Friday, May 30, 2014

Re: Journal: ACP
Title: Contribution of Airborne Dust Particles to HONO Sources
Author(s): N.A. Saliba et al.
MS No.: acp-2014-17
MS Type: Research Article

Dear Sergey,

Kindly consider the revised version of the article entitled: "Contribution of Airborne Dust Particles to HONO Sources". All reviewers' comments were addressed in the uploaded documents. This was a fruitful experience and will be ready to answer all the questions they might have in the second round (if any).

Should you need any additional information, please do not hesitate to contact me at the address shown below.

Sincerely,

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Answers to Reviewer #1

# Interactive comment on “Contribution of airborne dust particles to HONO sources” by N. A. Saliba et al.

**Anonymous Referee #1**

Received and published: 14 March 2014

The manuscript by Saliba et al. reports on the concentration of anions and trace gases sampled in air in the presence and absence of dust emanating from deserts in N. Africa or the Middle East. The focus of the paper is on providing insights on the mechanism of nitrous acid (HONO) formation on mineral dust (i.e., whether $NO_2$ hydrolysis is responsible and/or synergistic effects of other adsorbed anions such as sulfate play a role). A denuder method was used to sample gases (HONO, $HNO_3$, and $H_2SO_4$), while Teflon filters were used to sample particle chloride, nitrate, and sulfate. The authors attempt to draw correlations between anions and trace gases measured to identify sources of HONO in their samples and mechanisms are discussed to explain the correlations. The positive aspects of this manuscript are that it documents: (1) pollutant levels in a part of the globe where we lack data sets of atmospheric species; (2) captures dust events that potentially valuable provide insights into how surface chemistry influence atmospheric nitrogen and sulfur cycling; (3) it attempts to address the issue of HONO formation on mineral dust, which is far from being resolved. While the data sets are quite limited in their scope, much thought went into explaining the trends in the data.

Based on the recommendations of the two reviewers for the need of cations, anions, $NO_2$ and $SO_2$ data, the data of the 2013 field campaign which was analyzed after the submission of the original manuscript is presented. The details of the sampling dates and the results are shown below. Also, since no cation levels were available for the 2011 set of data, the results of this field campaign was removed. As for the 2009 study, only the Arabian dust episodes and its corresponding non-dusty days are presented. Hence, the revised manuscript and the answers to the reviewers present the chemical analysis of the gases and the chemical composition of PMs during non-dusty days and the Arabian dusty days of the summer and fall seasons.

That being said, it is my opinion that there are several important issues that need to be resolved. Specific issues are discussed below. The discussions of mechanism are highly speculative at times and there is not enough data to discern between the plethora of possible mechanisms. One of the most important aspects to consider in any study of anion/acid distribution in air samples is the pH of the dust/aerosol. Whether nitrous acid partitions between the aerosol and gas phase is highly dependent on the aerosol pH. It is well known that when ammonia is insufficiently abundant to neutralize sulfate in aerosols $HNO_3$ is driven into the gas phase, while excess ammonia will neutralize aerosol acidity. Unfortunately, the authors do not provide results of cation analyses (at very least, ammonium and sodium), which would allow one to estimate the pH of the dust or at least draw conclusions about whether the dust is acidic. This type of analysis may provide a more satisfying (and simplified) explanation for the observed trends, and it may be that the role of the dust is simply to provide a nucleus onto which gas phase pollutants adsorb onto.

I concur with the reviewer that the manuscript was missing cations data. In answer, we have included the cations concentrations for the 2009 campaign and introduced the data of the campaign conducted in 2013 for which cations were quantified. Since no cations data are available for the field measurements conducted in 2011, we decided to remove the data pertaining to 2011 and replace them with data collected in 2013. Hence, the Table 1 corresponds to listing the new concentrations and the Figures 1-3 are adjusted accordingly.

*Table 1. PM and acid gas concentrations collected during Arabian dusty and non-dusty days in 2009 and 2013 field campaign measurements. Size segregated (UF (ultrafine), ACC (Accumulation), and CPM (Coarse particulate matter) concentrations are shown for the 2013 field campaign and values corresponding to measurements of PM10 are listed for the 2009 field campaign.*

| **2013** | RH | UF | ACC | CPM | PM |
|---|---|---|---|---|---|
| | | | **Non Dusty** | | |
| **23-Jul-13** | 70.97 | 26.33 | 15.46 | 25.59 | **67.38** |
| **29-Jul-13** | 69.14 | 12.97 | 6.58 | 14.85 | **34.40** |
| **22-Aug-13** | 66.81 | 17.94 | 7.32 | 15.50 | **40.76** |
| **4-Sep-13** | 64.48 | 13.79 | 5.94 | 23.99 | **43.72** |
| **10-Sep-13** | 64.39 | 22.26 | 6.34 | 22.44 | **51.03** |
| | | | **Arabian Dusty Days** | | |
| **23-Oct-13** | 30.00 | 21.64 | 10.39 | 29.10 | **61.14** |
| **5-Nov-13** | 69.03 | 19.78 | 38.44 | 63.41 | **121.63** |
| **7-Nov-13** | 74.18 | 18.99 | 42.44 | 74.52 | **135.95** |
| **12-Nov-13** | 58.87 | 16.71 | 33.59 | 36.58 | **86.88** |
| **19-Nov-13** | 55.92 | 24.24 | 15.22 | 18.97 | **58.43** |

