



Heterogeneous  
reactions of  $N_2O_5$   
with  $TiO_2$

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# Heterogeneous reaction of $N_2O_5$ with airborne $TiO_2$ particles and its implication for stratospheric particle injection

M. J. Tang<sup>1,2</sup>, P. J. Telford<sup>1,4</sup>, F. D. Pope<sup>3</sup>, L. Rkiouak<sup>1,5</sup>, N. L. Abraham<sup>1,4</sup>,  
A. T. Archibald<sup>1,4</sup>, P. Braesicke<sup>1,4,\*</sup>, J. A. Pyle<sup>1,4</sup>, J. McGregor<sup>6</sup>, I. M. Watson<sup>2</sup>,  
R. A. Cox<sup>1</sup>, and M. Kalberer<sup>1</sup>

<sup>1</sup>Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, UK

<sup>2</sup>School of Earth Sciences, University of Bristol, Bristol BS8 1RJ, UK

<sup>3</sup>School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham B15 2TT, UK

<sup>4</sup>National Centre for Atmospheric Science, NCAS, UK

<sup>5</sup>Department of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge CB2 3RA, UK

<sup>6</sup>Department of Chemical and Biological Engineering, University of Sheffield, Sheffield S1 3JD, UK

\* now at: IMK-ASF, Karlsruhe Institute of Technology, Karlsruhe, Germany

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Correspondence to: M. Kalberer (markus.kalberer@atm.ch.cam.ac.uk)

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## Abstract

Injection of aerosol particles (or their precursors) into the stratosphere to scatter solar radiation back into space, has been suggested as a solar-radiation management scheme for the mitigation of global warming.  $\text{TiO}_2$  has recently been highlighted as a possible candidate particle because of its high refractive index, but its impact on stratospheric chemistry via heterogeneous reactions is as yet unknown. In this work the heterogeneous reaction of airborne sub-micrometre  $\text{TiO}_2$  particles with  $\text{N}_2\text{O}_5$  has been investigated for the first time, at room temperature and different relative humidities (RH), using an atmospheric pressure aerosol flow tube. The uptake coefficient of  $\text{N}_2\text{O}_5$  onto  $\text{TiO}_2$ ,  $\gamma(\text{N}_2\text{O}_5)$ , was determined to be  $\sim 1.0 \times 10^{-3}$  at low RH, increasing to  $\sim 3 \times 10^{-3}$  at 60% RH. The uptake of  $\text{N}_2\text{O}_5$  onto  $\text{TiO}_2$  is then included in the UKCA chemistry climate model to assess the impact of this reaction on stratospheric chemistry. While the impact of  $\text{TiO}_2$  on the scattering of solar radiation is chosen to be similar to the aerosol from the Mt. Pinatubo eruption, the impact of  $\text{TiO}_2$  injection on stratospheric  $\text{N}_2\text{O}_5$  is much smaller.

## 1 Introduction

Injection of aerosol particles (or their precursors) into the stratosphere to scatter solar radiation back into space, has been suggested as a solar-radiation management (SRM) scheme for the mitigation of global warming due to the increasing concentrations of greenhouse gases (see, e.g. Shepherd, 2009). Most of the stratospheric particle injection research to date has focused on the use of sulfuric acid particles (Crutzen, 2006; Ferraro et al., 2011) because of their natural presence in the stratosphere (SPARC, 2006). During periods of low volcanic activity there is a background sulphate aerosol layer with a global loading of  $0.65 \pm 0.2 \text{ Tg}$  (SPARC, 2006). However, after large explosive volcanic eruptions the concentration increases dramatically. For example, after the Mt. Pinatubo eruption in the Philippines in 1991 it is estimated that at peak there was

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~ 30 Tg H<sub>2</sub>SO<sub>4</sub> in the stratosphere (Guo et al., 2004; McCormick et al., 1995). Several minerals, including TiO<sub>2</sub>, have recently been suggested as possible alternative candidate particles to be injected into the stratosphere for SRM (Pope et al., 2012), due to their high light scattering ability by virtue of a high refractive index. For instance, the refractive index at 550 nm is 2.5 for TiO<sub>2</sub> compared to 1.5 for the naturally occurring 70wt% H<sub>2</sub>SO<sub>4</sub> particles. The scattering ability of aerosol particles is also dependent upon the size of the particles. Assuming that the size can be optimized, it is estimated that, to achieve the same scattering effect, the use of TiO<sub>2</sub> for SRM requires a factor of ~ 3 less in mass (and a factor of ~ 7 less in volume) than that of H<sub>2</sub>SO<sub>4</sub> aerosols (Pope et al., 2012).

Stratospheric particle injection for SRM would increase the burden of stratospheric aerosols and thus also the surface area available for heterogeneous reactions. The production and/or removal of gas-phase species via heterogeneous reactions could perturb the stratospheric chemistry and impact the stratospheric O<sub>3</sub> level (Molina et al., 1996; Solomon, 1999; Tilmes et al., 2008). Following the eruption of Mt. Pinatubo, low levels of stratospheric ozone were observed, and at the same time also reduced mean global surface temperature (Dutton and Christy, 1992; McCormick et al., 1995).

While the heterogeneous reactions of sulfuric acid particles in the stratosphere are well characterized (Ammann et al., 2013; Sander et al., 2011), the heterogeneous reactivity of mineral surface towards stratospherically important trace gases has seldom been investigated (Crowley et al., 2010), and this impedes us from a reliable assessment of their impact on stratospheric chemistry, and more specifically, stratospheric O<sub>3</sub> (Pope et al., 2012). The heterogeneous reaction of N<sub>2</sub>O<sub>5</sub> (Reaction R1), one of the most important heterogeneous reactions in the stratosphere, converts reactive nitrogen oxides (NO and NO<sub>2</sub>), which are involved in catalytic cycles leading to stratospheric O<sub>3</sub> depletion, to non-reactive nitric acid (Solomon, 1999):



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It has been shown that after the eruption of Mt. Pinatubo, the uptake of  $\text{N}_2\text{O}_5$  onto sulfuric acid particles led to significant change in the partitioning of nitrogen species in the stratosphere (Fahey et al., 1993; Solomon, 1999).

Mineral dust particles are the most abundant aerosol particles in the troposphere on a mass basis (Huneeus et al., 2011; Textor et al., 2006). Tropospheric mineral dust aerosols have a large impact on direct and indirect radiative forcing (Balkanski et al., 2007; Cziczo et al., 2013), and their heterogeneous reactions with several trace gases can significantly influence tropospheric photochemistry (Dentener et al., 1996) and modify the composition of dust particles (Sullivan et al., 2007).  $\text{TiO}_2$ , an important component in natural mineral dust particles (Hanisch and Crowley, 2003; Usher et al., 2003), is of particular interest because heterogeneous reactivity towards some trace gases (e.g.  $\text{NO}_2$ ,  $\text{O}_3$ ) is significantly enhanced under illuminated conditions (Ndour et al., 2008; Nicolas et al., 2009).  $\text{TiO}_2$  is also a well-established photocatalyst for a wide-range of reactions (Linsebigler et al., 1995; Nakata and Fujishima, 2012), including the conversion of  $\text{NO}_x$  species (Bedjanian and El Zein, 2012; Ndour et al., 2008).

