

Abstract

Recent laboratory studies indicate that while a dimethylamine concentration ([DMA]) of several pptv can substantially enhance nucleation rates, such an enhancement drops significantly as [DMA] decreases below a few pptv. Here we study global distributions of amines with a chemistry transport model. DMA's lifetime is quite short (1–2 h in some regions) due to aerosol uptake and oxidation. Aerosol uptake is important over regions of high anthropogenic emissions, while the decrease of the uptake coefficient (γ) from 0.03 to 0.001 in these regions increases the modeled amine concentrations by a factor of ~ 5 . Further decrease of γ from 0.001 to 0 has a small ($< 10\%$) effect on the predicted amine concentrations. With the estimated global emission flux, from the reference, our simulations indicate that [DMA] in the surface layer is generally less than 1 pptv over major continents and below 0.1 pptv over oceans, decreasing quickly with altitude. Total concentrations of methylamines are about one order of magnitude higher than that of DMA. A comparison of simulated and observed [DMA] shows that the values of the simulated [DMA] are close to the measured values for the various urban sites but are substantially lower (by 1–2 orders of magnitude) than those measured at the rural, coastal, and marine sites.

1 Introduction

In recent years, gaseous amines have attracted more attention due to theoretical, laboratory, and field measurements indicating that amines may considerably enhance particle formation and growth (Kurten et al., 2008; Nadykto et al., 2011, 2014; Almeida et al., 2013; Berndt et al., 2010; Zhao et al., 2011; Erupe et al., 2011; Chen et al., 2012; Wang et al., 2010; Yu et al., 2012). Amines are organic compounds and derivatives of ammonia wherein one or more hydrogen atoms are replaced by a substituent such as an alkyl or aryl group. About 150 amines have been identified in the atmosphere; the most common and abundant amines being the low-molecular-weight methylamines like

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monomethylamine (MMA), dimethylamine (DMA), and trimethylamine (TMA) (Ge et al., 2011a). Concentrations of amines can exceed several parts-per-billion-volume (ppbv) near their sources (Ge et al., 2011a; Schade and Crutzen, 1995) but are expected to be low farther away as a result of their short lifetime due to oxidation by OH (Atkinson et al., 1978) and uptake by particles (Qiu and Zhang, 2013).

While amines are stronger bases than ammonia and ternary $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ -amine clusters are more stable (Kurten et al., 2008; Nadykto et al., 2011, 2014; Almeida et al., 2013), the relative role of amines vs. ammonia in enhancing particle formation in the atmosphere is yet to be determined (Zollner et al., 2012). This is because the concentration of amines in the atmosphere is generally much lower than that of ammonia (by 2–3 orders of magnitude or more) (Ge et al., 2011a; Hanson et al., 2011). Recent measurements taken during the CLOUD (Cosmics Leaving Outdoor Droplets) chamber experiments at CERN (Almeida et al., 2013) indicate that a [DMA] of above ~ 5 parts-per-trillion-volume (pptv) enhances nucleation substantially, but enhancement drops significantly as [DMA] decreases below that level.

In order to determine the contribution of ternary nucleation involving amines to atmospheric particle production, it is critical to know the concentrations of key amines and their variations in the atmosphere. Due to their high reactivity and low concentrations, measurements of gaseous amines in the background atmosphere are very limited (Ge et al., 2011a). Several studies show [DMA] is below 1 pptv in urban areas (Grönberg et al., 1992a, b) while several others observed [DMA] around a few pptv in rural and coastal areas (Hanson et al., 2011; VandenBoer et al., 2011, 2012; Van Neste et al., 1987; Gibb et al., 1999). Although TMA is generally more abundant (Ge et al., 2011a), the concentration of TMA needed to substantially enhance nucleation remains to be studied.

In addition to in-situ measurements, numerical modeling is also needed to integrate the various processes controlling amine concentrations and ultimately assess the impact of amines on global nucleation, aerosol properties, and climate. While limited measurements of amines are available, modeling of atmospheric amines is basically

non-existent. In the present work and for the first time (to our knowledge), we aim to simulate the global distributions of amines in the air with a global chemistry transport model. The key processes controlling amine concentrations (including emission, transport, oxidation, deposition, and aerosol uptake) are considered and the simulated results are compared to the limited measurements available.