| **2009** | RH | UF | ACC | CPM | PM |
|---|---|---|---|---|---|
| | | | **Non Dusty** | | |
| 6-Sep-09 | 60.00 | | | | **46.15** |
| 24-Sep-09 | 49.00 | | | | **30.65** |
| 30-Sep-09 | 44.00 | | | | **44.54** |
| 6-Oct-09 | 78.00 | | | | **56.89** |
| 12-Oct-09 | 56.00 | | | | **42.66** |
| 30-Oct-09 | 91.00 | | | | **62.87** |
| 29-Nov-09 | 76.00 | | | | **37.08** |
| | | | **Arabian Dusty Days** | | |
| 18-Oct-09 | 12.00 | | | | **129.52** |
| 24-Oct-09 | 30.00 | | | | **83.55** |
| 11-Nov-09 | 43.00 | | | | **80.86** |
| 23-Nov-09 | 33.00 | | | | **77.47** |

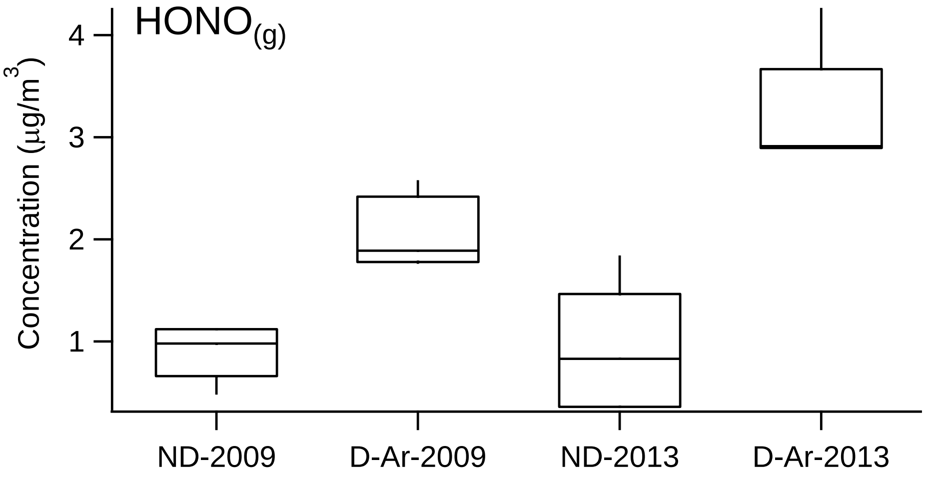

Figure 1 Box plots of concentrations of acid gase HONO during Arabian dusty and non-dusty days. Where ND stands for non-dusty and D-Ar stands for dusty Arabian.

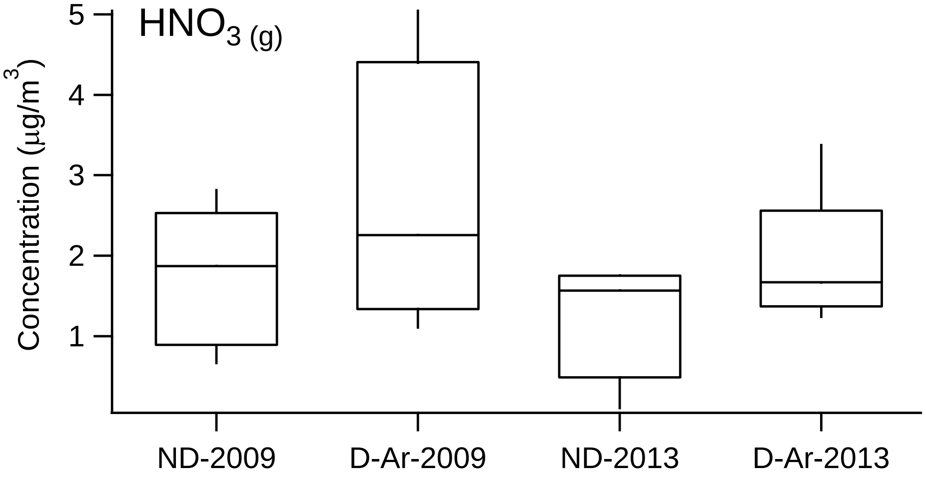

Figure 2 Box plots of concentrations of acid gase $HNO_3$ during Arabian dusty and non-dusty days. Where ND stands for non-dusty and D-Ar stands for dusty Arabian.