$\text{N}_2\text{O}_5$ , mainly formed at nighttime due to the reaction of  $\text{NO}_2$  with  $\text{NO}_3$  radicals (Wayne et al., 1991), is an important temporary reservoir for  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ), and its uptake onto aerosol particles contributes to the removal of  $\text{NO}_x$  and the formation of particulate nitrate (Brown et al., 2006; Brown and Stutz, 2012), and the production of  $\text{ClNO}_2$  (Phillips et al., 2012; Thornton et al., 2010), an important precursor of Cl atoms in the troposphere.

Although the kinetics of the uptake of  $\text{N}_2\text{O}_5$  onto desert dust particles and their surrogates (e.g. Arizona Test Dust, illite) has been reported by several previous studies (Karagulian et al., 2006; Mogili et al., 2006; Seisel et al., 2005; Tang et al., 2010, 2012, 2014; Wagner et al., 2008, 2009), to the best of our knowledge, the reaction of  $\text{N}_2\text{O}_5$  with  $\text{TiO}_2$  has never been studied. In this work an aerosol flow tube was deployed to investigate the kinetics of the heterogeneous reaction of  $\text{N}_2\text{O}_5$  with airborne submicron  $\text{TiO}_2$  particles at room temperature and at different relative humidities (RH).

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Telford et al. (2009) used the UMUKCA chemistry-climate model to attribute ozone changes due to volcanic aerosol after the Mt. Pinatubo eruption in 1991. Here, we use a successor of this model to assess the effect of N<sub>2</sub>O<sub>5</sub> uptake onto TiO<sub>2</sub> particles on the stratospheric composition. We construct a case study based on the eruption of Mt. Pinatubo, comparing the effects of TiO<sub>2</sub> to those from the volcanic sulfate and to a situation with only background aerosol amounts present. The changes in reactive nitrogen species and ozone due to the heterogeneous reaction of TiO<sub>2</sub> with N<sub>2</sub>O<sub>5</sub> are assessed relative to sulfate aerosol impacts.

## 2 Methodologies

### 2.1 Experimental section

A new atmospheric pressure aerosol flow tube was deployed to investigate the heterogeneous reaction of N<sub>2</sub>O<sub>5</sub> with airborne TiO<sub>2</sub> particles. The schematic diagram of the aerosol flow tube is shown in Fig. 1. Since it is presented for the first time, a detailed description of the aerosol flow tube is given in this study. All experiments were carried out at 296 ± 2 K, and N<sub>2</sub> was used unless otherwise stated.

#### 2.1.1 Aerosol flow tube

The atmospheric-pressure aerosol flow tube (AFT) is a horizontal-mounted Pyrex tube with an inner diameter of 30 mm and a length of 100 cm. The total flow in the AFT, was 1550 mL min<sup>-1</sup> at 1 bar and room temperature, resulting in a linear flow velocity of 2.36 cm s<sup>-1</sup>, a maximum residence time of ~ 40 s, and a Reynolds number of 46, i.e. the flow was laminar. The entrance length required to develop the laminar flow and the mixing length were calculated to be ~ 8 cm and ~ 13 cm, respectively (Keyser, 1984), using a diffusion coefficient of 0.085 cm<sup>2</sup> s<sup>-1</sup> for N<sub>2</sub>O<sub>5</sub> (Wagner et al., 2008). For all the experiments, only the middle part of the flow tube (30–80 cm) where the gases have

been well mixed and the laminar flow has been fully developed was used to measure the uptake kinetics.

TiO<sub>2</sub> aerosols, after being adjusted to the desired RH, were introduced into the top of the AFT via the side arm, and N<sub>2</sub>O<sub>5</sub> was delivered into the center of the flow tube via a stainless-steel injector. The position of the stainless-steel sliding injector (outer diameter: 6 mm) could be adjusted to vary the interaction time of N<sub>2</sub>O<sub>5</sub> with airborne TiO<sub>2</sub> particles. The inner wall of the AFT was coated with an inert FEP (Dupont FEP 121A) film to reduce the loss of gaseous N<sub>2</sub>O<sub>5</sub> onto the wall. The RH and the total flow rate in the flow tube were measured both before and after each experiment.

### 2.1.2 Aerosol generation and characterization

TiO<sub>2</sub> aerosols were generated by atomizing a P25 TiO<sub>2</sub>/water suspension (with a TiO<sub>2</sub> mass fraction of 1–2%) with ~3 bar N<sub>2</sub> using a commercial constant output atomizer (Model 3076, TSI, USA). The TiO<sub>2</sub>/water suspension was constantly stirred using a magnetic stirrer, in order to keep the suspension homogeneous so that the generated aerosol would have a constant number concentration and stable size distribution. The resulting aerosol flow (~3000 mL min<sup>-1</sup>) was delivered through 1–3 (depending on the desired RH in the flow tube) diffusion dryers in series. The aerosol flow then passed through a Berner cascade impactor (not shown in Fig. 1) with a cut-off size of 1 μm at a flow rate of 3000 mL min<sup>-1</sup>, in order to remove super-micrometer particles. A fraction of the aerosol flow was then pumped away (F1). The remaining aerosol flow was either delivered through a filter (not shown in Fig. 1) to remove all the particles, or alternatively the filter could also be bypassed. The aerosol flow was conditioned to desired RH and diluted to a total flow of 1800 mL min<sup>-1</sup> (by F2 and F3, as shown in Fig. 1). After that, 300 mL min<sup>-1</sup> of the aerosol flow was sampled into an SMPS to measure the number concentration and size distribution, and the remaining 1500 mL min<sup>-1</sup> flow was delivered into the aerosol flow tube via the side arm. Metal (outer diameter: 0.25") or conductive silicone (TSI, inner diameter: 0.19") tubing was used to deliver aerosols, in order to minimize the loss of TiO<sub>2</sub> particles during transport.

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A Scanning Mobility Particle Sizer (SMPS) was used to characterize the number concentration and size distribution of  $\text{TiO}_2$  aerosol particles online. It consists of a Differential Mobility Analyzer (TSI 3081), and a Condensation Particle Counter (TSI 3775) which was operated at a sampling flow rate of  $300 \text{ mL min}^{-1}$ . The sheath flow in the DMA was set to  $3000 \text{ mL min}^{-1}$ , resulting in a detectable mobility size range of 14–672 nm. The time resolution of the SMPS measurement is 150 s. The measured number concentration and size distribution were quite stable, and the variation of aerosol surface area concentration is typically  $< 5\%$  during each experiment (typically  $\sim 60$ –80 min), as shown in Table 1. A typical size distribution of  $\text{TiO}_2$  aerosols used in this study is shown in Fig. 2, suggesting that the contribution of undetected larger particles (with mobility diameters  $> 672 \text{ nm}$ ) to the total surface area concentration is negligible. For  $\text{TiO}_2$  aerosols used in this work,  $dN/d\ln D_d$  maximizes around 150 nm, and the average surface area of one  $\text{TiO}_2$  particle is  $\sim 9.0 \times 10^{-10} \text{ cm}^2$ . The mobility diameters measured by the SMPS are used to calculate the surface area which is then used to calculate the uptake coefficient, though we note that  $\text{TiO}_2$  particles used in this work are non-spherical and thus the mobility diameter based surface area can be different from the true surface area. The BET surface area was determined to be  $8.3 \text{ m}^2 \text{ g}^{-1}$ ,  $\sim 60\%$  larger than the mobility diameter based surface area, i.e.  $\sim 5.7 \text{ m}^2 \text{ g}^{-1}$ .

