding 100 % (Kulmala et al., 1997; Laaksonen et al., 1998; Kokkola et al., 2003). During cloud formation, RH increases relatively rapidly, and as it exceeds 100 %, the largest aerosols start activating to cloud droplets. With still increasing RH, smaller and smaller particles activate until condensation of water to already activated particles depletes water from the air, peak RH is reached, and further activation ceases, leaving still smaller particles unactivated. The activated fraction of the total aerosol can vary from less than 1 % to close to 100 %, depending on ambient conditions, and the concentration, size distribution and composition of the aerosol itself. Nitric acid influences the activation process because its condensation onto an aerosol particle increases the particle's hygroscopic mass and enables the particle to activate at lower RH. Furthermore, the acid condenses more efficiently to smaller particles with higher surface-to-volume ratio, and as a result, a larger fraction of the aerosol is able to activate (Kulmala, 1993; Xue and Feingold, 2004). Recent ambient observations from a polluted region in China (with

**Effect of nitric acid  
on cloud forcing**

R. Makkonen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



HNO<sub>3</sub> mixing ratios as high as 5 ppb) indicate that nitric acid contributes to persistent clouds which may activate even at RH's slightly below 100 % (Ma et al., 2010), which is in agreement with the earlier theoretical calculations of Kulmala et al. (1997) and Laaksonen et al. (1998). Experimental evidence of the role of HNO<sub>3</sub> in cloud drop formation has also been obtained by Henin et al. (2011).

It can be speculated that nitric acid will play an even more important role in the future with decreasing primary aerosol and SO<sub>2</sub> emissions. Nitrogen oxides are formed during fuel combustion at high temperature and pressure, main sources being traffic, power generation and industry. In the IPCC scenario IS92a, annual NO<sub>x</sub> emissions were estimated to increase substantially from 28 Tg (N) (year 2000) to 72 Tg (N) (year 2100). Later, the IPCC SRES scenarios showed a large spread in emission estimates for the year 2100 (28–151 Tg (N) yr<sup>-1</sup> in the A1 scenario family). All SRES scenarios expect an increase in NO<sub>x</sub> emissions for a few decades (until 2040–2050), following stabilization (A1 and B2 scenario families), decline (by NO<sub>x</sub> emission control technologies and alternatives for fossil-fuel) or continued increase until 2100 (fossil-fuel intensive and high-population scenarios). The NO<sub>x</sub> emission pathways for the next IPCC report emission scenario development (Lamarque et al., 2011) indicate a range from 16 (van Vuuren et al., 2007) to 26 (Riahi et al., 2007) Tg (N) for the year 2100, corresponding to a 30–60 % decrease in NO<sub>x</sub> emissions from present-day levels. However, the ratio of global NO<sub>x</sub>/SO<sub>2</sub> emissions is increasing throughout the 21st century (Lamarque et al., 2011).

Beyond nitric acid also other other semivolatile compounds affect the cloud droplet formation. It has been shown that the effect of nitric acid is enhanced by the co-condensation of ammonia, which as a base neutralizes the solution and thus condensation takes place at the lower relative humidity compared to nitric acid condensation alone (Hegg, 2000; Romakkaniemi et al., 2005). With high enough concentrations and/or low temperatures the co-condensation leads to the formation of ammoniumnitrate. However, as shown by Romakkaniemi et al. (2005) it is difficult to estimate how much ammonia enhances activation as partitioning of ammonia and nitric acid between

**Effect of nitric acid  
on cloud forcing**

R. Makkonen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



different sized particles is highly dependent on the air mass history. Also some organic compounds are semivolatile, and in the recent study it was shown that they also have a lot of potential to affect cloud droplet formation (Topping and McFiggans, 2011).

We study the effect of nitric acid on cloud droplet activation with a global climate model, and show the importance of nitric acid on the present-day indirect forcing. We also explore how the effect can change with projected decreases in particle number concentrations.