The methods of the present study (including sources, sinks, and model representation) are described in Sect. 2. The modeling results, comparisons with measurements, and sensitivity studies are given in Sect. 3. Section 4 is the summary and discussion.

2 Methods

2.1 Sources

Amines are ubiquitous atmospheric organic bases, and are emitted from a wide range of sources including animal husbandry, biomass burning, motor vehicles, industry, meat cooking, fish processing, sewage treatment and waste incineration, protein degradation, vegetation, soils, and ocean organisms (Ge et al., 2011a). On a global scale, little is known about the flux of most amines, especially various aromatic amines (Ge et al., 2011a). Among about 150 amines identified in the atmosphere, methylamines (MMA, DMA, and TMA) are most common and abundant. Schade and Crutzen (1995) estimated the global emission fluxes of MMA, DMA, and TMA to be 83 ± 26 , 33 ± 19 , and 169 ± 33 Gg N yr⁻¹, respectively. The total methylamine flux of 285 ± 78 Gg N yr⁻¹ is more than two orders of magnitude smaller than the estimated global ammonia flux of $50\,000 \pm 30\,000$ Gg N yr⁻¹ (Schade and Crutzen, 1995).

2.2 Sinks

The main sinks of amines emitted into the atmosphere include dry and wet deposition, gas phase reactions, and heterogeneous uptake. Since most of the amines are highly soluble, wet deposition is an important process to bring amines in the air to the surface.

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As organic compounds, gaseous amines undergo oxidation reactions with OH, NO_x, or O₃ (Nielsen et al., 2012; Lee and Wexler, 2013). The lifetimes of amines with respect to OH oxidation are typically a couple of hours, much shorter than those by reactions with O₃ and NO_x. The gaseous methylamines, which are strong bases, may also undergo rapid acid-base reactions to form salt particles in the presence of inorganic acids (HCl, HNO₃, H₂SO₄) (Murphy et al., 2007). In addition, amines may react with organic acids to form amides (Barsanti and Pankow, 2006). A detailed discussion of the chemistry of amines in the atmosphere can be found in several recent review articles (Nielsen et al., 2012; Lee and Wexler, 2013).

Owing to their high aqueous solubility and strong basicity, gaseous amines can efficiently enter into a particulate phase via direct dissolution and acid-base reactions. The importance of amines with regard to gas/particle partitioning has been supported by the reactive uptake of TMA into ammonium nitrate particles (Lloyd et al., 2009) and amine exchange into ammonium bisulfate and nitrate nuclei (Bzdek et al., 2010). Laboratory studies show that heterogeneous reactions of gaseous alkylamines on H₂SO₄ nanoparticles resulted in the formation of alkyl ammonium sulfates and particle growth (Wang et al., 2010a, b). It has also been observed that methylamine could react with glyoxal in drying cloud droplets to form SOA (De Haan et al., 2009a) and stable ammonium salts could be formed by amine and organic acids in the aerosols (Williams et al., 2010). The thermodynamic properties of amines that control their partitioning between the gas and the particle phase in the atmosphere are examined in a review paper (Ge et al., 2011b). An overview of laboratory progress in the multiphase chemistry of amines can be found in Qiu and Zhang (2013).

2.3 Model representation

A numerical model is needed to integrate the various processes influencing the concentrations of amines in the atmosphere. In the present study, we employ GEOS-Chem, a global 3-D model of atmospheric composition driven by assimilated meteorological data from the NASA Goddard Earth Observing System 5 (GEOS-5) (e.g.,

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Bey et al., 2001). The GEOS-Chem model has been developed and used by many research groups and contains a number of state-of-the-art modules treating various chemical and aerosol processes with up-to-date key emission inventories (for details, see the model webpage <http://geos-chem.org/>). While ammonia is simulated in detail in GEOS-Chem, amines are not considered prior to this study. Here, to represent gas phase amines, we add a tracer in GEOS-Chem V8.3.2 with an advanced particle microphysics (APM) model incorporated (Yu and Luo, 2009).

There exist large uncertainties in the estimated emission fluxes of amines and detailed emission inventories of amines from various sources are currently not available. In the present study, we use the estimated methylamine fluxes given in Schade and Crutzen (1995) but approximate the spatial distribution and seasonal variations of amine emissions following those of ammonia. Such a first order approximation enables us to simulate the typical concentrations of amines in the global atmosphere. The dry and wet deposition, as well as horizontal and vertical transport of amines, is also considered in GEOS-Chem, following the approaches for ammonia.