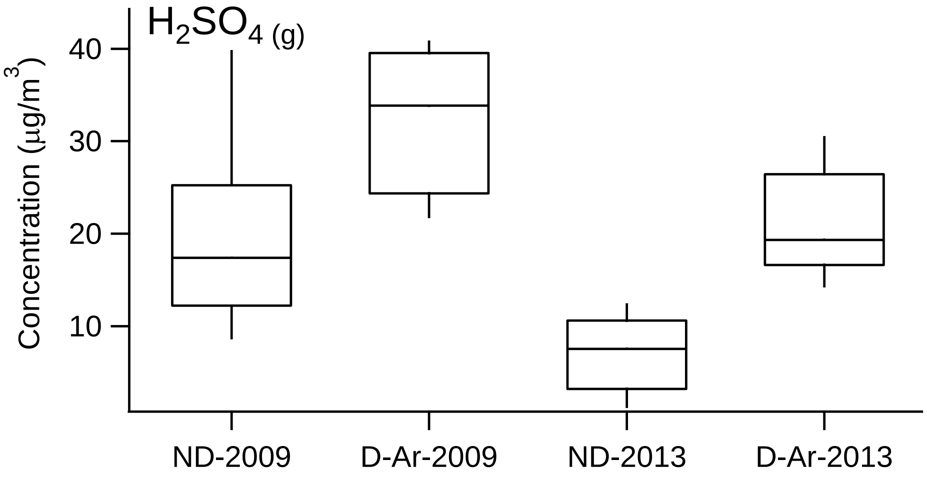

Figure 3 Box plots of concentrations of acid gas $H_2SO_4$ during Arabian dusty and non-dusty days. Where ND stands for non-dusty and D-Ar stands for dusty Arabian.

Increased acidity during dusty days is mostly noticed in the accumulation and coarse modes with no variation in the UF mode (Table 2). Acidity is calculated (Kerminen et al., 2001;Schwab et al., 2004)

$$[H^+] = [SO_4^{2-}] + [NO_3^-] - [NH_4^+]$$

It is important to note that both campaigns showed increased in acidity.

The extent to which acidic aerosol is neutralized is approximated as per Stevens et al., 1980 by:

$$f = \frac{[H^+]}{[H^+] + [{NH_4}^+]}$$

It is considered that when *f* = 0, there is full neutralization by $NH_4^+$, if *f* = 1, no neutralization has occurred. At *f* = 0.5, the bulk aerosol is a mixture of chemical species of properties similar to $NH_4HSO_4$(Stevens et al., 1980). In light of the acid ([$H^+$]) and neutralization factor calculation (*f*), the text reads:

*A drop in the neutralization factor of the 2013 field campaign (drop from 0.7 to 0.5) (Table 4), mostly noticed in the ACC mode, was counterfeited by an increase in the aerosol acidity (calculated as* $[H^+] = [SO_4^{2-}] + [NO_3^-] - [NH_4^+]$*)(Kerminen et al., 2001;Schwab et al., 2004). This increase was observed in both the 2009 and 2013-*$PM_{10}$ *field measurements (Table 4). As a result of that, the particle-gas conversion and hence the increase in acid gases during dusty days becomes enhanced.*

Table 2. Acidity [$H^+$] and neutralization factor (*f*) of size-segregated aerosols (UF (ultrafine particles), ACC (Accumulation) and CPM (coarse particulate matter) during dusty and non-dusty days PM for the 2013 field campaign and PM10 for the 2009 field campaign.

| | **[$H^+$] (mol/m$^3$)** | | | | ***f* (mol/m$^3$)** | | | | | **[$H^+$] (mol/m$^3$)** | ***f* (mol/m$^3$)** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Date** | **UF** | **Acc** | **CPM** | **PM10** | **UF** | **Acc** | **CPM** | **PM10** | **Date** | **PM** | **PM** |
| | | | | **2013** | | | | | | **2009** | |
| | | | | **Non-dusty** | | | | | | | |
| 23-Jul-13 | 0.04 | 0.05 | 0.03 | **0.12** | 0.49 | 0.7 | 0.65 | **0.61** | 6-Sep-09 | **0.28** | **0.80** |
| 29-Jul-13 | 0.04 | 0.01 | 0.04 | **0.09** | 0.62 | 0.7 | 0.85 | **0.71** | 24-Sep-09 | **0.10** | **0.83** |
| 22-Aug-13 | 0.05 | 0.03 | 0.04 | **0.12** | 0.45 | 0.88 | 0.89 | **0.65** | 30-Sep-09 | **0.17** | **0.80** |
| 4-Sep-13 | 0.02 | 0.09 | 0.03 | **0.14** | 0.79 | 0.94 | 0.85 | **0.9** | 6-Oct-09 | **0.18** | **0.84** |
| 10-Sep-13 | 0.01 | 0.01 | 0.04 | **0.06** | 0.22 | 0.3 | 0.79 | **0.5** | 12-Oct-09 | **0.21** | **0.80** |
| | | | | | | | | | 30-Oct-09 | **0.06** | **0.61** |
| | | | | | | | | | 29-Nov-09 | **0.28** | **0.83** |
| **Dusty** | | | | **Dusty** | | | | | | | |
| 5-Nov-13 | 0.03 | 0.09 | 0.17 | **0.29** | 0.51 | 0.37 | 0.97 | **0.61** | 18-Oct-09 | **0.39** | **0.91** |
| 7-Nov-13 | 0.03 | 0.11 | 0.18 | **0.32** | 0.45 | 0.4 | 0.97 | **0.6** | 24-Oct-09 | **0.37** | **0.89** |
| 12-Nov-13 | 0.03 | 0.1 | 0.01 | **0.13** | 0.57 | 0.36 | 0.43 | **0.39** | 11-Nov-09 | **0.54** | **0.91** |
| 19-Nov-13 | 0.05 | 0.04 | 0.03 | **0.12** | 0.38 | 0.52 | 0.7 | **0.48** | 23-Nov-09 | **0.06** | **0.53** |