## 2 Methods

We use the aerosol-climate model ECHAM5.5-HAM2 (Zhang et al., 2012) extended by a two-moment cloud microphysics scheme (Lohmann et al., 2007). The model horizontal resolution is T42, corresponding to approximately  $2.8^\circ$  grid. We use 31 vertical levels between the surface the 10 hPa. Aerosols are activated as cloud droplets with the scheme of Abdul-Razzak and Ghan (Abdul-Razzak and Ghan, 2000; Stier et al., 2012). The updraft velocity is calculated from the grid-mean vertical velocity, turbulent kinetic energy and convectively available potential energy. The aerosol microphysics model M7 (Vignati et al., 2004) considers the dominant aerosol compounds: dust, sea salt, black carbon, particulate organic matter and sulfate. Atmospheric new particle formation is modeled with a parameterization of binary water-sulphuric acid nucleation (Vehkamäki et al., 2002). The model does not include nitrate aerosols.

The effect of nitric acid is parameterized according to Romakkaniemi et al. (2005), based on results from a detailed numerical air parcel model. The parameterization is applied after the calculation of activated fraction without nitric acid ( $F_0$ ). The parameterization calculates the activated fraction ( $F_x$ ) with a certain nitric acid volume mixing ratio from the aerosol size distribution, gas phase nitric acid concentration, temperature, total pressure, updraft velocity and the activated fraction without nitric acid. The effect of nitric acid is considered only for two aerosol modes, soluble Aitken and accumulation modes.

## Effect of nitric acid on cloud forcing

R. Makkonen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Effect of nitric acid  
on cloud forcing**

R. Makkonen et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Natural emissions of sea salt (Schulz et al., 2004), dust (Tegen et al., 2002) and DMS (Kettle and Andreae, 2000) are calculated online, i.e. based on model meteorology. Both eruptive (Halmer et al., 2002) and non-eruptive (Andres and Kasgnoc, 1998) volcanic sulfur emissions are included. Emissions of biogenic VOCs are prescribed monthly averages according to Guenther et al. (1995). Present-day anthropogenic aerosol and precursor emissions are taken from AeroCom emission inventory for the year 2000 (Dentener et al., 2006). The nitric acid concentration fields are monthly mean volume mixing ratios for the year 2000 from the RETRO study calculated with the chemistry global circulation model ECHAM5\_MOZ (Rast et al., 2012). For the future simulation, we apply one scenario from the “Representative Concentration Pathways” (RCPs), which are used for the emission scenario development process of IPCC AR5 (Moss et al., 2010; Lamarque et al., 2011). The selected pathway is RCP 3-PD (van Vuuren et al., 2007), which is the most optimistic one regarding emissions of SO<sub>2</sub>, with an emission reduction of 90 % until the year 2100. Makkonen et al. (2012) have shown that the emissions of RCP 3-PD lead to a strong decrease in aerosol concentrations and the total aerosol forcing. We will only apply the aerosol and precursor emissions from the RCP 3-PD pathway: the nitric acid concentrations are for the year 2000 in all simulations.

We use two separate methods to analyze the effect of nitric acid on cloud albedo forcing and on total indirect forcing. To obtain the effect on cloud albedo, we run the ECHAM5-HAM model for 5 yr without coupling nitric acid to cloud microphysics. Instead, at each timestep we calculate the increase in cloud droplet number concentration (CDNC) due to nitric acid and we perform the radiation calculations twice, with and without nitric acid. The instantaneous change in radiative fluxes at top-of-atmosphere is diagnosed as cloud albedo forcing. Since the nitric acid is prescribed as monthly average 3-D-fields, the variation in the cloud albedo forcing is rather small, and a 5-yr model integration is sufficient. For the total indirect effect, two separate simulations are needed. One control simulation is done without nitric acid included. A second simulation is carried out, where the nitric acid is allowed to change the actual CDNC used

in cloud microphysics. The perturbation in CDNC can then lead to changes in e.g. cloud albedo, cloud lifetime and precipitation. The total indirect effect is analyzed as the difference in the top-of-atmosphere short-wave fluxes between the two simulations. Although the overall climate is constrained by prescribed sea-surface temperatures, the coupling of nitric acid and CDNC can alter cloud fields significantly. Hence, the two simulations are integrated for 20 yr to reduce the effect of the climate model's internal variability. The latter method used to obtain the total indirect forcing is essentially equivalent to quasi-forcing or fixed-SST-forcing calculated as radiative flux perturbation (Rotstajn and Penner, 2001).