### 2.1.3 $\text{N}_2\text{O}_5$ generation

Crystalline  $\text{N}_2\text{O}_5$  was synthesized by mixing a small flow of pure NO with  $500 \text{ mL min}^{-1}$   $\text{O}_3/\text{O}_2$  in a glass reactor and trapping the product at  $-78^\circ\text{C}$  using a cold finger immersed in an ethanol-dry ice bath.  $\text{O}_3$  was generated by electrical discharge of  $\text{O}_2$  which had been delivered through a  $\text{P}_2\text{O}_5/\text{silica}$  gel scrubber to remove any residual water vapour before entering the electrical discharger. After mixing NO with  $\text{O}_3/\text{O}_2$  in the glass reactor, brown colour appeared initially, indicating the formation of  $\text{NO}_2$  (Reaction R2). The brown colour mostly disappeared at the end of the reactor, suggesting



that most of the NO<sub>2</sub> was converted to N<sub>2</sub>O<sub>5</sub> (Reactions R3 and R4a):



The synthesised N<sub>2</sub>O<sub>5</sub> crystals were stored in an ethanol bath kept at  $-50^\circ\text{C}$  using a cryostat. In order to further purify the N<sub>2</sub>O<sub>5</sub> sample, the following procedure was repeated a few times after the cryostat was warmed to  $-20^\circ\text{C}$ : (i) the cold finger was connected to the vacuum line; (ii) the cold finger was disconnected from the vacuum line (by shutting the valve) and the cold finger was filled with dry N<sub>2</sub> (which was passed through a P<sub>2</sub>O<sub>5</sub>-silica gel scrubber) to  $\sim 1$  bar; (iii) the cold finger was disconnected from the dry N<sub>2</sub> flow, and then connected to the vacuum line. This procedure was found to largely reduce the NO<sub>2</sub> level associated with N<sub>2</sub>O<sub>5</sub>. A small N<sub>2</sub> flow (F5 in Fig. 1, usually  $5\text{--}10\text{ mL min}^{-1}$ ) was passed through a P<sub>2</sub>O<sub>5</sub>/silica scrubber (to remove any residual water vapour) and then used to elute gaseous N<sub>2</sub>O<sub>5</sub> from the crystalline sample. The resulting N<sub>2</sub>O<sub>5</sub> flow was diluted by another N<sub>2</sub> flow (F6) to a total flow of  $50\text{ mL min}^{-1}$  and then delivered into the centre of the aerosol flow tube through a 1/8" Teflon tube in the sliding injector.

#### 2.1.4 N<sub>2</sub>O<sub>5</sub> detection

The bottom 30 cm of the AFT was coaxially inserted into another FEP-coated Pyrex tube with a length of 60 cm and an inner diameter of 43 mm. A sheath flow of  $1500\text{ mL min}^{-1}$  (F4) was fed into the annular space between the two coaxial Pyrex tubes. The aerosol flow in the flow tube had the same linear flow velocity as the sheath flow in order to minimize the turbulence when they were mixed at the end of the AFT. Gases, including N<sub>2</sub>O<sub>5</sub>, could exchange between the sheath flow and the aerosol flow because their diffusion coefficients are around  $0.1\text{ cm}^2\text{ s}^{-1}$ , while airborne particles remain in the centre due to their very small diffusion coefficients ( $10^{-7} - 10^{-6}\text{ cm}^2\text{ s}^{-1}$ ,

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Hinds, 1996). At the end of the larger Pyrex tube,  $\sim 500 \text{ mL min}^{-1}$  was sampled through a  $1/4''$  Teflon tube which intruded 1–2 mm into the inner wall of the larger tube. The sampled flow was checked by a CPC and the measured particle number concentration was less than  $10 \text{ cm}^{-3}$  even when the number concentration of the TiO<sub>2</sub> aerosols in the AFT reached  $\sim 1 \times 10^7 \text{ particles cm}^{-3}$ . This novel gas-particle separation method in the aerosol flow tube study was first presented by Rouviere et al. (2010), and the current design was previously described by Tang et al. (2012).

The  $500 \text{ mL min}^{-1}$  particles-free air sampled from the AFT was mixed with a small flow ( $\sim 5 \text{ mL min}^{-1}$ , controlled by a mass flow controller) of NO (100 ppmv in N<sub>2</sub>) and then delivered into a glass reactor which was heated to 100 °C. N<sub>2</sub>O<sub>5</sub> was thermally decomposed to NO<sub>2</sub> and NO<sub>3</sub> radicals (Reaction R4b), which was then titrated by NO to form NO<sub>2</sub> (Reaction R5):



The change in NO concentration, is equal to the N<sub>2</sub>O<sub>5</sub> concentration. The glass reactor used in this work has a volume of  $\sim 30 \text{ cm}^3$  (with a length of 10 cm and an inner diameter of 2 cm), leading to a residence time of  $\sim 3 \text{ s}$  at a flow rate of  $\sim 500 \text{ mL min}^{-1}$ . At atmospheric pressure and 90 °C, the lifetime of N<sub>2</sub>O<sub>5</sub> with respect to thermal decomposition (Reaction R4b) is around  $\sim 0.05 \text{ s}$  and the lifetime of NO<sub>3</sub> radicals due to the titration by 1 ppmv NO (Reaction R5) is  $\sim 0.002 \text{ s}$ , as detailed by Wagner et al. (2008). The residence time in the reactor is much longer than the lifetime of N<sub>2</sub>O<sub>5</sub> and NO<sub>3</sub> under our experimental condition, ensuring that all the N<sub>2</sub>O<sub>5</sub> should be decomposed and then titrated by NO.

The NO concentration was measured by a chemiluminescence-based nitrogen oxides analyzer (Model 200E, Teledyne Instruments, USA), which has a sampling flow rate of  $500 \text{ mL min}^{-1}$  ( $\pm 10\%$ ) and a detection limit of  $\sim 0.5 \text{ ppbv}$  with a time resolution of 1 min. The NO measurement was calibrated using a certificated NO standard.

## 2.1.5 Chemicals

Pure NO (with a purity of > 99 %) in a lecture bottle and the 100 ppmv NO in N<sub>2</sub> (with actual mixing ratio within ±1 % deviated from the stated value) were both supplied by CK Gas (UK). N<sub>2</sub> and O<sub>2</sub> were provided by BOC Industrial Gases (UK). P25 TiO<sub>2</sub> particles were purchased from Degussa-Hüls AG (Germany) as dry powder, and have an anatase to rutile ratio of 3 : 1.