In the proposed $NO_2$ hydrolysis mechanism, the suggestion that *"the role of the dust is simply to provide a nucleus onto which gas phase pollutants adsorb onto"* still holds and relates to the adsorption of $NO_2$ which leads to the formation of HONO and $HNO_3$. If it is a simple physisorb mechanism, we should be able to detect nitrite in the particle phase. This is was not the case in the current and previous studies done in our lab (Saliba and Chamseddine, 2012).

*p. 4828, lines 16-17: The logic of the phrase, "This study implies that the NOx reactivity on mineral oxide surfaces leads to a higher mixing level of OH" may be unclear to readers since it is not mentioned how the OH can be formed. I recommend rewriting this to say: "This study implies that enhanced NOx conversion on mineral oxide surfaces leads to a higher mixing level of HONO, which would then photolyze to produce OH radicals."*

Upon the reviewer's suggestion, the sentence was modified.

This study implies that enhanced NOx conversion on mineral oxide surfaces leads to a higher mixing level of HONO, which would then photolyze to produce OH radicals.

*p. 4830, Methods Section: Missing is a full description of the sampling site(s). It is unclear where the samples were taken, only that the sampling site was influence by dust from Africa and the Middle East. Were they taken in Lebanon, in an urban area, on a roof top, out of a window, etc.? Please include sampling dates, location, description of the sampling site, etc. The sampling methodology for this study is prone to artefacts due to secondary and surface reactions on the denuder walls or filter, especially when samples are collected over 24 hours as indicated. In my opinion, a thorough discussion of these artifacts and how they might affect the data interpretation (or not) needs to be provided.*

As per the reviewer's comment, a detailed description on the sampling site has been added as follows:

**Sampling Location**

*Samples were collected on the roof-top of the Chemistry department at the American University of Beirut; North-West Beirut, Lebanon. The site is around 40 m above sea level. South of the site is the university's green belt of shrubbery and trees, and faces the Mediterranean Sea from the North. The location is considered to be an urban background site affected mainly by sea breeze; it is far from any industrial pollution sources and the closest roadway is located around 150 m north-east. The site is described fully by Baalbaki et al 2013 and Daher et al 2013 (Daher et al., 2013;Baalbaki et al., 2013)*

The sampling method has been modified to describe the steps followed during the 2009 and the 2013 sampling campaigns.

The denuder coating and extraction were done in a $N_2$ 99.0% glove-box closed compartment to minimize contamination. Some negative artifacts might appear during the removal of acidic gases by denuders; and it is expected that the HONO would be underestimated due to its oxidation to $HNO_3$ during the 24h sampling period by atmospheric ozone. However, 1% glycerol solution has been added to the coating solution and it has been shown that the former has the capacity to minimize the occurrence of such oxidation reactions and therefore the loss of HONO would be minimal/acceptable (Febo et al., 1987). The glycerol solution also increases the denuder capacity towards $SO_2$ and $HNO_3$ (Spurny, 1999)(and references therein). The same denuder-coating and denuder-extraction procedure has been employed for many previous acidic gases collection purposes (Baek and Aneja, 2004;Perrino et al., 1990).

Other artifacts that should be taken into consideration are the ammonium loss due to an increase in temperature (29 - 35 degrees Celsius) of packed Teflon filters(Appel and Tokiwa, 1981). For that, filters are stored at 4 degrees C. Also, possible gas-particle and particle-particle interactions appear during 24h sampling periods leading to over and underestimation of certain involved species (nitrates and aerosol acidity); however, Teflon filters used for aerosol collection have shown to cause minimal loss and are widely used for atmospheric analysis purposes (Appel et al., 1984) .

The modified sample collection method is as follows:

### Collection techniques

*The aerosol and gas samples are collected using a Rupprecht & Patashnick Partisol 2300. Sampling occurred between two different campaigns, detailed in Table 1. Soluble acidic gases (HONO, $HNO_3$ and $H_2SO_4$) were sampled for 24hr using a diffusion denuder system; where the reported $H_2SO_4$ is a combination of converted $SO_2$ and atmospheric $H_2SO_4$. The system is based on two Honey Comb denuders (HC) coated with 1% $NaCO_3$ and 1% glycerol in 50:50 water: methanol solution and placed in series in Rupprecht & Patashnick (R&P) Chemcomb™ cartridges. Sampling and analysis of trace gases is fully described in Saliba and Chamseddine (Saliba and Chamseddine, 2012).*

*During the first sampling campaign (2009), aerosol collection extended over 24 hours using pre-weighed 37mm Teflon filter housed between two Teflon meshes downstream the gas collecting denuders in $PM_{10}$ inlets Harvard cartridges. The flow rate was set at 10 l/min. Following collection and gravimetric calculation of PM concentrations, the filters are cut into four equal pieces that are stored at 4℃ until ready for chemical analysis (Kouyoumdjian and Saliba, 2006;Saliba et al., 2009;Saliba et al., 2010).*

