

Dear reviewers,

Please find the enclosed revision of our manuscript '*Is the photochemistry activity weak during haze events? — A novel exploration on the photoinduced heterogeneous reaction of NO₂ on mineral dust*'. The point-by-point replies to the comments are attached on the following pages. We colored **red** in the revised manuscript to the corrections. Thank you for your valuable suggestions.

Sincerely yours,

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Anonymous Referee #1

This study evaluates the formation of nitrite and nitrate by light-induced heterogeneous reactions of gaseous NO₂ on TiO₂ used as a proxy for mineral dust. The obtained laboratory results are compared with the behavior of nitrite and nitrate from sampled ambient aerosols. There are number of previous studies on this topic and the results from this study add to the current knowledge on this topic. This study is within the scope of Atmospheric Chemistry and Physics. The work presented here is overall well done, however I am still reluctant to follow the authors' general conclusion in the importance of illumination conditions for nitrite and nitrate formation, mainly due to a few shortcomings of the study that need to be addressed and clarified before the paper should be considered for publication.

General comments:

(1) The light intensities are given in mW cm⁻². How were these values measured? Are they integrated values in certain wavelength range? How do they correlate with the solar actinic flux?

Answer:

Thanks for your comments.

The light intensity in laboratory experiments were measured using an optical power meter. We have added details into the method section (line 102-104). *'Herein, ten light intensity levels (0.0, 0.3, 5.4, 17.5, 23.8, 30.5, 54.5, 98.5, 128.1, and 160.0 mW·cm⁻²) were referred based on the measurement by an optical power meter (CEL-NP2000, Beijing Ceaulight Co., LTD, China).'*

The wavelength distribution of the Xenon lamps are consistent with that of solar irradiation (Figure S3). Hence, the light from these lamps is comparable with the real sunlight. The unit of light intensity is mW/cm², defined as the solar energy per contact area.

(2) The NO₂ mixing ratio of 15 ppm is extremely high. The authors mentioned Langmuir-Hinshelwood mechanism but in a number of previous studies it was demonstrated that the NO₂ uptake coefficients decrease with the increasing NO₂ mixing ratios up to 100 ppb. Higher mixing ratios than 100 ppb do not influence the uptake coefficients.

Answer:

Langmuir-Hinshelwood was mentioned to explain the nitrite oxidation under dark condition (line 197-199). *'The nitrite would react with another surface nitrite in a Langmuir-Hinshelwood*

mechanism (R.3) or gaseous NO₂ in an Eley-Rideal mechanism (R.4) to form nitrate in the absence of illumination (Tang et al., 2018; Underwood et al., 1999).'

According to the concentration dependence experiments, the photoinduced heterogeneous uptake of NO₂ on particles can be viewed as pseudo-first-order reaction (Section S5). Many previous studies confirmed this as well (**Goodman et al., 1998; Guan et al., 2014**). Hence, the uptake coefficients obtained under high NO₂ concentrations are still authentic and valuable for atmospheric cases with lower NO₂ concentrations. We have emphasized this in the revised manuscript (line 234-236). *'Since the reaction is first order with respect to NO₂ concentration under various light intensities (Figure S8), the γ -values would still be authentic for atmospheric reactions with lower NO₂ concentrations.'* In addition, authentic dust (Kaolin) has been considered and was exposed to a much lower NO₂ concentration (mixing ratio=0.9 ppm) for better understanding the reactions in the atmospheric environment (see section 3.3 in the revised manuscript).

It is difficult to simulate low mixing ratios like 100 ppb in the laboratory research. However, since the NO₂ mixing ratios in most urban areas are higher than 100 ppb, the estimated uptake coefficients remain valuable.

(3) Generally, the data presented in this work had no error bars, therefore no uncertainties of those data can be evaluated. I generally feel that more solid evidences are need to arrive the conclusion.

Answer:

In this study, each independent variable was determined via five or more replication measurements. Based on these, Monte Carlo (MC) simulation were carried out to present the data in a more accurate way. All uptake coefficients were estimated by the MC method, and the percentile values were provided in Table S2. For the convenience of interactive comparison, we have added the Mean \pm SD values in the Supporting Information (Table S3).

Additionally, we have added more solid evidences to support the conclusion. The experiments on authentic dust under lower NO₂ concentration are available to make the conclusion more believable. More details are present in Section 3.3 in the revised manuscript.

Specific comments:

Line77: It is not mentioned what brand was used for the ultrapure water and how was tested the

purity of the water?

Answer:

We have added the description for ultrapure water in the revised manuscript (line 83-85). *'Ultrapure water (specific resistance $\geq 18.2 M\Omega cm$) produced from a deionizer (Direct-Q5-UV, MERCK, Germany) was used throughout the research process.'*

A conductivity meter was coupled with the water purifier to ensure the specific resistance above $18.2 M\Omega cm$.

Line 79: It is not mentioned the purity of the air bottle. What is the level of VOCs in this bottle?

Answer:

The purity of the N_2 and O_2 is 99.9999%, and the purity of NO_2 calibration gas is 99.999%. We have added the purity information in the revised manuscript (line 86-88). *'High-pure air (79% N_2 and 21% O_2 , 99.9999% purity, Shanghai TOMOE Co., LTD, China) and 300 parts per million (ppm) NO_2 (N_2 dilution, 99.999% purity, Shanghai Qingkuan Co., LTD, China) were included in this research.'*

Scarcely any impurities (e.g. VOCs) were included because the high-pure air was sent into molecular sieve for purification before coming into the gas supply system. *'Prior to coming into the gas supply system, high-pure air went through silica gel and molecular sieve for drying and purification, respectively.'*

Line 119: How was derived this equation? Where does it come from?