In the present study, we only take into account the oxidation of methylamines by OH as the oxidation of amines by NO_3 and O_3 is small. There have been limited measurements of the kinetics of OH reactions with simple alkyl amines (Ge et al., 2011a; Nielsen et al., 2012; Lee and Wexler, 2013). In this study we use the reaction coefficient ($6.54 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) reported by Atkinson et al. (1978). The uptake of amines by particles is considered, using the particle surface areas calculated from particle size distributions predicted by GEOS-Chem-APM. One key uncertainty about the heterogeneous uptake is the uptake coefficient (γ), defined as the ratio of gas surface collisions that result in loss of the amines onto the surface to the total gas surface collisions. Lloyd et al. (2009) reported a reactive uptake coefficient of 2×10^{-3} for the uptake of TMA by ammonium nitrate aerosols at 20 % RH. Wang et al. (2010b) studied the uptake of alkylamines (MMA, DMA and TMA) on sulfuric acid surfaces and found uptake coefficients in the range of $(2.0 - 4.4) \times 10^{-2}$. In a laboratory study of the heterogeneous reactions between alkylamines (MMA, DMA and TMA) and ammonium salts

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Figure 1 shows the horizontal distributions of DMA emissions assumed in the present study. As mentioned earlier, we use the estimated DMA emission flux of 33 Gg N yr^{-1} as given in Schade and Crutzen (1995) but approximate the spatial distribution and seasonal variations of DMA emissions following those of ammonia. Again, this should be considered as a first order approximation, as the emission rates of amines from various sources may be quite different from those of ammonia. With the understanding of this limitation, we can see from Fig. 1 that DMA emission rates are in the range of ~ 0.2 to $10 \text{ kg N km}^{-2} \text{ yr}^{-1}$ over major continents and below $0.2 \text{ kg N km}^{-2} \text{ yr}^{-1}$ over oceans. In Fig. 1 we also marked the locations of sites where some kind of DMA measurements are available, as summarized in Table 1. It should be noted that sites A, B, D, and G are close to each other and overlap in Fig. 1. Similarly, sites E and F overlap in Fig. 1. Sites J and K are the same location but measurements were taken during different time periods. A comparison of simulated and observed DMA concentrations is discussed later.

Figure 2 shows the simulated horizontal distributions of annual mean DMA lifetime (τ) and concentration ($[\text{DMA}]$) in the model surface layer (0–150 m above surface) under two aerosol uptake coefficients: Fig. 2a and b $\gamma = 0$ (i.e., oxidation only) and Fig. 2c and d $\gamma = 0.03$ (uptake by sulfuric acid particles). The corresponding zonally averaged vertical distributions of τ and $[\text{DMA}]$ are given in Fig. 3. The oxidation only condition (i.e., no aerosol uptake) leads to a DMA lifetime of 2–5 h in most parts of lower and middle latitude regions, from the surface to the upper troposphere. The oxidation lifetime is relatively long (10–50 h) over the high latitude regions due to low OH concentrations there. The aerosol uptake with $\gamma = 0.03$ (upper limit, corresponding to the uptake by sulfuric acid particles) cuts the lifetime of DMA by half or more over the major continents, resulting in a DMA lifetime less than one hour over central Europe, east Asia, and the eastern US (Fig. 2c). Our sensitivity study indicates that τ values decrease with increasing γ when $\gamma > 0.001$ but become insensitive to γ when $\gamma < 0.001$, as oxidation dominates the lifetime under this condition.

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As a result of short the DMA lifetime, high [DMA] are generally confined to the source regions (Figs. 1 and 2b, d). Depending on the uptake coefficients, [DMA] in the surface layer over major continents is in the range of 0.1–1 ppt when $\gamma = 0.03$ and 0.5–10 ppt when $\gamma = 0$. [DMA] decreases quickly for altitudes (Fig. 2b and d), with zonally averaged values dropping below 0.1 ppt a few hundred meters above the surface (Fig. 3). [DMA] over oceans are below 0.05 ppt and these DMA are emitted from marine organisms (Fig. 1) rather than transported from continents. [DMA] over polar regions is below 0.01 ppt (Figs. 2 and 3) due to the lack of emissions there (Fig. 1).