*During the second campaign (2013), sampling followed the procedure of Daher et al. (Daher et al., 2013). Aerosols were sampled for 24hr using Sioutas Personal Cascade Impactor Samplers (Sioutas PCIS, SKC Inc., Eighty Four, PA, USA) preceded by denuder containing $PM_{10}$ inlets and operating at 9 l/min. Dust particles were collected according to their size fractions; 10–2.5 µm (coarse particulate matter) and 2.5–0.25 µm (accumulation PM) were collected on 25mm Teflon filters and <0.25 µm (quasi-ultrafine PM) were collected on 37 mm Teflon filters. Total $PM_{10}$ was calculated by the sum of these three size fractions.*

*Ion Chromatography*

*Coated denuders are extracted by a 20mL of Deionized water. One quarter of each Teflon filter used during the first campaign is extracted in 15 ml deionized water and sonicaton for 50 min. Both extracts are micro-filtered and analyzed by ion chromatography (IC) (Saliba and Chamseddine, 2012). During the 2013 sampling campaign, denuder extraction followed the same procedure. Each size resolved filter was extracted in 20ml Deionized water and sonicated for 50min then analyzed using ion chromatography model Metrohm 850 professional IC AnCat with 858 Professional Sample Processor.*

*Gas Monitoring Station*

*The monitoring station is mounted at the same sampling location. It is equipped with Thermo Environmental analyzers used to nitrogen oxides (Model 42i, Chemiluminescence Principle) and sulfur dioxide (Model 43i, Pulsed Fluorescence Principle). The analyzers are calibrated using the Thermo Environmental Multigas Calibrator (Model 146i) for both zero and span concentrations. Zero air is provided from the Thermo Zero Air Generators (Model 111) connected to the Thermo Dual Reactor (Model 1150). Span gases are provided from standard gas bottles for NO, and $SO_2$.*

*The Met One instruments (http://www.metone.com/meteorology.php) were used to setup the weather at a logging interval of 1 min. It is placed on a pole that was lifted about 5 m above the monitoring station at the AUB-Chemistry roof top.*

p. 4831, line 1: The authors indicate that some of the sampling days were influenced by dust from Africa or Arabia, but there is no evidence for this. In principle, any air mass traveling through a polluted city could also have high PM and anion levels. The best way to confirm that mineral dust dominated the samples is to do elemental/mineralogical analysis of the collected particles and match that to the geology of a region. However, in the absence of this I would recommend providing figures showing the actual back trajectories for both non-dusty and dusty days and linking them to their sources. These back trajectories should have enough geospatial coverage to clearly show where the dust is coming from and labeling of populated areas to provide information on whether the air parcels passed through urban or remote spaces. A more thorough discussion of the back trajectories would strengthen the discussion.

I agree with the reviewer that the episode characterization as dusty or non-dusty section does not show enough information. All backwards trajectories were calculated according to the method just described. Samples of HYSPLIT backward air mass trajectory pertaining to the 2013 dusty and non-dusty episodes have been added in the supplementary material and the section has been expanded and modified as follows:

*Soluble gases and size resolved aerosols were sampled at ambient level during Arabian non-dusty days. Dusty days were predicted using the NOAA-Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model of 48h isobaric backward trajectories (Draxler and Rolph, 2013). HYSPLIT was run at three different altitudes between 1 and 10 km, the height of an average dust event. Arabian dust outbreaks have low initial heights (2 to 4 km) (Notaro et al., 2013;Dada et al., 2013). Dust episodes were confirmed using BSC Dream Atmospheric Dust Forecast System. Wind speed and direction, local weather and visibility were used as other indications to the occurrence of dust-rich episodes.*

*p. 4831, lines 15-18: After describing that African dust storms are accompanied by humid air masses, the authors state, "The presence of water on the surface acts as a shield preventing the interaction of NO2 and SO2 directly with the active sites on the particle surface. This is confirmed by the correlation between gaseous HONO and HNO3 (R=0.52)." It is not clear how the correlation (which is actually relatively poor) supports the first sentence.*

All interpretations pertaining to the African dust were removed from the manuscript. The focus of the study remains on the mechanisms pertaining to Arabian dust.

*p. 4831, lines 22-25: It is difficult to understand how a correlation between gas phase HONO and particle sulfate mean that the NO2 hydrolysis mechanism is active in producing HONO.*

*There are many other compounding and interdependent factors that could lead to this correlation. Please clarify.*

Also, as per the removal of the African episodes' interpretations from the manuscript the paragraph pertaining to this sentence has been removed.