Answer:

The reactive uptake coefficients (γ) for the heterogeneous adsorption of tracer gases were deduced from the DRIFTS experiments, and is frequently used in the similar studies (**Li et al., 2006; Wu et al., 2011**). We have introduced the definition in the revised manuscript (line 127-128). *'The reactive uptake coefficient, γ , is defined as the ratio of the reactive gas-surface collision rate ($d[NO_3^-]/dt$) to the total gas-surface collision rate (Z).'*

Line 125: It would be better the equation to be presented as $(2.1 \pm 0.2) \cdot 10^{15}$

Answer:

We have changed the sentence to ‘*The conversion factor (f), estimated to be $(2.09 \pm 0.16) \times 10^{15}$ (ion · K-M unit⁻¹) in this study.*’ (line 138)

Line 131: “Based on earlier finds”: : :.should state “Based on earlier findings”

Answer:

‘Based on earlier findings’ is the correct expression. However, we have added more details into the section (line 146-147). The original sentence has been changed into ‘*We performed independent runs at 1500, 3000, 5000, and 10000 iterations with each parameter. The results showed that 5000 iterations are sufficient to ensure the stability of the results.*’

Line 169: The wavelength should be ≤ 390 nm.

Answer:

We have changed it to ‘*wavelength ≤ 390 nm*’ in the revised manuscript (line 186).

Line 172: The dot on hydroxyl radical should be on O atom and not on H atom.

Answer:

We have changed it into ‘*OH*’. (line 189)

Line 197-198: These two questions are not properly formulated. For example “Whether” does not fit here. I am not native English speaker but I think the English language usage must be substantially improved in the core of the manuscript.

Answer:

We have revised them. Actually, we added another section discussing the reactions on authentic dust Kaolin. These two questions were inferred in the end of the section 3.3 of the revised manuscript (290-293). ‘*Generally, two questions become more interesting when discussing the heterogeneous process on mineral surrogates or authentic dust: What is the association between nitrate and nitrite in atmospheric particulates? What is the proposed mechanism behind these illumination effects? We may discuss these issues in the following sections.*’

We have also consulted native speaker to improve the language.

Line 235: On which basis is this statement that “the irradiation tends to be weaker in winter”? Where is this applied? What solar zenith angle, latitude? Etc.

Answer:

According to the regression analysis on the uptake coefficients, the $d\gamma_{\text{geo}}/dI$ values can be obtained by derivation to distinguish the illumination effects varying with light intensity. The solar irradiation intensities of Shanghai, China was adopted as an example for better comparisons as explained in the revised manuscript (line 256-257). *‘In Shanghai (31°11’E, 121°29’W), the 3h-average solar irradiation intensities are mostly lower than 80 mW/cm² (NOAA data, <https://www.arl.noaa.gov/>), indicating noticeable sunlight impacts.’*

The comparisons between solar intensities in cold and warm seasons can be obtained from Figure 2d. We have revised the legend of Figure 2d for better understanding.

Lines 293-295: The authors stated “low and high NO₂ concentration of 9.20 ppm and 21.45 ppm. These values are not concentrations but mixing ratios and both values are extremely high.

Answer:

Herein, we adopted mixing ratio to represent the adding amount of NO₂ gas, in consistent with earlier studies. We have changed the ‘concentration’ to ‘mixing ratio’ in the revised manuscript.

In this work, the mixing ratios of NO₂ are higher than the common levels in the troposphere. However, laboratory research frequently adopted mixing ratios in these levels (**Tan et al., 2017; Yang et al., 2015**). To make the experimental situation closer to the real atmosphere, we conducted experiments on authentic dust (Kaolin) under a much lower NO₂ mixing ratio (0.9 ppm). More details can be found in the added Section 3.3 in the revised manuscript.

Lines 313-314: This definition is very strange, “polluted aerosols” and “carcinogenic aerosols”. Please change this.

Answer:

We have changed the definitions in the revised manuscript (line 382-382). *‘Nitrite-rich and nitrate-rich products may occupy the mainstream under faint sunlight and strong irradiation, respectively.’*

Supporting Information

On Y axis should be the intensity or spectral irradiance. It depends what values the authors measured and how were these values measured (see my general comment above).

Answer:

Figure S3 presents the spectral distribution of the Xenon lamp light measured by a fiber optic spectrometer (AULTT-P4000, Beijing Ceaulight Co., LTD, China). For the Y axis, the original 'Intensity' should be changed to 'Relative intensity' to represent the relative spectral distribution under any light intensity.

Table S1: It is stated the velocity of SO₂ instead of NO₂.

Answer:

It is a mistake. We have changed 'SO₂' to 'NO₂'.

Table S2: The presentation of data is not scientific here. Please change.

Answer:

We have added the Mean±SD into Table S2.

Conclusions and Implications

I would be very careful to claim the importance of sunlight during the haze events, as you merely tested a few aerosol samples, and they cannot represent all aerosols types. Note your experimental conditions are often not atmospherically relevant (high NO₂ mixing ratios and light intensities). The findings should not be over-interpreted and stated with caveats.

Answer:

Firstly, we did statistical tests on the field data, with results (*p* value and R²) present in Figure 4 of the revised manuscript. We will do more field observations to support the results.

Secondly, the NO₂ mixing ratios in the original manuscript is extremely high. In the revised manuscript, we have added many experimental results to illustrate the heterogeneous process on Kaolin particles with a much lower NO₂ mixing ratio (0.9 ppm). We think the 'authentic dust-low NO₂ mixing ratio' system could provide strong evidences to the uneven illumination effect. The experimental results on Kaolin are shown in Section 3.3 of the revised manuscript.

Moreover, light intensities higher than 100 mW/cm² were adopted for TiO₂ particles to explore the main reaction mechanism. For the authentic particles Kaolin, the light intensities for all tests were lower than 100 mW/cm² (line 109-110, section 2.3). *‘In each test, 50 mg Kaolin was put into the chamber, followed by the exposure to 0.90 or 15.33 ppm NO₂ under diverse light intensities (0, 10, 40, 70, and 100 mW/cm²).’*

Based on these findings, we can emphasize the importance of photochemistry in the atmosphere, especially the uneven illumination effects in the formation of nitrate and nitrite.