The analyzed flux perturbations correspond to changes in present-day cloud forcing when nitric acid is explicitly described in cloud activation. Since the used nitric acid fields also contain natural sources, the resulting change in radiative fluxes is not strictly the anthropogenic forcing. However, global anthropogenic  $\text{NO}_x$  emissions are almost fivefold compared to emissions from natural sources (Delmas et al., 1997), and in areas with clouds most affected by nitric acid, the influence of anthropogenic  $\text{NO}_x$  emissions is presumably even higher.

### 3 Results and discussion

#### 3.1 Nitric acid effect on activation

Figure 1 shows the distribution of activated fractions  $F_x$  and  $F_0$  at 8 different heights between 100 and 2000 m, taken from simulations without coupling of nitric acid and cloud microphysics. The scatter plot is generated by correlating  $F_x$  with  $F_0$  at each model grid point at a specific height. At low altitudes (100–200 m) the activated fraction  $F_0$  without nitric acid effect can easily reach values over 0.3, and Fig. 1 shows a large spread in the activated fraction  $F_x$  with nitric acid at these values. Nitric acid can not decrease the activated fraction at any point. The relative increase in activated fraction due to nitric acid increases monotonously with height, from about 10–20 % below 1 km

## Effect of nitric acid on cloud forcing

R. Makkonen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



to > 50 % above 3.5 km.

The zonal distribution of CDNC increase due to nitric acid is shown in Fig. 2. The strongest effect is seen in the mid-troposphere between 500–800 hPa and between 30° S–60° N, where nitric acid can increase CDNC by more than 10 % in large areas.

### 5 3.2 Present-day forcing due to nitric acid

Our simulations show a strong effect from the inclusion of nitric acid on total short-wave radiation fluxes at top-of-atmosphere:  $-0.32 \pm 0.01 \text{ W m}^{-2}$  for the cloud albedo effect and  $-0.46 \pm 0.26 \text{ W m}^{-2}$  ( $-0.42 \pm 0.28 \text{ W m}^{-2}$  when accounting for longwave radiation) for the total indirect effect. With the  $\text{NO}_x$  sources mostly confined to the Northern Hemisphere, the cooling from nitric acid has a strong zonal pattern. Figure 3 shows the cloud albedo effect peaking between 20–80° N, reaching a value of  $-0.90 \text{ W m}^{-2}$  around 50° N. The hemisphere-mean effect of nitric acid on cloud albedo forcing is  $-0.17 \text{ W m}^{-2}$  for the Southern Hemisphere and  $-0.43 \text{ W m}^{-2}$  for the Northern Hemisphere. Similarly to the cloud albedo effect, the total indirect effect shows a strong contrast between Southern ( $-0.20 \text{ W m}^{-2}$ ) and Northern ( $-0.59 \text{ W m}^{-2}$ ) Hemisphere. The 5-yr global averages of the total indirect forcing extracted from the 20-yr simulation are  $-0.38$ ,  $-0.49$ ,  $-0.38$  and  $-0.58 \text{ W m}^{-2}$ , so they all exceed the cloud albedo forcing of  $-0.32 \text{ W m}^{-2}$ . Figure 3 shows that the nitric acid induced perturbation to CDNC follows the nitric acid concentration, indicating that the fluctuations in total indirect effect are arising from changes in modeled cloud cover.