## 2.2 Model description

The UKCA chemistry climate model in its whole atmosphere configuration (Braesicke et al., 2014; Telford et al., 2014) was used to simulate the effects of the heterogeneous reaction of TiO<sub>2</sub> with N<sub>2</sub>O<sub>5</sub> in the stratosphere. This is a relatively new configuration that combines the well established tropospheric (O'Connor et al., 2014) and stratospheric (Morgenstern et al., 2009) versions of the model. It includes the O<sub>x</sub>, HO<sub>x</sub> and NO<sub>x</sub> chemical cycles and the oxidation of CO, ethane, propane, and isoprene in addition to chlorine and bromine chemistry including heterogeneous processes on polar stratospheric clouds (PSCs) and liquid sulfate aerosols.

We adopt an approach based on our previous study of the effects of the Pinatubo eruption on stratospheric ozone (Telford et al., 2009). Telford et al. (2009) used the UKCA model in a “nudged” configuration to constrain the dynamics of the model to observations (Telford et al., 2008, 2013), and examined the differences in ozone between scenarios with and without stratospheric sulfate aerosol caused by the Mt. Pinatubo eruption. Here we consider a further scenario in which we introduce raised levels of TiO<sub>2</sub> into the stratosphere.

It has been suggested that in order to achieve the same solar radiation scattering effect as the eruption of Mt. Pinatubo, 10 Tg TiO<sub>2</sub> aerosol particles with an assumed radius of 70 nm are needed (Pope et al., 2012). The total mass of TiO<sub>2</sub> particles (10 Tg) is converted to the total surface area, based on the known density (4.23 g cm<sup>-3</sup>) and radius (70 nm). In the model the global distribution of the surface area concentration of

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TiO<sub>2</sub> aerosol is derived from that of the Pinatubo aerosol, scaling to take account of differences in the global mass, particle size and density. The sulfate aerosol surface area concentration was derived from the SPARC climatology (SPARC, 2006). We perform two simulations for the TiO<sub>2</sub> scenario in which the uptake of N<sub>2</sub>O<sub>5</sub> onto TiO<sub>2</sub> aerosols is included using two different uptake coefficients, i.e. 0.001 and 0.005, respectively. The two uptake coefficients used in the model are constrained by the experimental measurements, as detailed in Sect. 3. We compare these with a simulation with aerosols set to a background level and with a simulation with volcanically induced sulfate aerosols present. The 1990 stratospheric aerosol loading is chosen to represent the background condition (Telford et al., 2009). We examine the results over the course of 1992, as the effects of the eruption on the stratospheric chemistry were largest then, caused by the spread of the aerosols towards the poles (e.g. Telford et al., 2009). In our approach the loading of both sulfate and TiO<sub>2</sub> is then smaller than their peak loading. This contrasts with some of the figures given in Pope et al. (2012) that concentrate on a time horizon soon after the eruption when the radiative effect was greatest.

### 3 Results and discussion

#### 3.1 Uptake kinetics

The decay of N<sub>2</sub>O<sub>5</sub> in the aerosol flow tube is due to the removal of N<sub>2</sub>O<sub>5</sub> by the wall and its uptake onto the aerosol surface. Under pseudo first-order conditions, e.g. the number of reactive sites is in great excess of the gaseous reactant and hence does not change significantly during the trace gas-particle interaction time, the loss of N<sub>2</sub>O<sub>5</sub> in the aerosol flow tube can be described as

$$[\text{N}_2\text{O}_5]_t = [\text{N}_2\text{O}_5]_0 \cdot \exp[-(k_w + k_a) \cdot t] \quad (1)$$

where  $[\text{N}_2\text{O}_5]_t$  and  $[\text{N}_2\text{O}_5]_0$  are the measured N<sub>2</sub>O<sub>5</sub> concentrations at reaction times of  $t$  and 0, and  $k_w$  and  $k_a$  are the pseudo-first-order loss rates (s<sup>-1</sup>) of N<sub>2</sub>O<sub>5</sub> onto the flow

5 tube wall and the aerosol surface, respectively. In a typical experiment, the total loss rate,  $k_w + k_a$ , was determined by measuring the  $N_2O_5$  concentrations at five different injection positions (corresponding to five different reaction times) with  $TiO_2$  aerosols present in the flow tube. Before and after measuring the total loss rate, the wall loss rate,  $k_w$ , was determined in a similar way, except passing the aerosol flow through a filter to remove all the  $TiO_2$  particles before it was delivered into the flow tube via the side arm. The difference of  $k_w$  measured before and after introducing  $TiO_2$  aerosols in the AFT was insignificant, indicating that the  $N_2O_5$  wall loss did not change significantly during the uptake experiment.

10 A typical dataset of the measured  $N_2O_5$  mixing ratios at five different injection positions with and without  $TiO_2$  aerosols present in the flow tube is shown in Fig. 3. The measured  $N_2O_5$  loss rate with  $TiO_2$  aerosols present in the AFT was significantly larger than that of the experiments without  $TiO_2$  aerosols, and the difference is equal to  $k_a$ , the loss rate of  $N_2O_5$  onto the aerosol surface. The experimentally measured loss rate of a trace gas in a flow tube under the laminar flow condition is different from the true loss rate, due to the intrinsic non-plug flow condition and the axial and radial diffusion of the trace gas in the flow tube. This effect on the determined  $k_a$  can be corrected using the method described by (Brown, 1978) and it is widely used in aerosol flow tube studies, e.g. (Thornton et al., 2003). The effect is small, with the corrected  $k_a$  only < 5% larger than the measured value. The pseudo first-order loss rate of  $N_2O_5$  onto  $TiO_2$  aerosol surface in the flow tube (after being corrected for the non-plug flow effect, etc.),  $k_a$ , is related to the uptake coefficient of  $N_2O_5$  onto  $TiO_2$  particles by Eq. (2) (Crowley et al., 2010):

$$25 \quad k_a = 0.25 \cdot \gamma_{\text{exp}}(N_2O_5) \cdot c(N_2O_5) \cdot S_a \quad (2)$$

where  $\gamma_{\text{exp}}(N_2O_5)$  is the measured (also called effective) uptake coefficient of  $N_2O_5$ ,  $c(N_2O_5)$  is the average molecular speed of  $N_2O_5$  ( $24\,096\text{ cm s}^{-1}$  at 296 K, Houston, 2001), and  $S_a$  is the surface area concentration ( $\text{cm}^2\text{ cm}^{-3}$ ) of  $TiO_2$  aerosol in the flow tube.

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As shown in Table 1 for each RH 2–4 repeat experiments were performed and Eq. (2) was used to derive the uptake coefficient for each experiment. The surface area concentration of TiO<sub>2</sub> aerosols was varied by a factor of about 2. The uptake coefficients of N<sub>2</sub>O<sub>5</sub> onto TiO<sub>2</sub> particles are quite small ( $< 3 \times 10^{-3}$ ), and very high aerosol concentrations (up to  $4 \times 10^6 \text{ cm}^{-3}$ ) were needed to achieve a significant decay of N<sub>2</sub>O<sub>5</sub> due to the heterogeneous reaction with TiO<sub>2</sub> particles. Thus, it was not possible to vary  $S_a$  over a broad enough range to determine  $\gamma(\text{N}_2\text{O}_5)$  via the slope of a linear fit of  $k_a$  vs.  $S_a$ , equal to  $0.25 \cdot \gamma(\text{N}_2\text{O}_5) \cdot c(\text{N}_2\text{O}_5)$ , as it has been done in previous studies (McNeill et al., 2006; Thornton et al., 2003).