Figure 4 compares the simulated annual mean [DMA] with measurements at the sites listed in Table 1 and marked in Fig. 1. The modeling results under four γ values (0.03, 0.01, 0.001, and 0) are given. It is clear from Table 1 that, based on very limited measurements currently available, [DMA] in urban areas is smaller than those in rural and coastal areas. Over the Arabian Sea, measurements of two periods differ by a factor of 5, indicating a large temporal variation in amine concentrations. Figure 4 shows that the simulated [DMA] are close to the measured values for the various urban sites but are substantially lower than those at the rural, coastal, and marine sites. The underestimation can not be explained by the possible uncertainty in the uptake coefficients. It is unclear how much the underestimation is associated with the spatial ($4^\circ \times 5^\circ$ model grid box with a depth of ~ 150 m vs. measurements at given sites near surface) and temporal (model annual mean vs. measurements a few days to a few weeks) average. If the measurements are representative and reflect the real DMA concentrations, then our simulations suggest that the DMA emissions in the rural, coastal, and marine areas could be much larger than those shown in Fig. 1.

To examine the effect of emissions on amine concentrations, we increase the emission flux of DMA to the total methylamine flux of 285 Gg N yr^{-1} , as estimated by Schade and Crutzen (1995). The resulting horizontal distributions of amine concentrations in the surface layer under four different uptake coefficients ($\gamma = 0.03, 0.01, 0.001, \text{ and } 0$) are presented in Fig. 5. The results in Fig. 5 can be viewed either as the impact of emission flux on [DMA] or the effect of uptake coefficients on methylamines concentra-

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tions. A comparison of Figs. 5a with 2b and 5d with Fig. 2d shows that, as expected, [DMA] is proportional to the emission flux. DMA emissions in certain regions could be much larger while, in other regions, much lower than those shown in Fig. 1. Due to the short lifetime of amines, long range transport is not important, thus the observed amine concentrations can be used to estimate the emission strength in the region. The under-prediction of DMA by one to two orders of magnitude in the rural and coastal areas (Fig. 4) may indicate that the DMA emissions in these regions are one to two orders of magnitude larger than those shown in Fig. 1. Apparently long-term measurements of amines at more locations are needed to evaluate the potential importance of amines.

Figure 5 also shows that, with total estimated flux of 285 Gg N yr^{-1} , the concentration of methylamines in the surface layer over major continents is $\sim 1\text{--}10$ ppt when $\gamma = 0.03$ and can reach up to $5\text{--}50$ ppt if aerosol uptake is not considered (i.e., $\gamma = 0$). Aerosol uptake is most important in the regions of high anthropogenic emissions (North America, Asia, and Europe) and the decrease of γ from 0.03 to 0.001 increases the modeled amine concentrations by a factor of ~ 5 over these regions. As mentioned earlier, further decreases of γ from 0.001 to 0 has small effects on the predicted amine concentrations (Fig. 5a and b). Methylamine concentrations in the surface layer over oceans are below 0.5 ppt and are not affected by γ values as the uptake of amines by sea salt is not considered in the present study.

4 Summary and discussion

As a result of the substitution by one or more organic functional groups, amines have stronger basicity than ammonia and may participate in new particle formation in the atmosphere. To integrate the various processes controlling amines concentrations and understand the concentrations of key amines and their spatiotemporal variations in the atmosphere, we simulate the global distributions of amines in the air with a global

chemistry transport model (GEOS-Chem), focusing on dimethylamine (DMA) in particular and methylamines in general.