*p. 4832-4833: The authors note that gas phase HONO is correlated with gas phase H2SO4 during an Arabian dust storm accompanied by dry air. They suggest that the correlation indicates a synergistic mechanism of adsorption and reaction between NO2 and SO2 on dust surfaces. I think it is fine to discuss this mechanism. However, it is a somewhat unproven mechanism that was arrived at from laboratory experiments carried out at high concentrations (hundreds of ppm); see Ma et al. 2008 and the Liu et al. 2012 papers. I think the authors should keep in mind that it is difficult to extrapolate these mechanisms to atmospheric conditions.*

It is true that it is very difficult to extrapolate, yet we tried to prove the proposed mechanism based on field measurements repeated 3 years consecutively (2009 -2010), 2011 and 2013 (Although 2011 was omitted due to the lack of cation data, the correlations were still consistent with the other 2 years). It is important to note that due to the scarcity of field measurements for HONO formation during dust storms, we relied on mechanism of HONO formation from laboratory studies. However, the formation of HONO on dust particles is well documented in literature (Grassian and coworkers). In a paper published in ACP 2011 by Broske et al, the authors discussed that the enrichment of sulfate is favored on dust enriched with calcium and in a previous study in our lab (Saliba and Chamseddine, 2012) we showed that indeed the Arabian dust storms are enriched with calcium. Also, in the 2013 data we showed that the HONO/$NO_2$ data increased by 100% during dusty days. Based on the $SO_2$ and $NO_2$ data and analysis the paragraph has been modified as:

*"Gas phase composition: The average gas phase HONO, $HNO_3$, and $H_2SO_4$ (sum of $SO_2$ and $H_2SO_4$ captured by the denuders) levels for the sampling periods are shown in Figure 1. During dusty days, a burst of HONO was measured, where in the present sets of data, more than a twofold increase of HONO levels was observed during Arabian dust storms in comparison to non-dusty days. Also, $HNO_3$ and $H_2SO_4$ levels exhibit a clear increase during dusty days. Concomitantly, an increase in $NO_2$ and $SO_2$ gas levels is observed for the 2013 experimental data (Figure 2). During dusty days, the $NO_2$ increase might be explained by the accumulation of locally emitted $NO_2$ pollutants in the stagnant atmospheric environment. Although $NO_2$ and its precursor, NO, could be considered a source of HONO, the trend does not explain the two-fold increase of HONO. In fact, the HONO/$NO_2$ doubles (from an average of 0.03 during non-dusty to 0.06 during dusty days) during dusty days despite the increase in $NO_2$ levels. The higher value of HONO/$NO_2$ of 0.06 remains typical of urban environments (Stutz et al., 2004). Also, the HONO/$HNO_3$ ratio goes up from 1.3 in non-dusty to 1.9 during Arabian dusty days. Similar trend for HONO/$HNO_3$ is observed in 2009 data, where the ratio increases from 0.7 in non-dusty to 1.0 in dusty days. The increase in both ratios (HONO/$NO_2$ and HONO/$HNO_3$) during dusty days indicates that HONO production is due to sources other than $NO_2$. Furthermore, it is important to note that HONO does not correlate with RH during Arabian dusty days while it highly*

*correlates with RH during non-dusty days ($R^2$ = 0.4 in 2009 and $R^2$ = 0.9 in 2013) suggesting that $NO_2$ heterogeneous conversion which leads to HONO and $HNO_3$ is a possible mechanism during non-dusty days (Stutz et al., 2004) as illustrated in equations (R2)-(R4).*

$$2NO_2\ (g) \xleftrightarrow{surface} N_2O_4\ (surface) \qquad (R2)$$

$$N_2O_4\ (surface) \rightarrow ONONO_2\ (surface) \rightarrow NO^+NO_3^-\ (surface) \qquad (R3)$$

$$NO^+NO_3^- \xrightarrow{H2O} HONO\ (g) + H^+ + NO_3^- \qquad (R4)$$

*The increase in $H_2SO_4$ and $SO_2$ alongside HONO and $NO_2$, during dusty days, could be due to similar or independent factors. In fact, a poor correlation between $SO_2$ and $NO_2$ ($R^2$ = 0.4) during non-dusty days suggests the two gases have a low probability that they originate from similar sources or undergo synergistic reactions. However, the enhancement of this correlation during dusty days (correlation between $SO_2$ and $NO_2$ ($R^2$ = 0.7)) and the high correlations between $SO_2$ and $H_2SO_4$ ($R^2$ = 0.6) and $SO_2$ and HONO ($R^2$ = 0.85, descending) suggests that $SO_2$ plays a role in the formation of HONO during dust. One possible explanation is the synergistic mechanism of adsorption and reaction between $NO_2$ and $SO_2$ that could be enhanced by dust particles; mainly mineral oxides according to (R5).*

$$SO_2 + NO_2 + 2H_2O \xrightarrow{H_2O} HONO\ (g) + H_2SO_{4(g,\ particle)} \qquad (R5)$$

*Such effect has been shown to exist in laboratory experiments. For instance, Ma et al. (2008)(Ma et al., 2008) showed that adsorption of $NO_2$ on alumnia was altered in the presence of $SO_2$. In similar studies, co-adsorption of $SO_2$ and $NO_2$ showed that the intermediate $N_2O_4$ leads to nitrates and sulfates in pathways different than the formation of $NO^+NO_3^-$ on the surface (Liu et al., 2012).*

*p. 4832, line 18-20: I believe it is more appropriate to describe these as ligand substitution reactions rather than nucleophilic substitution, which is more common with organic molecules. NO2 and SO2 are termed acidic molecules in the manuscript; it may be clearer to specify them as Lewis acids.*

The proposed mechanism based on surface reactions was omitted from the manuscript as recommended by the reviewer.