Anonymous Referee #2

Overview. The paper by Wang et al. mostly describes laboratory experiments and some field data exploring the role of heterogeneous chemistry involving nitrogen dioxide (NO₂) on surrogate mineral dust and ambient aerosols. The study is comprised of three parts: (1) an FTIR study of NO₂ adsorption to titanium dioxide (TiO₂; industrial grade photocatalyst) in the dark and when irradiated with UV-visible light; (2) development of a parameterization of the NO₂ uptake coefficients as a function of light intensity as a potential approach for describing NO₂-to-nitrite and nitrate conversion on mineral dust. This work is based on the abovementioned FTIR studies and Monte Carlo simulations were used to estimate error (details on this part are scarce); and (3), results of a field campaign showing that nitrate and nitrite concentration in aerosols are positively correlated at night, but inversely related when they are collected during the day. The authors conclude that FTIR study shows that the nitrite: nitrate ratios observed in ambient aerosol are due to heterogeneous chemistry involving NO₂ conversion on mineral dust surfaces containing TiO₂. There are several major issues with this manuscript that make it unacceptable for publication. These are outlined below.

General Comments on the Study.

The authors choose as a surrogate for mineral dust Degussa TiO₂ which is mixture of rutile and anatase that is designed to be highly reactive. However, the photoactive mineral anatase is one of the scarcest Ti minerals in Earth's crust. For this reason, I feel that Degussa TiO₂ is not a suitable surrogate for photochemical studies of mineral dust heterogeneous chemistry. That being said, it is probably as good as SiO₂ or alumina for use as a surrogate for non-photochemically active mineral

surfaces.

Answer:

Thanks for your comments.

Firstly, titanium dioxide is ubiquitous in the atmosphere, originating mainly from natural processes and human activities (**Chen et al., 2012**). The suspended TiO_2 is most likely from windblown mineral dust. Approximately 0.7 wt % TiO_2 is found in the continental dust (**WEDEPOHL, 1995**). In general, TiO_2 is found in mineral dust at mass mixing ratios ranging from 0.1% to 10% depending on the exact location from where the particles were uplifted (**Ndour et al., 2008**). Besides the TiO_2 in mineral dust, there are additional sources of airborne PM containing TiO_2 from industrial processes, including the nanotechnology industry, that could contribute significantly to TiO_2 in the atmosphere. Hence, TiO_2 was employed to represent the ubiquitous atmospheric metal oxides.

Meanwhile, many previous studies focused on pure TiO_2 or Degussa TiO_2 during the atmospheric research (**El Zein and Bedjanian, 2012; Kebede et al., 2013; Tang et al., 2016**). Ponczek et al., investigated the photooxidation of butanol on mineral dust and considered TiO_2 the main effective component in the primary particles (**Ponczek and George, 2018**). Actually, SiO_2 and Al_2O_3 occupy greater shares in atmospheric mineral dust. However, there is no generation of electron-hole pairs in the conduction and valence bands of these metal oxides under solar irradiation. The study is aimed at exploring the photoinduced formation of nitrate and nitrite on mineral dust. We have improved the introduction section on mineral dust to highlight the importance of atmospheric TiO_2 (line 48-58). *‘As a complex mixture, mineral dust is composed of various metal components, such as SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , TiO_2 , etc. Compared to the non-semiconducting components in mineral dust, TiO_2 has direct environmental implications for its photocatalysis (**Nanayakkara et al., 2014**). TiO_2 is found in mineral dust at mass mixing ratios ranging from 0.1% to 10% depending on the exact location from where the particles were uplifted (**Ndour et al., 2008**). Prior studies have indicated the photoinduced oxidation of trace gases by TiO_2 an essential role in the chemical balance of the atmosphere (**Chen et al., 2012**). TiO_2 -coated surfaces are frequently used in the vicinity of buildings or urban infrastructure (**Ballari et al., 2010; Ballari et al., 2011**). It is suggested that these self-cleaning materials have a great chance of entering into the environment and then triggering series of atmospheric reactions (**Balajka et al., 2018; Langridge***

et al., 2009; Monge et al., 2010; Yang et al., 2018). Accordingly, TiO₂ is usually representative of the ubiquitous semiconducting components in atmospheric environment (Kebede et al., 2013; Moon et al., 2018; Ponczek and George, 2018).’

Last but not the least, more experiments have been conducted on authentic dust (Kaolin) under a much lower NO₂ mixing ratio (0.9 ppm) to evaluate the heterogeneous processes in the real atmospheric environment. The uneven promotion effect under illumination and the negative correlation between nitrite and nitrate can be found on the authentic dust as well. Hence, TiO₂ could represent the atmospheric metal dust in photoinduced reactions, and the experiments on Kaolin highlight the atmospheric implications. More details have been included in the Section 3.3 of the revised manuscript.

The FTIR product study of NO₂ adsorption and photochemistry on TiO₂ surfaces is parameterized and used to explain the aerosol field results. However, this presumes that the aerosols collected contain mineral dust containing an appreciable amount of anatase surface sites. Unfortunately, the ambient aerosols have not been characterized (e.g., with elemental analysis and crystallographic methods) and therefore, there is nothing supports the validity of using Degussa anatase to represent the aerosol chemistry occurring in the collected ambient aerosol samples. Indeed, the relationships between nitrate and nitrite for these field samples could as easily be explained through, by now, well established non-TiO₂ chemistry. For example, nighttime data can be explained by uptake of NO₂ into aqueous droplets, or onto non-TiO₂ mineral surfaces, while daytime chemistry can be explained by aerosol phase nitrate photolysis. For example, Xianliang Zhou et al. have published results showing that aerosol nitrate is a major source of nitrite and HONO in aerosols and all evidence suggests that TiO₂ is not necessarily needed for this chemistry.

Answer:

Herein, TiO₂ is regarded as the surrogate of mineral dust for its ubiquitous existence in the atmosphere and the photocatalytic activity under solar irradiation. Meanwhile, we have added the latest results on Kaolin particles into the revised manuscript (Section 3.3). The uneven promotion effect under illumination and the negative association between nitrite and nitrate can be found on Kaolin particles as well. Hence, these two illumination effects really exist in the atmospheric environment.