As shown in Fig. 4, there are differences between the spatial distributions of  $\text{HNO}_3$  concentration and the simulated cloud albedo forcing. In addition to the nitric acid concentration, the nitric acid effect on cloud droplet concentration depends on the aerosol distribution, temperature, updraft velocity and activated fraction. The annual average  $\text{HNO}_3$  mixing ratio at the 750 hPa level (Fig. 4a) reaches > 1 ppb in polluted regions (middle Africa, India, China) and is mostly between 0.1–1 ppb over continents. Although surface concentrations are even higher close to  $\text{NO}_x$  sources (annual average several ppb), the 750 hPa level shows clearly the transport of  $\text{HNO}_3$  over oceans. The

## Effect of nitric acid on cloud forcing

R. Makkonen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





transport of  $\text{HNO}_3$  has been observed from satellites, and  $\text{HNO}_3$  has been suggested as a reservoir of  $\text{NO}_x$  (Wespes et al., 2007). In large parts of the North Atlantic,  $\text{HNO}_3$  levels are between 0.3–0.5 ppb. The outflow from Africa establishes even 0.5–1 ppb of  $\text{HNO}_3$  over the South Atlantic. The overall effect of  $\text{HNO}_3$  on cloud droplet number concentration is largest over continents, especially over polluted regions. The cloud albedo effect ranges from  $-1.5$  to  $-2 \text{ W m}^{-2}$  over Eastern US, Europe, Central Africa and Japan. The forcing is stronger than  $-0.2 \text{ W m}^{-2}$  over all continental regions except for Northern Africa, Middle East and Greenland. At certain locations, even a high  $\text{HNO}_3$  concentration is not enough to produce a strong cooling: e.g. in India, the annual average  $\text{HNO}_3$  concentration of 1 ppb or more leads to a forcing from only  $-0.2$  to  $-0.7 \text{ W m}^{-2}$ . The cooling over India is most prominent during summer months, when the simulated aerosol concentrations are lower than average. With high enough aerosol number concentrations, the amount of nitric acid partitioned in each particle, and subsequent effect on activation, is small (Nenes et al., 2002).

The nitric acid inclusion leads to a global annual-mean increase of 7% in CDNC, which is a clear signal of the nitric acid effect and sufficient for a significant cloud albedo perturbation. The zonal averages in Fig. 3 show that this CDNC increase follows the nitric acid concentration. However, the zonal averages of the total indirect forcing (Fig. 3) and especially its horizontal distribution (Fig. 4d) differ substantially from the cloud albedo effect. Indeed, Fig. 4d shows that locally, the total indirect effect can be either stronger or weaker negative than the cloud albedo effect, and even positive at many locations. The areas with positive (strong negative) total indirect forcing generally correspond to reduced (increased) cloudiness. For the most part, the changes in the horizontal distribution of cloudiness (not shown) are statistically insignificant, that is, they are undistinguishable from the internal variability of the model's climate. Thus the small-scale patterns seen in Fig. 4d are not robust. However, the nitric acid induced changes in global-mean low cloud fraction and middle cloud fraction (0.38% and 0.40%, respectively) are both significant at higher than 99.9% level of confidence. This is consistent with the global-mean total indirect effect being larger than the cloud

**Effect of nitric acid  
on cloud forcing**

R. Makkonen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



albedo effect, and provides evidence that at least in this model, nitric acid acts to increase the average cloud lifetime.

### 3.3 Effect of decreasing future aerosol concentration

To study the impact of decreasing aerosol concentration on the effect of nitric acid, we show results from simulations with aerosol and precursor emissions of the year 2100, but with present-day nitric acid concentrations. Low emissions of the RCP 3-PD pathway lead to a strong decrease in CCN (0.2 %) concentration (Fig. 5a,b), except for high-latitude regions. In continental Northern Hemisphere, the decrease in CCN (0.2 %) concentration is generally over 50 %, while in South America, Africa and Australia the decrease is slightly smaller. More details on changing number concentration under RCP 3-PD can be found in Makkonen et al. (2012). Note that the shown CCN concentrations are unperturbed by nitric acid.