Our simulations show that the oxidation only (i.e., no aerosol uptake) leads to a DMA lifetime of 2–5 h in most part of low and middle latitude regions, from the surface to the upper troposphere. The oxidation lifetime is relatively longer (10–50 h) over the high latitude regions due to low OH concentration there. The aerosol uptake with uptake coefficient (γ) of 0.03 (corresponding to the uptake by sulfuric acid particles) cuts the lifetime of DMA by half or more over the major continents, resulting in DMA lifetime less than one hour over central Europe, East Asia, and Eastern US. As a result of the short lifetime, high [DMA] are generally confined to the source regions. Depending on the uptake coefficients, [DMA] in the surface layer over major continents is in the range of 0.1–1 ppt when $\gamma = 0.03$ and 0.5–10 ppt when $\gamma = 0$. [DMA] over oceans are below 0.05 ppt and [DMA] over polar regions is below 0.01 ppt. [DMA] decreases quickly with altitudes, with zonally averaged values dropping below 0.1 ppt a few hundred meters above the surface. Our simulations indicate that total concentrations of methylamines are about one order of magnitude higher. Aerosol uptake is most important in the regions of high anthropogenic emissions (North America, Asia, and Europe) and the decrease of γ from 0.03 to 0.001 increases the modeled amines concentrations by a factor of ~ 5 over these regions. Further decrease of γ from 0.001 to 0 has small effects on the predicted amines concentrations. Simulated [DMA] are close to the measured values for several urban sites but are substantially lower than those at the rural, coastal, and marine sites. The underestimation can not be explained by the possible uncertainty in the uptake coefficients and long range transport. The under-prediction of DMA by one to two orders of magnitude in the rural and coastal areas may indicate that the DMA emissions in these regions are one to two orders of magnitude higher than those assumed in this study. It should be noted that DMA measurements are very limited and subject to large uncertainty as well because of its low concentration and short lifetime.

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Amines have been suggested to be the most likely compound to sequester carbon dioxide and there exists concern about the potential impacts of substantial increases in future amine emissions (Nielsen et al., 2012). Our study indicates that the impact of amine emissions from carbon sequestration is likely to be local rather than global as a result of their short lifetime. The low concentrations of amines away from source regions ($< 0.1\text{--}1$ ppt) suggest that the impact of amines on global new particle formation may be quite limited. Nevertheless, amines can exceed a few ppt over the main source regions and thus may substantially enhance new particle formation. It should be noted that about 150 amines have been identified in the atmosphere and amines of different kinds are likely to have different abilities in stabilizing pre-nucleation clusters. It is important to identify those amines with abundant concentrations in the atmosphere and study their ability in enhancing new particle formation. We would like to emphasize that the present global simulations of methylamines are subject to uncertainties associated with emissions, uptake coefficients, and chemistry. Further laboratory study, field measurement, and numerical modeling are needed to advance our understanding of spatiotemporal distributions of key amines and to evaluate their contributions to new particle formation in the global atmosphere.

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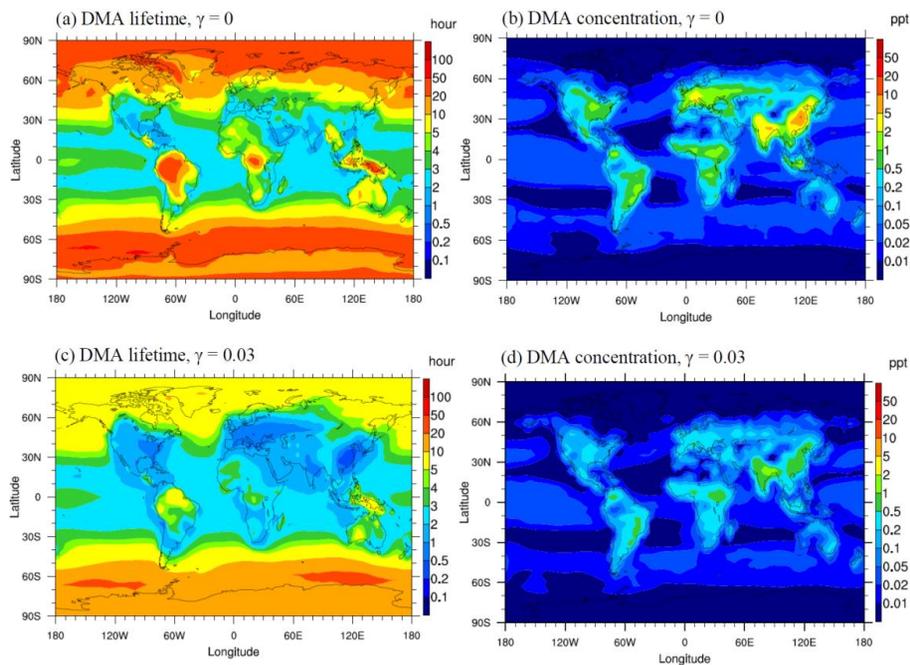


Figure 2. Simulated horizontal distributions of annual mean DMA lifetime and concentration ($[DMA]$) in the model surface layer (0–150 m above surface) under two aerosol uptake coefficients: **(a–b)** $\gamma = 0$ (i.e., oxidation only) and **(c–d)** $\gamma = 0.03$ (uptake by sulfuric acid particles).