The oxidation of nitrite by photocatalytic components in mineral dust is a nice explanation for the results of aerosol samples. More importantly, we have noticed two papers focusing on the photolysis of nitrate and nitrite aerosols, as well as some similar studies on this topic (Ye et al., 2017; Ye et al., 2016). The photolysis may lead to the negative dependence in another aspect. We have emphasized these valuable points in the revised manuscript (line 319-327). *'It is universally acknowledged that atmospheric nitrate may undergo photolysis (R.8-10) under acidic conditions (Goldstein and Rabani, 2007; Schuttlefield et al., 2008; Ye et al., 2016). These two processes (photolysis of nitrate and oxidation of nitrite) may contribute to the negative association in different aspects. Yet, the nitrite oxidation seems to be more easily to take place because some semiconductor in the atmosphere can be excited by visible light, while the nitrate photolysis mainly occurs under ultraviolet light (Benedict et al., 2017; Ye et al., 2017). The exact contributions of these two processes to this negative correlation are still not very clear. Noticeably, some aerosol samples indicate low nitrite levels accompanied by slight nitrate pollution in the presence of sunlight. Besides the photolysis of nitrate and nitrite, HONO formation in acidic media (R.11) is another sink of surface nitrous acid (Liu et al., 2015; Su et al., 2011; Wang et al., 2015; Zhang et al., 2012).'*

Concentrations of NO₂ used for the FTIR study are in the range of 9-21 parts-permillion (ppm). These concentrations are unheard of in the natural or even urban environment unless one considers the chemistry occurring within the engine of a car or a power plant stack. Therefore, such data cannot be extrapolated to environmental conditions where ambient NO_x levels are orders of magnitude lower; for this reason, the parameterizations they develop are only applicable to Degussa TiO₂ under the conditions of their study.

By now it has been well established that at high concentrations of NO₂, the heterogeneous mechanism involves dimerization of NO₂ followed by autoionization of N₂O₄ and reaction with water (see the review article by Finlayson-Pitts et al, PCCP, 2003, which the authors seem to not be aware of based on their citations). While this mechanism explains much of the thermal chemistry in the manuscript by Wang et al., under ambient concentrations, it is too slow to explain NO_x-to-nitrite chemistry under ambient levels of NO₂; under ambient conditions, the mechanism likely rather proceeds with the mediation by aerosol components that are more abundant than TiO₂ and can also occur in the absence of mineral dust.

In my opinion, the suggested mechanisms are not thought out carefully and in some cases are inaccurate. For example, the authors suggest that negative OH stretches in the FTIR difference spectrum indicate that NO₂ conversion to nitrite and nitrate on TiO₂ in the dark involves reactivity at the Ti-OH sites (that is involvement of hydride anions), which would imply breaking the Ti-O bond. The energetics of this is likely not favorable based on bond strength considerations; the involvement of water is more likely. Caution should be used in interpreting negative peaks in the OH stretching region in the FTIR difference spectrum as they also develop when the H-bonding environment changes. Again, the authors should refer to the Finlayson-Pitts et al. review article in PCCP (2003) for more discussion for mechanism at such high NO₂ concentrations.

Answer:

Based on the concentration dependence experiments, the photoinduced heterogeneous uptake of NO₂ on TiO₂ particles can be viewed as pseudo-first-order reaction. Hence, the γ -values would still be authentic for atmospheric reactions with lower NO₂ concentrations. We have explained it in the revised manuscript (line 234-236). *‘Since the reaction is first order with respect to NO₂ concentration under various light intensities (Figure S8), the γ -values would still be authentic for atmospheric reactions with lower NO₂ concentrations.’* In addition, we conducted the experiments on authentic particles under lower NO₂ mixing ratio (0.9 ppm). The results on Kaolin were similar with those of the TiO₂ particles. In general, the high NO₂ concentrations may not influence the kinetics evaluation, and the much lower mixing ratio has been used on authentic dust in order to confirm the illumination effects.

N₂O₄ (~1700 and 1300 cm⁻¹) was not observed in the DRIFTS spectra. We assumed that the N₂O₄ existed in the initial stage of the whole reaction and was consumed immediately along with the oxidation of nitrite species. Liu et al., observed the similar phenomenon (Liu et al., 2012). We have added the possible mechanism about N₂O₄ in the revised manuscript (line 207-214). *‘Different with previous studies, the dimer of NO₂, namely N₂O₄, was not observed in these spectra around 1745 and 1295 cm⁻¹. It has been confirmed that N₂O₄ could isomerize and autoionize to NO⁺NO₃⁻, and then react with adsorbed water to generate HNO₃ and HONO (Syomin and Finlayson-Pitts, 2003). Meanwhile, N₂O₄ may exist in the initial stage of the whole reaction and be consumed immediately along with the oxidation of nitrite species. Liu et al., investigated the consumption of N₂O₄ during the oxidation of adsorbed SO₂ (Liu et al., 2012). Herein, the proposed process can be*

described by (R.6-7). Furthermore, Kaolin particles have been referred to explain the relevant mechanism. Hence, the mechanism would take place on both mineral surrogate and authentic dust.

Actually, TiO₂ is fairly stable in chemical processes. We didn't mention any information on the OH stretches.

The work is also not novel. The TiO₂-NO_x system has been exhaustively studied by numerous groups over the years in both the catalysis and atmospheric chemistry community. Previous papers presented detailed mechanisms that are not accurately considered or interpreted in the current manuscript. One interesting discussion is that of how adsorbed nitrite can be oxidized to nitrate by the reaction of NO_x on the surface, an observation that is nonetheless well documented in the literature (see numerous papers by Szyani et al.) and is shown to occur under high NO_x concentrations by researchers studying catalytic converter technology.

Answer:

We have emphasized the innovation and importance of this study in the revised manuscript (line 63-68). *'Most remarkable studies concerned the photocatalytic effects under ultraviolet light while the intensity dependence under simulated solar irradiation was rarely explored (Dupart et al., 2014; Guan et al., 2014; Li et al., 2010; Shang et al., 2010). Some researchers (El Zein and Bedjanian, 2012) noticed the uneven illumination effect on the heterogeneous reaction of NO₂ on TiO₂ particles while ignored the reaction process on authentic dust and the reaction mechanism behind the variation.'* Additionally, we further employed authentic dust (Kaolin) and a much lower NO₂ concentration to explain the uneven promotion effect under illumination and the negative dependence between nitrate and nitrite in the revised manuscript (Section 3.3), which also presents novelty.