A gradient of the N<sub>2</sub>O<sub>5</sub> concentration close to the particle surface is formed due to the uptake of N<sub>2</sub>O<sub>5</sub> onto the particle surface, leading to the decrease of effective uptake coefficient,  $\gamma_{\text{exp}}(\text{N}_2\text{O}_5)$ , compared to the true uptake coefficient,  $\gamma(\text{N}_2\text{O}_5)$ . This effect can be corrected by using the Fuchs–Sutugin equation (Fuchs and Sutugin, 1970; Poschl et al., 2007):

$$\frac{1}{\gamma(\text{N}_2\text{O}_5)} = \frac{1}{\gamma_{\text{exp}}(\text{N}_2\text{O}_5)} - \frac{0.75 + 0.286Kn}{Kn \cdot (Kn + 1)} \quad (3)$$

where  $Kn$  is the Knudsen number. For mono-dispersed aerosol particles,  $Kn$  given by

$$Kn = \frac{6D(\text{N}_2\text{O}_5)}{c(\text{N}_2\text{O}_5) \cdot d} \quad (4)$$

where  $D(\text{N}_2\text{O}_5)$  is the diffusion coefficient of N<sub>2</sub>O<sub>5</sub> ( $0.085 \text{ cm}^2 \text{ s}^{-1}$  at 1 atm and 296 K, Wagner et al., 2008), and  $d$  is the diameter of the particle (cm), which is assumed to be the mobility diameter measured by the SMPS. For poly-dispersed aerosol particles, e.g. TiO<sub>2</sub> particles used in this work,  $Kn$  can be calculated by

$$Kn = \frac{\sum [Kn(i) \cdot N(i)]}{\sum N(i)} = \frac{6D(\text{N}_2\text{O}_5)}{c(\text{N}_2\text{O}_5)} \cdot \frac{\sum [N(i)/d_i]}{\sum N(i)} \quad (5)$$



coefficient of  $\text{H}_2\text{O}_2$  (Pradhan et al., 2010).  $\gamma(\text{HCHO})$  onto  $\text{TiO}_2$  particles under irradiated conditions (340–420 nm) increases with RH when RH is below 40 %, and a further increase in RH causes the reduction of  $\gamma(\text{HCHO})$  (Sassine et al., 2010).

A close inspection of Fig. 4 further suggests that  $\gamma(\text{N}_2\text{O}_5)$  may decrease with increasing RH between 5–20 % RH and reaches a minimum around 20 % RH, and above that  $\gamma(\text{N}_2\text{O}_5)$  starts to increase with RH. The heterogeneous uptake of  $\text{N}_2\text{O}_5$  onto mineral surfaces is suggested to proceed with two pathways: the reaction of  $\text{N}_2\text{O}_5$  with surface OH groups or the heterogeneous hydrolysis of  $\text{N}_2\text{O}_5$  by surface adsorbed water, whereas the reaction with surface OH groups is faster (Seisel et al., 2005; Tang et al., 2014). FTIR observations showed that surface OH groups on Saharan dust particles were depleted during the exposure to  $\text{N}_2\text{O}_5$ , leading to the decrease of  $\gamma(\text{N}_2\text{O}_5)$  with reaction time (Seisel et al., 2005). The uptake coefficient of  $\text{N}_2\text{O}_5$  onto illite was found to decrease with increasing RH, and this is suggested to be due to the coverage of OH groups by adsorbed water at high RH (Tang et al., 2014). The minimum of  $\gamma(\text{N}_2\text{O}_5)$  onto  $\text{TiO}_2$  at 20 % RH may indicate that the increase of RH up to 20 % could cause the more reactive surface OH groups to be covered by surface adsorbed water, while further increase in RH will promote the heterogeneous hydrolysis of  $\text{N}_2\text{O}_5$  by surface-adsorbed water, i.e. the overall effect of the two competing roles of surface adsorbed water results in a minimum of  $\gamma(\text{N}_2\text{O}_5)$  at  $\sim 20$  % RH.

### 3.3 Comparison with other relevant surfaces

$\text{TiO}_2$  is an important component in tropospheric mineral dust aerosols, and this work is the first time that the heterogeneous reaction of  $\text{N}_2\text{O}_5$  with  $\text{TiO}_2$  aerosols has been investigated. It is interesting to compare  $\gamma(\text{N}_2\text{O}_5)$  onto  $\text{TiO}_2$  particles with that onto other mineral dust particles. Only results reported by aerosol flow tube studies are compared here. Real desert dust and clay minerals show much higher heterogeneous reactivity towards  $\text{N}_2\text{O}_5$ : the uptake coefficient of  $\text{N}_2\text{O}_5$ ,  $\gamma(\text{N}_2\text{O}_5)$ , is  $(1-2) \times 10^{-2}$  for Saharan dust (Tang et al., 2012; Wagner et al., 2008), and  $(4-9) \times 10^{-2}$  for illite (Tang et al., 2014), explained by the high density of surface OH groups in illite (Hatch et al., 2011).  $\gamma(\text{N}_2\text{O}_5)$

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effect of temperature on the heterogeneous reaction of N<sub>2</sub>O<sub>5</sub> with minerals. The weak dependence of  $\gamma(\text{N}_2\text{O}_5)$  onto sulfuric acid particles on temperature, leads us to believe that  $\gamma(\text{N}_2\text{O}_5)$  onto TiO<sub>2</sub> particles under typical lower stratosphere conditions (temperature: 200–220 K; RH: < 40 %) (Dee et al., 2011) should not be larger than a factor of 5 compared to that at room temperature, i.e.  $< 5 \times 10^{-3}$ .

Stratospheric ice particles, an important component in polar stratospheric clouds (PSCs), show significant reactivity towards N<sub>2</sub>O<sub>5</sub>, with  $\gamma(\text{N}_2\text{O}_5)$  of 0.02 at 190–200 K (Crowley et al., 2010), and the reactivity of NAT, another important type of particles in PSCs is much lower, with  $\gamma(\text{N}_2\text{O}_5)$  of around  $\sim 6 \times 10^{-4}$  at 190–200 K (Hanson and Ravishankara, 1991). In addition, a  $\gamma(\text{N}_2\text{O}_5)$  of  $\sim 6.5 \times 10^{-3}$  was measured for sulfuric acid tetrahydrate (SAT) and ranges from  $4 \times 10^{-4}$  to  $1.65 \times 10^{-3}$  (RH dependent) for sulfuric acid monohydrate (SAM) (Crowley et al., 2010).

To summarize, under the conditions investigated P25 TiO<sub>2</sub> particles show much lower reactivity towards N<sub>2</sub>O<sub>5</sub> than sulfuric acid and ice particles and significantly higher reactivity than NAT, and their reactivity towards N<sub>2</sub>O<sub>5</sub> is on the same order of magnitude as SAT and SAM.