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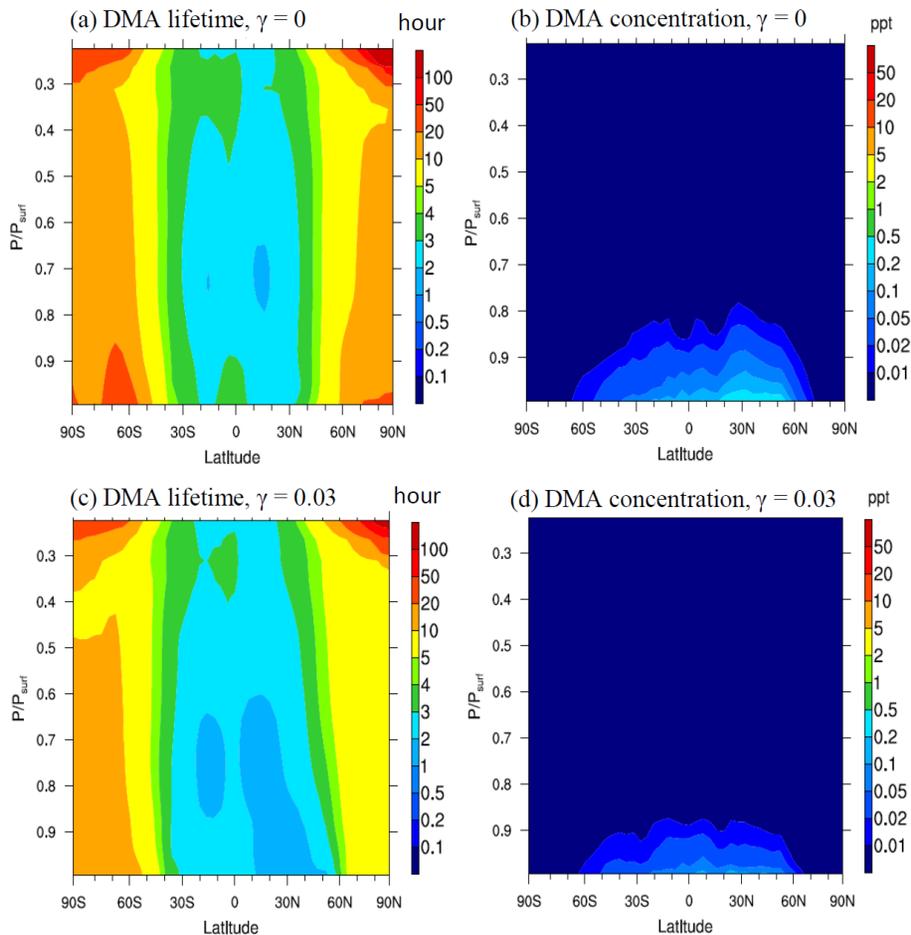


Figure 3. Same as Fig. 2 but for zonally averaged values. Vertical axis is the ratio of pressure (P) at the model layer to the pressure at the surface (P_{surf}).