We have read many papers from Szyani's groups (Desikusumastuti et al., 2008; Ozensoy et al., 2005; Szanyi et al., 2005; Yi et al., 2007; Yi and Szanyi, 2008). The experimental conditions (temperature, concentrations) and surfaces (catalytic materials) are quite different from the atmospheric conditions. Hence, the mechanism in these papers may not be suitable for explaining the atmospheric process. However, we found some knowledge on FT-IR analysis meaningful and cited these papers in the revised manuscript (line 174-176). *'Bridging bidentate nitrate can be recognized by the shoulder peak at 1602 cm⁻¹ (Du et al., 2019; Goodman et al., 1998; Sun et al.,*

2016; Szanyi et al., 2005; Yi et al., 2007).’

Nitrite oxidation on mineral dust occurs via two pathways. Under dark condition, the nitrite would react with another surface nitrite in a Langmuir-Hinshelwood mechanism or gaseous NO_2 in an Eley-Rideal mechanism to form nitrate in the absence of illumination (line 197-198). While under illumination, the oxidation by photoinduced active species (PAS) becomes an important pathway, as evidenced by the oxidation of NaNO_2 to NaNO_3 on TiO_2 under solar irradiation (Section S9).

Conclusions are made that are not supported by the results and overstate the importance of the results. For example, starting on line 297 the authors state, “*Generally, higher NO_2 concentrations suggest broader influence scope of illumination. Hence, current serious NO_2 pollution may increase the participation of solar irradiation in the formation of secondary aerosols.*” It is not clear how this work actually addresses formation of secondary aerosol since most of the work looked at NO_2 chemistry on TiO_2 and a rather limited study of nitrite and nitrate levels in ambient aerosols.

In another example, on line 322, the authors state, “*However, the nitrate formation on mineral dust is found to be more dependent on weak sunlight, indicated that photochemistry processes are still crucial in heavy haze.*” They further state as one of the main conclusions of the paper is that nitrate formation on mineral dust is “*more dependent on weak sunlight.*” Unfortunately, it was unclear to me how the authors can extract this conclusion from their data. It is well known that nitrate formation is driven by photochemical oxidation that converts NO_2 to nitric acid/nitrate in a radical termination step. This photochemical pathway is directly proportional to light intensity, which drives both OH and NO_x production rates. The nitrate formation rate on TiO_2 is also shown to increase with light intensity as shown in Figure 1G. The authors also suggest there is a “*nitrite burst accompanied by low nitrate concentrations*” that has not been considered by the atmospheric community. It is not clear what burst they are referring to, as this part of the discussion was quite unclear. The conclusion appears to come from the correlations observed in Figure 3, but those observations are expected and can be interpreted using known chemistry. For example the positive correlation between nitrite and nitrate at evening/night is expected since both stem from adsorption of N_2O_5 and NO_2 to particles, while a negative correlation is expected during the day since high photon flux generates high concentrations of more photochemically stable nitric acid/nitrate, but effectively photolyzes nitrite.

Answer:

Thanks for the valuable comments on conclusions and we have changed this section based on the revised discussion section. The current conclusion section contains four parts:

- (1) the summary of this study,
- (2) the uneven illumination effect and the associations between nitrite and nitrate species on TiO₂ and authentic dust (Kaolin)
- (3) the associations between atmospheric nitrite and nitrate
- (4) the importance of Monte Carlo simulation in the assessment of kinetics.

These four parts have contained the main contents of the revised manuscript. The conclusion section has been thoroughly improved in the revised manuscript (line 388-417).

The heterogeneous reaction of NO₂ on TiO₂ and Kaolin particles was investigated by means of in-situ DRIFTS experiments and ex-situ flow reactions, respectively. Photochemistry has traditionally been considered inapparent during haze events due to the weak sunlight near the ground caused by low visibility. Hence, light intensity is taken into consideration as an important index. For better illustration, size-segregated aerosol samples were collected in the absence and presence of sunlight.

Water-solvated nitrate is the main product on TiO₂ surfaces, followed by other species influenced by illumination conditions. The nitrate formation rate is enhanced by simulated solar irradiation with uneven promotion effect. The nitrate formation is sensitive to the variation of light intensity under weak illumination, while tends to be insensitive under strong irradiation. That is, the uptake coefficient for NO₂ adsorption under moderate sunlight is close to that under strong irradiation. The oxidation of nitrite can be observed under dark condition and is promoted by the appearance of light and the elevation of the intensity. Hence, a significant negative correlation exists between nitrate and nitrite products. Similar uneven promotion effect and negative dependence occur on authentic particles (Kaolin) as well. Based on the photo-electrochemical (PEC) tests and concentration dependence experiments, these illumination effects can be explained by the excess NO₂ adsorption under weak illumination while the sufficient photoinduced active species under strong irradiation.

The negative association between atmospheric nitrite and nitrate can be found in the presence of sunlight, along with the positive correlation in the absence of sunlight. The negative dependence

can be explained by either the photolysis of particulate nitrate or the photoinduced oxidation of nitrite, suggesting illumination an inducing factor in the atmospheric nitrogen cycling. Nitrate pollution has got much concern recently, while little attention has been paid to the high nitrite concentrations accompanied by low nitrate levels. Nitrite may induce adverse health risk for its close association with various cancer cases (Zhang et al., 2018). Compared to the nitrate-rich aerosols under strong irradiation, the nitrite-rich aerosols under faint sunlight may be more harmful to human health.

Actually, we discussed the γ -values based on the averaged experimental results while gave little care to various measurement errors. Compared to the arithmetic mean results, the percentile γ -values estimated by Monte Carlo simulation could be more suitable for modelling studies due to the differences between real atmosphere and the simulated laboratory condition. Furthermore, sensitivity analysis is helpful in explaining the determining factors involved in the assessment of uptake capacity. Generally, statistical simulation brings about more accurate evaluation and provides opportunities to explain the model discrepancy for secondary aerosols.'

In summary, The paper is poorly organized and written; there is no experimental evidence that the ambient aerosol N chemistry is driven by or can be linked to TiO₂ (anatase) chemistry; the TiO₂ study is not conducted under atmospherically relevant conditions on a substrate that is not atmospherically relevant; and some of the main mechanisms proposed are either inaccurate or lack experimental support and can rather be explained using well-established chemistry. For this reason, I do am unable to recommend this manuscript for further consideration. Moving forward, I would suggest that the authors place all of the TiO₂ data (which appears to be of good quality) into a concise manuscript (break the multi-panel figures up into more digestible figures) focused on the topic of photocatalytic reactions of N on TiO₂ surfaces, which could be submitted to a more specialized journal in the area of catalysis or environmental remediation.