### 3.4 Implication for stratospheric particle injection

The impact of N<sub>2</sub>O<sub>5</sub> uptake onto TiO<sub>2</sub> aerosols on the stratospheric trace gas composition is assessed using the UKCA model. Two values of  $\gamma(\text{N}_2\text{O}_5)$  onto TiO<sub>2</sub> aerosol particles were used in the model. The first one is 0.001, equal to the experimentally determined uptake coefficient at room temperature and low relative humidity. The second one is 0.005, which we believe represents the upper limit of  $\gamma(\text{N}_2\text{O}_5)$  onto TiO<sub>2</sub> aerosol particles under typical stratospheric conditions, taking into account the uncertainties associated with temperature (typically 200–220 K) and relative humidities (typically 0–40 %) (Pope et al., 2012).

We note that, at the present at least, the impact of stratospheric aerosols on trace gases is dominated by chlorine activation (Solomon, 1999). Thus, to fully assess the

impact of  $\text{TiO}_2$ , especially on ozone, these further reactions need to be taken into account. However, we can gain an understanding of the relative effect of  $\text{TiO}_2$  compared to sulfuric acid by considering its effect on  $\text{N}_2\text{O}_5$ . We also acknowledge that by choosing to constrain the dynamical changes to those observed after the eruption of Mt.

Pinatubo, whilst allowing us to focus on the changes in heterogeneous chemistry, we neglect differences in the dynamical response and their feedbacks onto the chemistry. The effects of stratospheric aerosols, including  $\text{TiO}_2$ , on stratospheric dynamics have been considered elsewhere (Pope et al., 2012) and we consider it is worthwhile exploring the impacts of heterogeneous chemistry in isolation before constructing case studies with a more elaborate set of feedbacks.

The surface area density of the additional sulfate (i.e., after the Mt. Pinatubo eruption) and  $\text{TiO}_2$  aerosols is shown in Fig. 5. The lower mass loading, higher density, and larger particle size of the  $\text{TiO}_2$  particles all contribute to the much lower surface aerosol density of the  $\text{TiO}_2$  aerosol compared to the Pinatubo sulfate aerosol. The higher density of  $\text{TiO}_2$  and lower projected mass are the main drivers of the decreases in the surface area density. Although our assumption of completely uniform particle size is not realistic, it allows to assess the effects of  $\text{N}_2\text{O}_5$  under idealized conditions.

Figure 6 shows the effects of these extra aerosols on the simulated  $\text{N}_2\text{O}_5$  averaged over 1992. The run with Pinatubo aerosols has lost almost all  $\text{N}_2\text{O}_5$  in the lower stratosphere, around 90 %, compared to the base run. The reductions with the addition of the  $\text{TiO}_2$  aerosols are much smaller, around 20–30 % in much of the lower stratosphere using the higher uptake coefficient (0.005), and only  $\sim 10$  % using the lower value (0.001). One region where there is slightly greater depletion is over Antarctica, and this may be a result of an overestimate of surface area densities caused by extrapolation over the poles. Overall the effects of our simulated  $\text{TiO}_2$  in the stratosphere are considerably lower than the effects of the Pinatubo eruption.

The impacts on ozone are also examined. As in previous model studies (Telford et al., 2009) we found the volcanic sulfate aerosols caused large decreases in ozone (up to 10 % in the northern extra-tropics) in the lower stratosphere caused by increased

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then studied the impact of introducing 10 Tg of TiO<sub>2</sub> into the stratosphere, which has been suggested to produce a radiative effect similar to that of the Mt. Pinatubo eruption (Pope et al., 2012). We found, whilst the aerosols produced appreciable reductions in N<sub>2</sub>O<sub>5</sub> concentration (up to 30% depending on the uptake coefficient), they were significantly smaller in size and extent than those seen after the Mt. Pinatubo eruption, where N<sub>2</sub>O<sub>5</sub> depletion was over 90% through much of the lower stratosphere.

The impact on ozone was also studied, with small increases (2–3%) simulated throughout the stratosphere. These increases are similar to the middle stratospheric increases we found in our previous study of the Mt. Pinatubo eruption, and here we do not calculate any lower stratospheric ozone reduction, which contrasts with the large depletions seen in the lower stratosphere after the Pinatubo eruption. This is the result of the omission of the activation of chlorine on TiO<sub>2</sub> particles in our simple experiment. Therefore, the heterogeneous reactions of TiO<sub>2</sub> with chlorine containing trace gases (e.g. ClONO<sub>2</sub>, HOCl, and HCl) in the stratosphere need to be investigated before we can fully assess the impact of TiO<sub>2</sub> on stratospheric ozone. One previous study (Molina et al., 1997) suggested that the uptake of ClONO<sub>2</sub> onto aluminium oxide and Pyrex glass in the presence of HCl is very efficient, with an uptake coefficient of 0.02, which is > 10 times larger than that onto stratospheric sulfuric acid aerosols. In addition, the uptake of N<sub>2</sub>O<sub>5</sub> onto HCl-doped sulfuric acid (Talukdar et al., 2012) and SiO<sub>2</sub> (Raff et al., 2009) leads to the formation of ClNO<sub>2</sub>, whose photolysis will release Cl atoms and therefore represent a pathway for chlorine activation (Ghosh et al., 2012). Additionally, the potential photocatalytic activity of TiO<sub>2</sub> is likely to play a role, as previous studies on atmospherically relevant mineral dusts indicated enhanced uptake and reactivity of TiO<sub>2</sub> towards NO<sub>2</sub> under irradiation (Ndour et al., 2008). Future studies will address this aspect.

Our simulations, which are designed to focus on chemistry effects, neglect feedbacks between the aerosol heating, the dynamics, and chemistry. However, the nudging has those feedbacks implicitly included for the volcanic aerosol case, which may or may not be a valid and good enough assumption for TiO<sub>2</sub>. Interactive feedbacks could also

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contribute to chemistry changes through factors such as the modification of the QBO (Telford et al., 2009), strengthening of polar vortices (Thomas et al., 2009) and increasing uplift (Rosenfield et al., 1997). Our description of the aerosol particles is also simple; obviously particles with uniform radii distributed as the products of the Pinatubo eruption would be impossible to obtain. Variations in the distribution and radii of the particles will change the surface area density, and thus the chemical and optical impacts. To fully quantify the effects of the injection of any aerosol into the stratosphere a more complete simulation would be required.

Much consideration is required before any solar radiation management scheme could be considered. This will include feasibility studies on the technical, political, social, and environmental feasibility of the scheme. One of the most important considerations is the effect of the scheme on the stratospheric chemistry and in particular the ozone layer. This work shows that the use of TiO<sub>2</sub> might offer benefits, when compared to sulfuric acid, by causing less perturbation to N<sub>2</sub>O<sub>5</sub> chemistry, but further studies are required to fully understand the chemical consequences as discussed above.