The change in nitric acid cloud albedo forcing between years 2000 and 2100 shown in Fig. 5 is clearly connected to the change in CCN (0.2 %) concentration. The cloud albedo forcing due to nitric acid is intensified by more than  $0.25 \text{ W m}^{-2}$  in North America, Central Africa, India, China and Eastern Europe, when moving from year 2000 to 2100. These areas show a simultaneous decrease in CCN (0.2 %) by more than 200 ( $\text{cm}^{-3}$ ) (a decrease of 50–80 %). Even though the simulated present-day cloud albedo forcing can reach high values even in rather polluted areas, the results indicate that cleaning the air from particulate pollutants intensifies the nitric acid effect. The resulting negative forcing could balance the loss in aerosol forcing. The present-day global average cloud albedo effect of  $-0.32 \text{ W m}^{-2}$  is increased to  $-0.37 \text{ W m}^{-2}$  in the year 2100.

It should be noted that our future simulation only focused on the effect of decreasing number concentrations on the magnitude of the nitric acid effect. Also, the number concentrations are simulated with a model without nitrate aerosols, hence the anthropogenic emission changes stem only from  $\text{SO}_2$ , BC and OC. The applied nitric acid concentration is identical for years 2000 and 2100, while the RCP 3-PD shows a

## Effect of nitric acid on cloud forcing

R. Makkonen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



60% decrease in anthropogenic  $\text{NO}_x$  emissions (Lamarque et al., 2011). RCP 3-PD also predicts a 70% increase in ammonia emissions, however the global ammonium aerosol burden is decreasing due to a decrease in  $\text{NO}_x$  (Lamarque et al., 2011). To fully quantify the effect of nitric acid condensation in the future aerosol forcing requires simulations with coupled aerosol-chemistry models.

## 4 Conclusions

We have presented global model simulations with explicit inclusion of the effect of nitric acid condensation on cloud droplet activation. The increased soluble material increases cloud droplet number concentrations significantly, leading to a  $-0.32 \pm 0.01 \text{ W m}^{-2}$  cloud albedo forcing and a total indirect forcing of  $-0.46 \pm 0.26 \text{ W m}^{-2}$  with present-day emissions. While the cloud albedo effect is spatially coupled to nitric acid concentrations, the total indirect forcing is dominated by changes in low and middle cloud cover. The spatial distribution of cloud cover changes can be very much model dependent, nonetheless the total indirect effect qualifies for an estimate for cloud effects beyond the cloud albedo effect.

We also showed that with decreasing aerosol number concentrations in the future, the effect of nitric acid could play a more important role. The applied future pathway with over 50% reductions in CCN concentrations led to a nitric acid cloud albedo forcing of  $-0.37 \pm 0.01 \text{ W m}^{-2}$  in year 2100. While the simulation did not take into account changes in  $\text{NO}_x$ , nitrate aerosol or ammonia, it serves as indication on the effect of particle number reductions. Despite the benefits from added cooling, other environmental impacts (acid rain, ozone production) and health issues speak for reduction measures of  $\text{NO}_x$  emissions. To account for the total effect of  $\text{NO}_x$  on aerosols and clouds, one should also consider  $\text{NO}_x$  as a source of ozone.

## Effect of nitric acid on cloud forcing

R. Makkonen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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## Effect of nitric acid on cloud forcing

R. Makkonen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Effect of nitric acid  
on cloud forcing**

R. Makkonen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Effect of nitric acid  
on cloud forcing**

R. Makkonen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Effect of nitric acid  
on cloud forcing**

R. Makkonen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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## Effect of nitric acid on cloud forcing