Answer:

We have noticed some probable shortcomings in the original manuscript and then made major revisions based on your comments.

Firstly, the particles.

TiO₂ was selected as the mineral surrogate. However, more and more studies found the limited

representativeness of TiO₂ in mineral particles for its scarce existence in the atmosphere. In the revised manuscript, we added the latest experimental results on Kaolin particles. The uneven promotion effect under illumination and the negative dependence between nitrite and nitrate can still be found on the authentic particles. Hence, these new illumination effects should be admitted in the atmospheric research.

Secondly, the atmospheric condition.

In the original manuscript, the mixing ratio of NO₂ for TiO₂ particles was relatively high (~15.33 ppm). However, for the new sections on Kaolin particles, we adopted a much lower NO₂ mixing ratio (~0.9 ppm) to get close to the real atmospheric condition. Simultaneously, because the low NO₂ mixing ratio hinders the product observation via in-situ DRIFTS, a new-style quartz flow reactor has been designed and employed in the Kaolin-related exploration. We believe that the experiments under lower NO₂ mixing ratios are beneficial to explain the illumination effects.

Thirdly, the mechanism for NO₂ adsorption.

N₂O₄ was not observed by *in-situ* DRIFTS, and may exist in the very initial stage of the reaction. We have added the discussions on N₂O₄ and the possible reaction processes triggered by it in the revised manuscript (line 207-214).

Furthermore, we expanded the association between nitrite and nitrate to the atmospheric aerosols. However, the negative dependence in the presence of sunlight may result from the photolysis of particulate nitrate and nitrite. We ignored the important knowledge in the original manuscript, and have added some discussions into the revised manuscript (line 319-331).

Additionally, the mechanism on the photoinduced heterogeneous reaction of NO₂ on mineral dust has been widely investigated. However, the **uneven promotion effects** under illumination were seldom studied. Meanwhile, little information can be found in literatures about atmospheric nitrite species and the association with nitrate. Hence, this paper is novel in its community and would provide more opportunities for the further studies. We have emphasized these points in the revised manuscript (line 63-71). *‘Most remarkable studies concerned the photocatalytic effects under ultraviolet light while the intensity dependence under simulated solar irradiation was rarely explored (Dupart et al., 2014; Guan et al., 2014; Li et al., 2010; Shang et al., 2010). Some researchers (El Zein and Bedjanian, 2012) noticed the uneven illumination effect on the heterogeneous reaction of NO₂ on TiO₂ particles while ignored the reaction process on authentic*

dust and the reaction mechanism behind the variation. Furthermore, nitrite owns an important position in atmospheric processes for its frequent appearance and great contributions to aerosol toxicity. However, there is little information available in literature about the pollution characteristics or reaction pathways of nitrite aerosols. Generally, how the illumination influences the uptake capacity and product species are questions urgently needs solving.'

We have improved the manuscript as perfect as possible. Generally, authentic dust, lower NO₂ mixing ratio, and more mechanism discussions have been added into the revised manuscript.

Specific Comments: Too many figures are shown in Figure 1. These figures can easily be broken up in a way to make a separate manuscript on its own (see above comment).

Answer:

Figure 1 is designed to exhibit the product observations on TiO₂ particles by means of DRIFTS, as well as the formation trends of nitrate and nitrite species. For better understanding the reactions, we have explained the general content of Figure 1 in the beginning of the section 3.1 (line 166-168). *'Figure 1 presents the product analysis for dark reaction (Figure 1a-c) and illumination process (Figure 1d-f) by means of DRIFTS spectra, along with the quantitative evaluation of nitrate and nitrite formation based on IC measurements (Figure 1g-i).'*

line 62: The authors state that some researchers have studied the effect of radiation on NO₂ uptake on TiO₂ but have ignored the reaction mechanism behind the trends in reactivity. However, after reading the papers cited and some that are not cited, I disagree.

Answer:

The mechanism of NO₂ adsorption on mineral dust has been exhaustively studied. However, little attention has been paid to the heterogeneous reaction influenced by light intensity, especially weak irradiation during heavy haze events. Some researchers noticed the uneven illumination effect on the heterogeneous reaction of NO₂ on TiO₂ particles under UV light while ignored the reaction process on authentic dust and the reaction mechanism behind the variation.

We have emphasized these details in the introduction section (line 63-67). *'Most remarkable studies concerned the photocatalytic effects under ultraviolet light while the intensity dependence under simulated solar irradiation was rarely explored (Dupart et al., 2014; Guan et al., 2014; Li*

et al., 2010; Shang et al., 2010). Some researchers (El Zein and Bedjanian, 2012) noticed the uneven illumination effect on the heterogeneous reaction of NO₂ on TiO₂ particles while ignored the reaction process on authentic dust and the reaction mechanism behind the variation.'

line 229-230. In figure 2c, the authors fit a polynomial function to the experimental data collected for NO₂ uptake coefficients plotted as a function of light intensity. They then provide an inset showing a near perfect correlation between experimental uptake coefficients and those making up the line they fit to it. This is unnecessary. I recommend omitting the inset and simply reporting the R-squared value for the polynomial fit. 237-238: The polynomial fits lack any physical meaning and are only applicable to the substrate and conditions of the experiment, which are not necessarily environmentally applicable (see above).

Answer:

The regression analysis is aimed at finding an accurate formula fitting the obtained curve. The polynomial was constructed for the better estimation of $d\gamma_{geo}/dI$ values. We have emphasized these details in the revised manuscript (line 253-255). *'Based on this, the $d\gamma_{geo}/dI$ values are obtained by derivation to distinguish the illumination effect varying with light intensity.'* Figure 2(c) makes it easier for readers to understand the generation of $d\gamma_{geo}/dI$ values.