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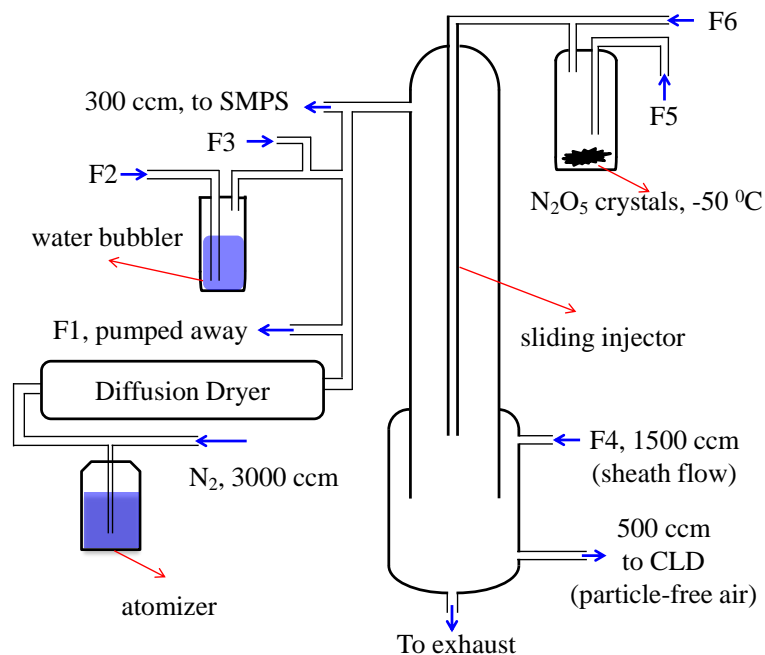
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**Table 1.** Loss rates of N<sub>2</sub>O<sub>5</sub> on TiO<sub>2</sub> ( $k_a$ ), total surface area of TiO<sub>2</sub> particles in the flow tube ( $S_a$ ) and uptake coefficients of N<sub>2</sub>O<sub>5</sub> onto TiO<sub>2</sub> aerosols,  $\gamma(\text{N}_2\text{O}_5)$  at different relative humidities. All the errors shown here are  $1\sigma$  statistically.

RH (%)	$k_a$ ( $\times 10^{-2} \text{ s}^{-1}$ )	$S_a$ ( $\times 10^{-3} \text{ cm}^2 \text{ cm}^{-3}$ )	$\gamma(\text{N}_2\text{O}_5)$ ( $\times 10^{-3}$ )	average $\gamma(\text{N}_2\text{O}_5)$ ( $\times 10^{-3}$ )
5 ± 1	3.02 ± 1.62	4.39 ± 0.26	1.15 ± 0.62	1.22 ± 0.21
	2.64 ± 0.58	3.79 ± 0.06	1.16 ± 0.26	
	2.44 ± 1.11	3.02 ± 0.10	1.35 ± 0.61	
12 ± 2	2.39 ± 0.40	2.75 ± 0.16	1.45 ± 0.24	1.34 ± 0.18
	2.86 ± 0.36	3.80 ± 0.52	1.26 ± 0.16	
	2.65 ± 0.22	2.89 ± 0.33	1.53 ± 0.13	
	1.84 ± 0.24	2.70 ± 0.14	1.14 ± 0.15	
23 ± 2	6.26 ± 0.20	1.75 ± 0.17	0.60 ± 0.19	0.68 ± 0.13
	2.27 ± 0.28	4.89 ± 0.21	0.77 ± 0.01	
33 ± 2	1.00 ± 0.37	2.27 ± 0.16	0.73 ± 0.27	0.86 ± 0.17
	1.27 ± 0.30	2.01 ± 0.12	1.06 ± 0.25	
	1.07 ± 0.26	2.23 ± 0.09	0.80 ± 0.20	
45 ± 3	1.29 ± 0.26	1.59 ± 0.33	1.36 ± 0.27	1.52 ± 0.34
	2.53 ± 0.60	3.00 ± 0.05	1.41 ± 0.31	
	2.91 ± 0.56	2.86 ± 0.05	1.70 ± 0.33	
	2.66 ± 0.58	2.75 ± 0.02	1.62 ± 0.35	
60 ± 3	5.22 ± 1.40	2.86 ± 0.06	3.08 ± 0.82	2.98 ± 1.36
	3.84 ± 1.04	2.24 ± 0.09	2.89 ± 0.78	



**Fig. 1.** Schematic diagram of the aerosol flow tube. SMPS: Scanning Mobility Particle Sizer; CLD: Chemiluminescence Detector, used to measure the  $\text{N}_2\text{O}_5$  concentration (measured as the change in the NO concentration). All the flows (except the flow applied to the atomizer) were controlled by mass flow controllers. Flow details are provided in text.

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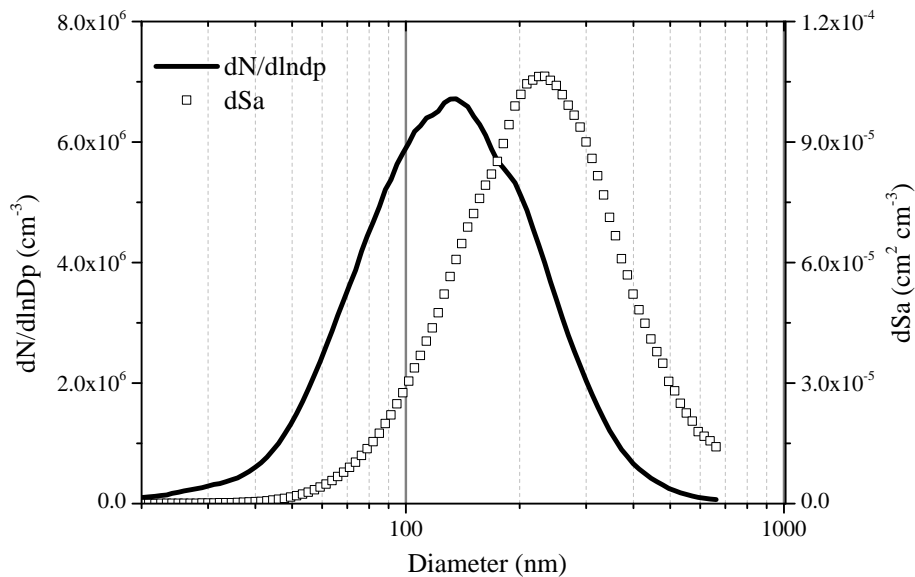
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**Fig. 2.** Typical number (left y axis) and surface (right y axis) size distribution (mobility diameter, measured by the SMPS) of  $\text{TiO}_2$  aerosols used in this study.