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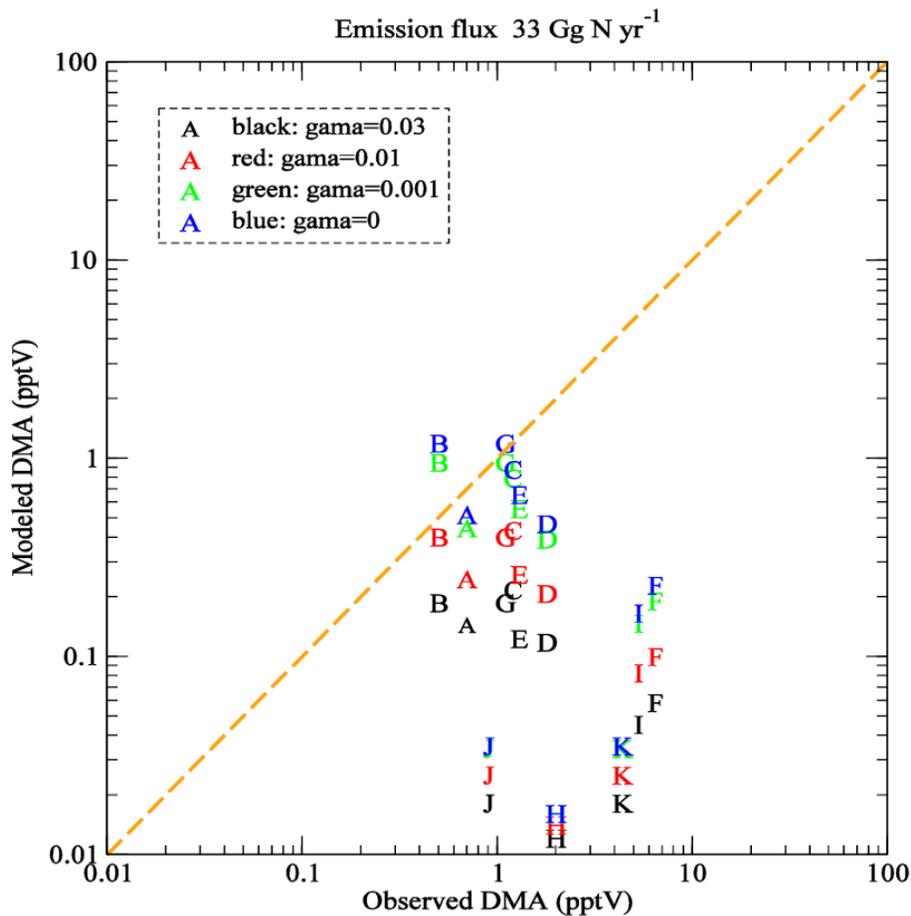


Figure 4. A comparison of simulated and measured [DMA] at the sites listed in Table 1 and marked in Fig. 1.

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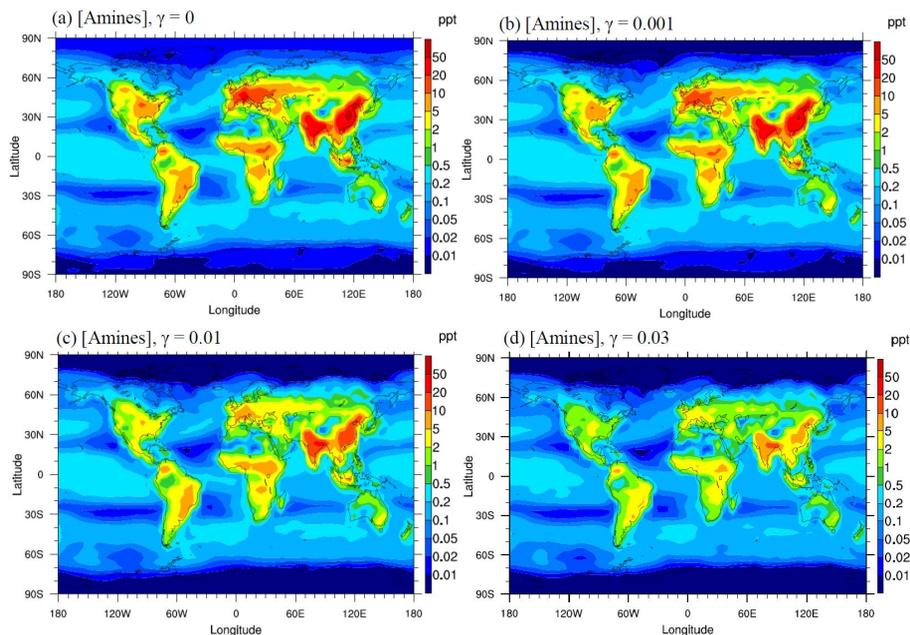


Figure 5. Horizontal distributions of methylamines in the surface layer under four different uptake coefficients ($\gamma = 0.03, 0.01, 0.001$, and 0), with total methylamine flux of 285 Gg N yr^{-1} as estimated in Schade and Crutzen (1995).

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