Figure 2: It would be more appropriate to plot concentration on an aerosol mass basis. Lastly, it is my opinion that the supplemental figures should be moved to the main manuscript. Alternatively one can construct a table showing acids/anions where R2 values for the various correlations are provided at the intersections of rows and columns. Also for Figures 1 and 2, I recommend using bar and whisker plots rather; this would convey the statistics more effectively.

As per the reviewer's comment, the tables and figures were modified and moved to the manuscript as shown in Table 1 and 2 and Figures 1-3.

## References

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Answers to Reviewer #2

# Interactive comment on “Contribution of airborne dust particles to HONO sources” by N. A. Saliba et al.

**Anonymous Referee #2**

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In the manuscript by Saliba et al. gas and particle phase measurements of some trace components in Lebanon were used to understand potential formation pathways of nitrous acid (HONO) in the atmosphere. Although some interesting data is presented, I have some major concerns with the manuscript, which should be considered before publication in ACP.

Major concerns:

Based on the recommendations of the two reviewers for the need of cations, anions, $NO_2$ and $SO_2$ data, the data of the 2013 field campaign which was analyzed after the submission of the original manuscript is presented. The details of the sampling dates and the results are shown below. Also, since no cation levels were available for the 2011 set of data, the results of this field campaign was removed. As for the 2009 study, only the Arabian dust episodes and its corresponding non-dusty days are presented. Hence, the revised manuscript and the answers to the reviewers present the chemical analysis of the gases and the chemical composition of PMs during non-dusty days and the Arabian dusty days of the summer and fall seasons.

- Measurements Method:

*In the present study,* ***dry denuder/filter pack measurements*** *were used which are unfortunately not explained in detail in the present manuscript and only a reference to another study (Saliba and Chamseddine, 2012) is given. When going back to this reference, only one denuder is used for basic gases (H3PO3) and one for acid gases (Na2CO3). If the same set-up is also used in the* ***present study*** *(?), than these measurements will be affected by well-known* ***artefacts*** *and especially the HONO data should not be used. For example, it is well known, that NO2 forms nitrite on the carbonate denuders, for which typically two carbonate denuder are used in series for correction (see studies by A. Febo). In addition, also the reaction of NO2+SO2, also discussed here as formation pathway on particles, will cause an* ***additional interference*** *(see again Febo and also Spindler et al.), which needs further corrections using also the SO2 data. Further, the* ***nitrite*** *which is sampled on the carbonate denuder is partially oxidized (e.g. by O2, O3, H2O2, :) to nitrate leading to a negative artefact.*
*Typically, HNO3 is first sampled on a NaCl denuder and the nitrate + nitrite signals from the carbonate denuder are used for HONO. Another issue to the denuder technique is that the authors have* ***measured SO2 and not H2SO4*** *like this is mentioned throughout the manuscript (s. e.g. page 4831, line 4). It is well known that most SO2 (depending on the oxidant level) is sampled as sulphate on the carbonate denuders (sampled as SO3(2-) and oxidized to SO4(2-)).*

*Since SO2 levels will be much higher than gas phase H2SO4 (see also vapour pressure of H2SO4 and uptake kinetics on particles: : :),* ***the sulphate signal of the denuder represents SO2****. Finally, here only 24 h data is considered from which formation mechanisms of HONO are derived. However, since HONO formation mechanisms are very different during day and night-time (see also specific comments below),* ***low resolution data should not be used.***

Upon the reviewer's suggestion, the employed sampling method during the 2009 and the 2013 sampling campaigns has been clarified and explained in details as per below.

Considering the artifacts, the denuder coating and extraction were done in a $N_2$ 99.0% glove-box closed compartment to minimize contamination. Some negative artifacts might appear during the removal of acidic gases by denuders; and it is expected that the HONO would be underestimated due to its oxidation to $HNO_3$ during the 24h sampling period by atmospheric ozone. However, 1% glycerol solution has been added to the carbonate-coating solution and it has been shown that the former has the capacity to minimize the occurrence of such oxidation reactions and therefore the loss of HONO would be minimal (Febo et al., 1987). The glycerol solution also increases the denuder capacity towards $SO_2$ and $HNO_3$ (Spurny, 1999)(and references therein).

As for the sulfuric acid part, I agree with the reviewer that $SO_2$ is collected as $H_2SO_4$, yet this is only the case when the denuders are extracted with $H_2O_2$ solution which aids the complete conversion of $SO_2$ to sulfate (Markovic et al., 2012). In the present set of data, the extraction procedure, followed in 2009 and 2013 sampling campaigns did not include $H_2O_2$ oxidizing agent and therefore the collected acidic gases represent the sum of converted $SO_2$ and original gas phase $H_2SO_4$. Hydrogen peroxide was not added to the extraction solution, as its presence leads to the oxidation of HONO into $HNO_3$, leading to an underestimation and overestimation of the latter, respectively. From here on, the collected $SO_2$ and $H_2SO_4$ on denuders will be referred to as $H_2SO_4$ (gas).