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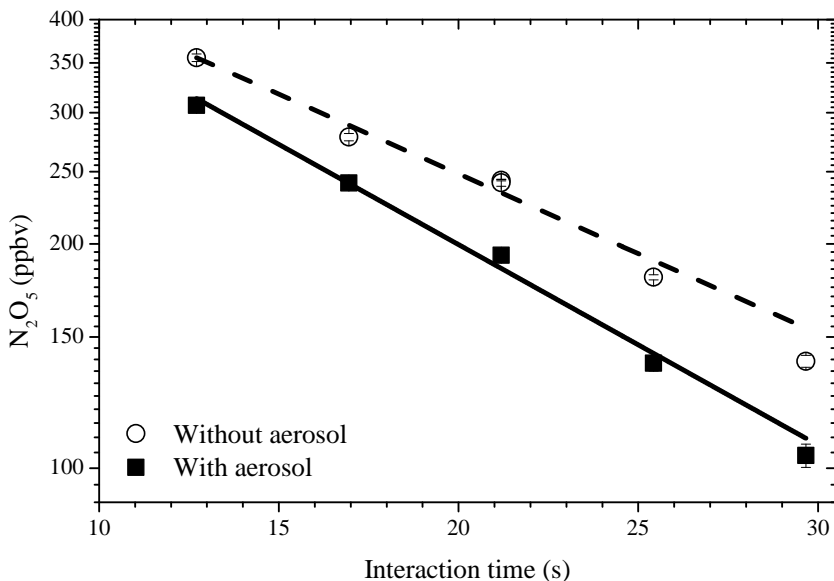
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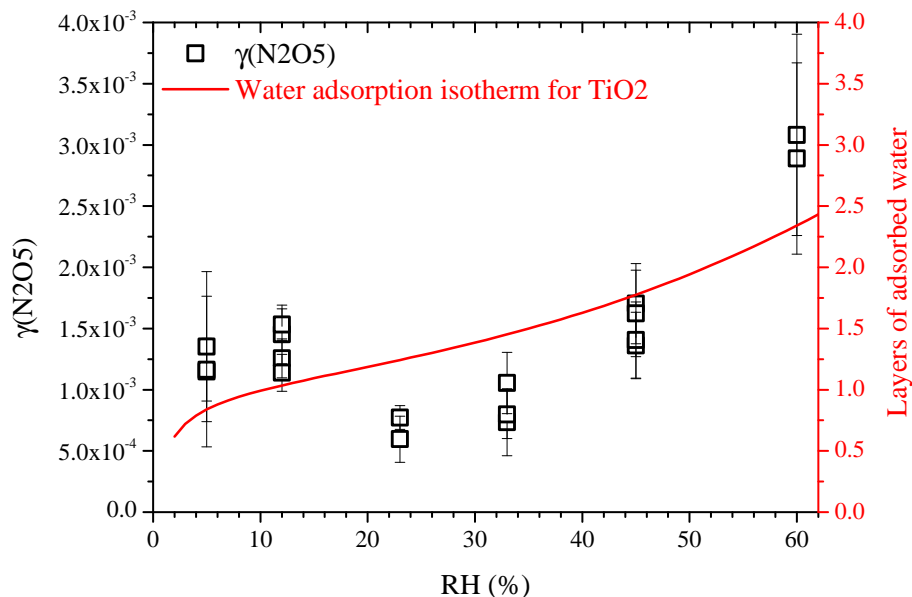


**Fig. 3.** Measured  $\text{N}_2\text{O}_5$  mixing ratios at different  $\text{N}_2\text{O}_5$ - $\text{TiO}_2$  interaction times, i.e. at different injection positions, with (solid squares) and without (open circles)  $\text{TiO}_2$  aerosols in the flow tube. The pseudo first order decay rates of  $\text{N}_2\text{O}_5$  are  $0.0493 \pm 0.0025$  and  $0.0619 \pm 0.0030 \text{ s}^{-1}$  without and with  $\text{TiO}_2$  aerosols in the flow tube, respectively.

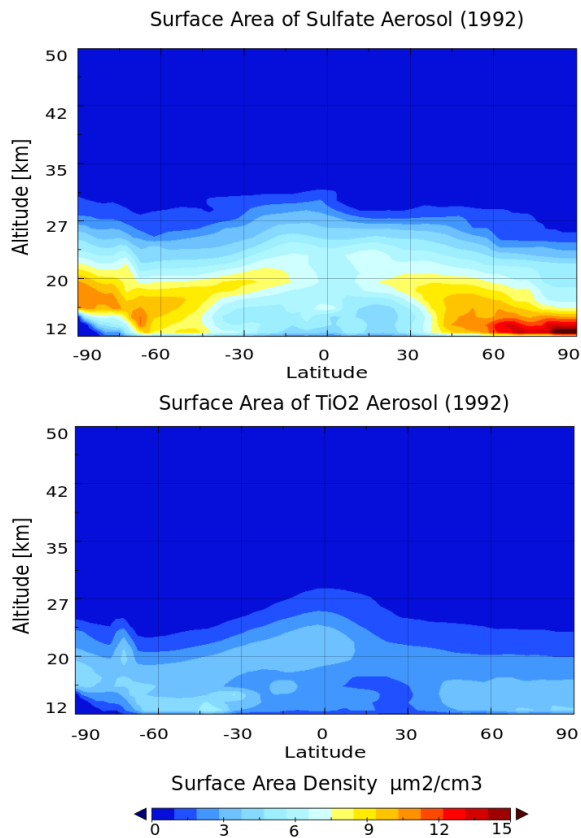
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**Fig. 4.** Uptake coefficients of  $\text{N}_2\text{O}_5$  onto airborne  $\text{TiO}_2$  particles (black squares, left x axis) at different relative humidities. The number of layers of the adsorbed water on  $\text{TiO}_2$  particles (red curve, right y axis) at 296 K, reported by Goodman et al. (2001), is also plotted as a function of RH.



**Fig. 5.** Surface area density ( $\mu\text{m}^2 \text{cm}^{-3}$ ) of sulfate particles after the Mt. Pinatubo eruption (top panel) and of  $\text{TiO}_2$  particles (bottom panel) which generate the same radiative effect as the sulfate particles in the top panel (Pope et al., 2012) and which were used in the simulations shown in Fig. 6.

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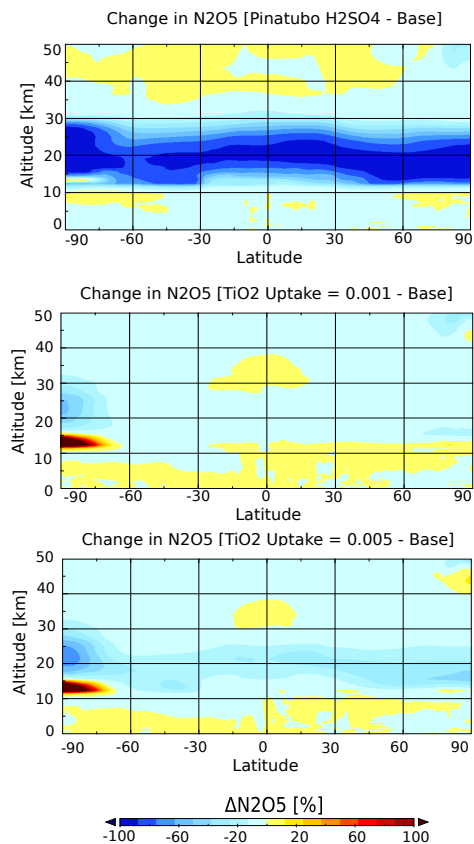
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**Fig. 6.** Simulated changes in  $N_2O_5$  concentrations caused by Mt. Pinatubo eruption (top), and  $TiO_2$  injection with  $\gamma(N_2O_5)$  of 0.001 (middle) and 0.005 (bottom).