R. Makkonen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

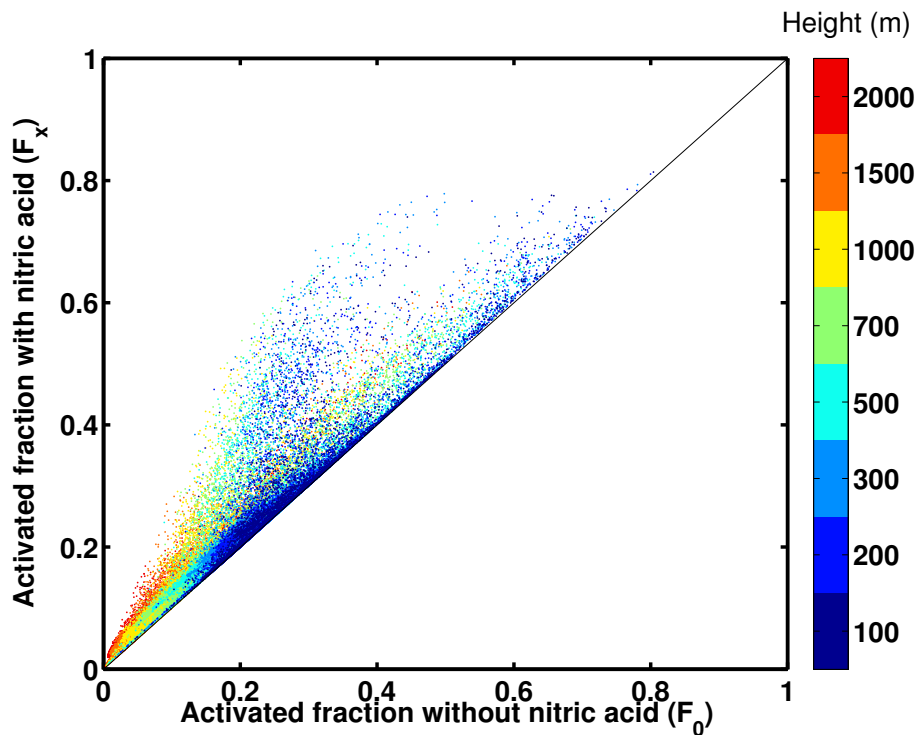
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Printer-friendly Version

Interactive Discussion







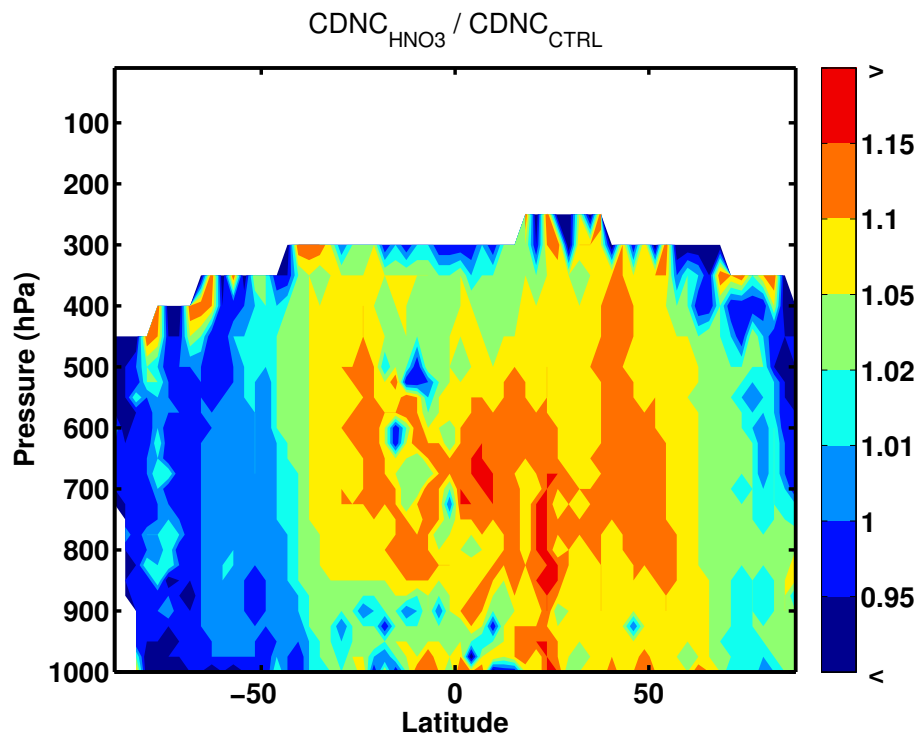
**Fig. 1.** Scatter plot of activated fraction with nitric acid ( $F_x$ ) plotted against activated fraction without nitric acid ( $F_0$ ) at 8 different heights. The scatter plots are generated by plotting 5-year average activated fractions in each grid point against each other. The data is from simulations without coupling of nitric acid and cloud microphysics.