For the similar data analysis on Kaolin experimental results, we ignored the process and presented uptake coefficients and $d\gamma_{geo}/dI$ values in the same figure (Figure 3c). Meanwhile, we provided only the R-square value in discussing the situation for Kaolin in the revised manuscript (line 277-278). *'Based on regression analysis ($R^2=0.994$), the $d\gamma_{geo}/dI$ values were estimated by derivation to distinguish the promotion effect influenced by light intensity.'*

Figure 3: It is entirely unclear what the rightmost column is depicting. What do the authors mean by "nitrite classification?" What do the color codes mean?

Answer:

The rightmost column exhibits the correlations between daily nitrite and nitrate concentrations in (c) coarse mode, (f) droplet mode, (i) condensation mode and (l) full-size particles. The insets present the associations between nitrite and nitrate based on the classification of nitrite levels.

The 'nitrite classification' was carried out to divide the aerosol samples into several groups

according to the nitrite concentration for better analysis. We have explained this process in the revised manuscript (line 301-302). 'For better comparison, the 26 daily samples were classified into several groups according to the nitrite concentrations.'

The color of the rightmost column was designed for the classification of nitrite concentration. We have added the color scale in the revised figure.

Anonymous Referee #3

This is a new contribution aiming at understanding the effect of mild illumination on mineral dust proxies and linking those observations with a limited set of environmental data. The claim having motivated this investigation can be found in the fact that previous studies have not seriously discussed the photochemistry under weak sunlight during haze conditions, and have thus ignored some underlying processes. I would certainly agree on such a statement, that I found quite interesting. However, I'm not fully convinced by the current version of the manuscript that would need significant revision to convey a better and stronger elaborated message.

First of all, I do need to admit that I found it difficult to read this manuscript which contains a series of awkward sentences, such: "The growth of nitrate formation rate tends to be slow after the initial fast with increasing light intensity. For example, the geometric uptake coefficient (γ_{geo}) under 30.5 mW/cm² (5.72×10^{-6}) has exceeded the 50 % of that under 160 mW/cm² (1.13×10^{-5}). This case can be explained by the excess NO₂ adsorption under weak illumination while the excess photoinduced active species under strong irradiation. Being negatively associated with nitrate ($R^2=0.748$, $P<0.01$), nitrite acts as the intermediate and decreases with: : :". This clearly weakens the content of this manuscript.

Answer:

Thanks for your comments. We have made major revisions on the abstract section. In the revised manuscript the paragraph has been changed as follows.

'Despite the increased awareness of heterogeneous reaction on mineral dust, the knowledge of how the intensity of solar irradiation influences the photochemistry activity remains a crucially important part in atmospheric research. Relevant studies have not seriously discussed the

photochemistry under weak sunlight during haze, and thus ignored some underlying pollution and toxicity. Here, we investigated the heterogeneous formation of nitrate and nitrite on mineral dust under various illumination conditions by laboratory experiments and field observations. Observed by in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), water-solvated nitrate was the main product on TiO₂ surfaces, followed by other species varying with illumination condition. The nitrate formation rate grows rapidly from the dark to faint sunlight, while becomes insensitive to light intensity variation under strong irradiation. For example, the geometric uptake coefficient (γ_{geo}) under 30.5 mW/cm² (5.72×10^{-6}) has exceeded the 50 % of that under 160 mW/cm² (1.13×10^{-5}). Additionally, being negatively associated with nitrate ($R^2=0.748$, $P<0.01$), nitrite acts as the intermediate and decreases with increasing light intensity via oxidation pathways. Heterogeneous reaction on authentic dust (Kaolin) exhibits the similar uneven promotion effect and photoinduced negative association, which can be explained by the excess NO₂ adsorption under weak illumination while the sufficient photoinduced active species under strong irradiation based on the photo-electrochemical tests and concentration dependence experiments. Similar negative dependence appears in coarse particles collected during daytime ($R^2=0.834$, $p<0.05$), accompanied by the positive association during nighttime ($R^2=0.632$, $P<0.05$), suggesting illumination a substantial role in the atmospheric nitrogen cycling. Overall, for the nitrate formation, the conspicuous response under slight illumination offers opportunities to explain the secondary aerosol burst during haze episodes with weak irradiation. Additionally, high nitrite levels accompanied by low nitrate concentrations may induce great health risk which was previously neglected. Further, Monte Carlo simulation coupled with sensitivity analysis may provide a new insight in the estimations of kinetics parameters for atmospheric modelling studies. ’

Then the link being made with the ambient measurements and the test on TiO₂ particles is far from being obvious, and would certainly need to more elaborated to make a stronger case.

Answer:

TiO₂ is representative of single-component mineral dust. Kaolin, consisting of SiO₂, Al₂O₃, Fe₂O₃, and TiO₂, is on behalf of the mineral dust with mixed components. In the revised manuscript, we made extra investigations on the heterogeneous adsorption of NO₂ on Kaolin particles (Section 3.3). The uneven promoting effect under illumination and negative association between nitrite and

nitrate formation have been observed on Kaolin particles as well. The negative dependence between nitrite and nitrate products on Kaolin provides a strong evidence to explain the oxidation of nitrite aerosols.

Most of the data presented have been made at quite high NO₂ concentrations (tens of ppm), corresponding to a concentration regime where N₂O₄ is known to be a significant intermediate for NO_x conversion on surfaces. While such concentrations are inherent to the DRIFT technique, one can still wonder how this could affect the findings reported here. It is stated that “Since no saturation effects were observed in the DRIFTS experiments, the NO₂ adsorption rate can be regarded as constant.”, but this is strong contrast with previous studies dedicated to NO₂ heterogeneous chemistry. Could that be to the involvement of N₂O₄?