**Effect of nitric acid on cloud forcing**

R. Makkonen et al.

Title Page	
Abstract	Introduction
Conclusions	References
Tables	Figures
◀	▶
◀	▶
Back	Close
Full Screen / Esc	
Printer-friendly Version	
Interactive Discussion	





**Fig. 2.** 20-yr zonal average ratio of CDNC between simulations with and without nitric acid.

**Effect of nitric acid on cloud forcing**

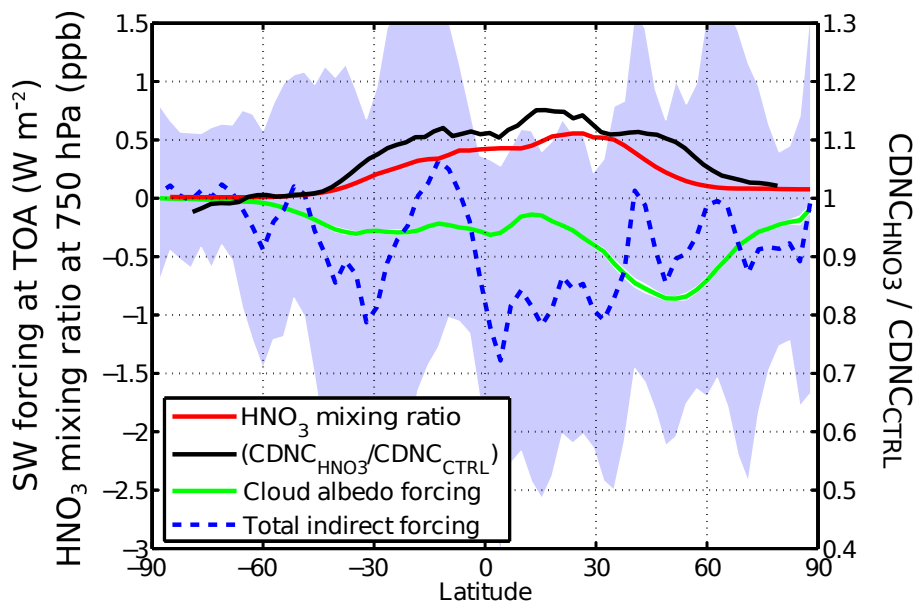
R. Makkonen et al.

Title Page	
Abstract	Introduction
Conclusions	References
Tables	Figures
◀	▶
◀	▶
Back	Close
Full Screen / Esc	
Printer-friendly Version	
Interactive Discussion	



## Effect of nitric acid on cloud forcing

R. Makkonen et al.



**Fig. 3.** Zonal average nitric acid mixing ratio at 750 hPa (ppb), cloud albedo forcing ( $\text{W m}^{-2}$ ) and total indirect forcing ( $\text{W m}^{-2}$ ) due to inclusion of nitric acid. Also shown is the relative change in CDNC at the 750 hPa level between total indirect effect simulations with ( $\text{CDNC}_{\text{HNO}_3}$ ) and without ( $\text{CDNC}_{\text{CTRL}}$ ) nitric acid. The blue shading corresponds to standard deviation of the total indirect forcing. The standard deviation is presented also for the cloud albedo forcing, but it is almost indistinguishable from the green line.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

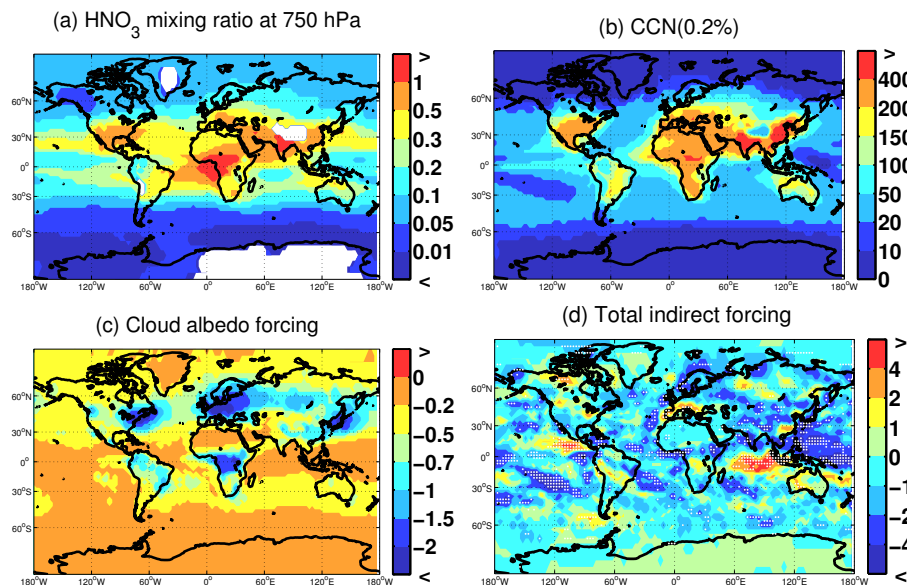
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Interactive Discussion



Effect of nitric acid  
on cloud forcing

R. Makkonen et al.



**Fig. 4.** (a) Annual average nitric acid mixing ratio at 750 hPa (ppb), (b) surface-level CCN (0.2%) ( $\text{cm}^{-3}$ ) (unperturbed by nitric acid), (c) cloud albedo forcing ( $\text{W m}^{-2}$ ) and (d) total indirect forcing ( $\text{W m}^{-2}$ ) due to inclusion of nitric acid. The cloud albedo forcing is averaged over 5 yr, the total indirect forcing over 20 yr. White dots in (d) indicate statistical significance with  $p < 0.05$ .

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

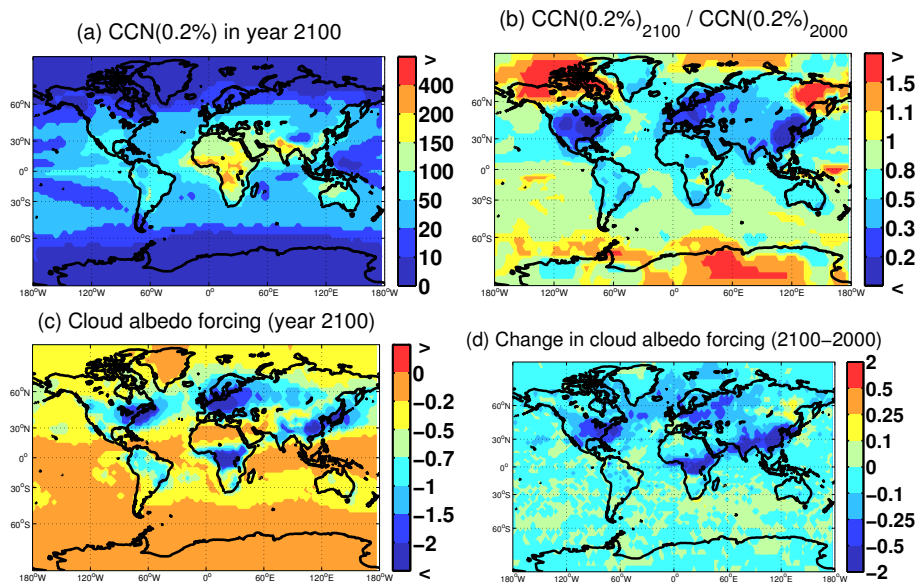
Printer-friendly Version

Interactive Discussion



## Effect of nitric acid on cloud forcing

R. Makkonen et al.



**Fig. 5.** (a) Surface-level CCN(0.2%) ( $\text{cm}^{-3}$ ) in year 2100, (b) ratio of CCN(0.2%) ( $\text{cm}^{-3}$ ) between years 2100 and 2000, (c) cloud albedo forcing ( $\text{W m}^{-2}$ ) due to nitric acid in year 2100, and (d) the change in cloud albedo forcing due to nitric acid ( $\text{W m}^{-2}$ ) between years 2000 and 2100 (negative values indicate more cooling due to nitric acid in year 2100).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