Answer:

N₂O₄ was not observed in the DRIFTS spectra. It is deduced that N₂O₄ formed in the initial stage of the whole reaction and then fade away during oxidation steps. Previous studies reported the oxidation of S(IV) species to S(VI) compounds along with the consumption of N₂O₄. Hence, N₂O₄ is considered as an promotor during the oxidation of nitrite. We have added some discussions in the revised manuscript (line 207-212). *‘Different with previous studies, the dimer of NO₂, namely N₂O₄, was not observed in these spectra around 1745 and 1295 cm⁻¹. It has been confirmed that N₂O₄ could isomerize and autoionize to NO⁺NO₃⁻, and then react with adsorbed water to generate HNO₃ and HONO (Syomin and Finlayson-Pitts, 2003). Meanwhile, N₂O₄ may exist in the initial stage of the whole reaction and be consumed immediately along with the oxidation of nitrite species. Liu et al., investigated the consumption of N₂O₄ during the oxidation of adsorbed SO₂ (Liu et al., 2012). Herein, the proposed process can be described by (R.6-7).’*

The original sentence ‘Since no saturation effects were observed in the DRIFTS experiments, the NO₂ adsorption rate can be regarded as constant.’ was aimed at explaining the continuous nitrate formation during each DRIFTS test. Based on this, we started the discussion on the balance between NO₂ adsorption and PAS generation, which results in the uneven promotion effect under illumination. N₂O₄ was not observed after the initial reaction stage, and was thus not considered in mechanism discussion. Additionally, the original sentence has been changed in the revised manuscript for better understanding (line 347-348). *‘Since no saturation effects were observed in*

each in-situ experiment, the NO₂ adsorption rate can be regarded as constant.'

In TiO₂ driven photocatalysis, it is known that the conversion rate is linear function of light intensity at low intensity, and then levels off at high power to reach steady state conditions. While this seems to be also observed here (inset of figure 2a) but not really discussed nor mentioned, why? In addition, one could argue that the light intensities used here are far from being small and I would not consider this as being photochemistry under mild conditions.

Answer:

Most TiO₂ photocatalytic experiments were conducted under UV light. Herein, TiO₂ is considered as the surrogate of mineral dust, and exposed to NO₂ under simulated solar irradiation. This study is aimed at exploring the heterogeneous reaction of NO₂ on mineral dust in the atmospheric environment. The nitrate formation rate grows rapidly from the dark to faint sunlight, while becomes insensitive to light variation under strong irradiation. This uneven promoting effect under illumination can be explained by the excess NO₂ adsorption under weak illumination while the sufficient photoinduced active species under strong irradiation. We have emphasized the difference between this study and others in the introduction section (line 63-65). *'Most remarkable studies concerned the photocatalytic effects under ultraviolet light while the intensity dependence under simulated solar irradiation was rarely explored.'* Meanwhile, we have explained the uneven illumination effect, which acts as one of the most important findings in section 3.5 of the revised manuscript.

The light intensities for TiO₂ particles are 0-160 mW/cm². At the global AM (air mass) 1.5 G (global) condition, 1 sun is defined as equal to 100 mW/cm² of irradiance (a standard used in solar cell research). We adopted some high light intensities on TiO₂ to investigate the general rules of the illumination effects. For the authentic dust Kaolin, we designed all tests under the light intensities of 0-100 mW/cm² with a much lower NO₂ mixing ratio (0.9 ppm). We have introduced this detail in the method section (line 109-110). *'In each test, 50 mg Kaolin was put into the chamber, followed by the exposure to 0.90 or 15.33 ppm NO₂ under diverse light intensities (0, 10, 40, 70, and 100 mW/cm²).'* Additionally, more details have been included in the section 2.3 of the revised manuscript. We believe the added experiments on Kaolin particles are providing more evidences to support the conclusions.

One of the key finding here is associated with the nitrite levels between sustained (or more important) under mild illumination, but the section “mechanism” does not provide a real explanation for that. You should try to define what you mean with cumulative uptake coefficients.

Answer:

In this paper, we summarized the reaction pathways after the analysis of DRIFTS spectra (section 3.1). In the mechanism section, we explained the uneven illumination effect and the negative association based on the concentration dependence experiments and photo-electrochemical tests. We have explained this in the beginning of the mechanism section in the revised manuscript (Line 342-343). ‘Detailed reaction pathways concerning the heterogeneous reaction of NO_2 on mineral dust have been included in previous sections.’ Meanwhile, the photolysis of nitrate and nitrite may also be used to explain the negative dependence between nitrite and nitrate. Hence, we changed the title of section 3.5 to ‘Proposed mechanism’.

Monte Carlo simulation was implemented to quantify the uncertainty and its impact on the kinetics assessment. Each independent variable was determined via five or more replication measurements and assumed to be normally distributed in the simulation. We performed independent runs at 1500, 3000, 5000, and 10000 iterations with each parameter. The results showed that 5000 iterations are sufficient to ensure the stability of the results. Hence, the phrase ‘cumulative uptake coefficients’, which was not mentioned in the manuscript, includes 5000 calculated results. Instead of the cumulative uptake coefficients, we have used the percentile values for each case based on the cumulative probability of uptake coefficients (Table S3, Table S4). Noticeably, arithmetic mean results are frequently used in this paper for better comparison with other papers.

A few chemical reactions are described in a simplified i.e., wrong way with unbalanced stoichiometry. This should be avoided.

Answer:

Numerous reaction processes were included when discussing the heterogeneous reaction on mineral dust. Some important reactions were summarized in the manuscript in a brief form, followed by some others listed in the Supporting Information. We have emphasized it in the revised manuscript (line 202-204). ‘The reactions **R1**, **R2**, and **R5** are presented in a brief way, followed by

detailed processes listed in *Section S8*.’

I did find Figure 3 quite difficult to understand and I am finally unsure about the message the authors want to convey with this illustration. This may need to be better discussed.

Answer:

The Figure 3 (Figure 4 in the revised manuscript) illustrates the associations between nitrite and nitrate aerosols varying with particle size (coarse mode, droplet mode, condensation mode, and full-size) and collection period (nighttime, daytime, and whole day). The insets present the associations based on the classification of nitrite levels. The classification has been explained in the revised manuscript (line 301-302). ‘*For better comparison, 26 daily samples were classified into several groups according to the nitrite concentrations.*’ Additionally, the color in the rightmost column reveals the classification of nitrite concentration. We have added the color scale in the revised figure.

Overall, this figure provides a strong evidence to the nitrite oxidation in the presence of illumination. We have summarized these results in the revised manuscript (line 332-334). ‘*Generally, atmospheric nitrite is positively correlated with nitrate in the absence of irradiation, whereas presents negative association with nitrate during daytime. The dependence is significant for coarse particles while turns to be inconspicuous in droplet mode and condensation mode.*’

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