The modified text pertaining to the sample collection method appears as follows:

### *Collection techniques*

*The aerosol and gas samples are collected using a Rupprecht & Patashnick Partisol 2300. Sampling occurred between two different campaigns, detailed in Table 1.*

*Table 1. PM and acid gas concentrations collected during dusty and non-dusty days in 2009 and 2013 field campaign measurements*

| **2013** | RH | UF | ACC | CPM | PM |
|---|---|---|---|---|---|
| **Non Dusty** | | | | | |
| **23-Jul-13** | 70.97 | 26.33 | 15.46 | 25.59 | **67.38** |
| **29-Jul-13** | 69.14 | 12.97 | 6.58 | 14.85 | **34.40** |
| **22-Aug-13** | 66.81 | 17.94 | 7.32 | 15.50 | **40.76** |
| **4-Sep-13** | 64.48 | 13.79 | 5.94 | 23.99 | **43.72** |
| **10-Sep-13** | 64.39 | 22.26 | 6.34 | 22.44 | **51.03** |
| **Arabian Dusty Days** | | | | | |
| **23-Oct-13** | 30.00 | 21.64 | 10.39 | 29.10 | **61.14** |
| **5-Nov-13** | 69.03 | 19.78 | 38.44 | 63.41 | **121.63** |
| **7-Nov-13** | 74.18 | 18.99 | 42.44 | 74.52 | **135.95** |
| **12-Nov-13** | 58.87 | 16.71 | 33.59 | 36.58 | **86.88** |
| **19-Nov-13** | 55.92 | 24.24 | 15.22 | 18.97 | **58.43** |

| **2009** | RH | UF | ACC | CPM | PM |
|---|---|---|---|---|---|
| **Non Dusty** | | | | | |
| 6-Sep-09 | 60.00 | | | | **46.15** |
| 24-Sep-09 | 49.00 | | | | **30.65** |
| 30-Sep-09 | 44.00 | | | | **44.54** |
| 6-Oct-09 | 78.00 | | | | **56.89** |
| 12-Oct-09 | 56.00 | | | | **42.66** |
| 30-Oct-09 | 91.00 | | | | **62.87** |
| 29-Nov-09 | 76.00 | | | | **37.08** |
| **Arabian Dusty Days** | | | | | |
| 18-Oct-09 | 12.00 | | | | **129.52** |
| 24-Oct-09 | 30.00 | | | | **83.55** |
| 11-Nov-09 | 43.00 | | | | **80.86** |
| 23-Nov-09 | 33.00 | | | | **77.47** |

### *Collection techniques*

*Soluble gases and size resolved aerosols were sampled at ambient level during Arabian dusty and during non-dusty days. Dusty days were predicted using the NOAA-Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model of 48h isobaric backward trajectories (Draxler and Rolph, 2013). HYSPLIT was run at three different altitudes between 1 and 10 km, the height of an average dust event. Arabian dust outbreaks have low initial heights (2 to 4 km) and show east and south-east trajectories (Notaro et al., 2013;Dada et al., 2013). Dust episodes were confirmed using BSC Dream Atmospheric Dust Forecast System (http://www.bsc.es/earth-sciences/mineral-dust-forecast-system/bsc-dream8b-forecast/). Wind speed and direction, local weather and visibility were used as other indications to the occurrence of dust-rich episodes.*

The aerosol and gas samples are collected using a Rupprecht & Patashnick Partisol 2300. Sampling occurred between two different campaigns, detailed in Table 1. Soluble acidic gases (HONO, $HNO_3$ and $H_2SO_4$) were sampled for 24hr using a diffusion denuder system. The system is based on two Honey Comb denuders (HC) coated with 1% $NaCO_3$ and 1% glycerol in 50:50 water: methanol solution and placed in series in Rupprecht & Patashnick (R&P) Chemcomb™ cartridges. Sampling and analysis of trace gases is fully described in Saliba and Chamseddine (Saliba and Chamseddine, 2012).

During the first sampling campaign (2009), aerosol collection extended over 24 hours using pre-weighed 37mm Teflon filter that is housed between two Teflon meshes downstream the gas collecting denuders in $PM_{10}$ inlets Harvard cartridges. The flow rate was set at 10 l/min. Following collection and gravimetric calculation of PM concentrations, the filters are cut into four equal pieces that are stored at 4℃ until ready for chemical analysis (Kouyoumdjian and Saliba, 2006;Saliba et al., 2009;Saliba et al., 2010).

During the second campaign (2013), sampling followed the procedure of Daher et al. (Daher et al., 2013). Aerosols were sampled for 24hr using Sioutas Personal Cascade Impactor Samplers (Sioutas PCIS, SKC Inc., Eighty Four, PA, USA) preceded by denuder containing $PM_{10}$ inlets and operating at 9 l/min. Dust particles were collected according to their size fractions; 10–2.5 μm (coarse particulate matter) and 2.5–0.25 μm (accumulation PM) were collected on 25mm Teflon filters and <0.25 μm (quasi-ultrafine PM) were collected on 37 mm Teflon filters.

## Ion Chromatography

Coated denuders are extracted by a 20mL of Deionized water. One quarter of each Teflon filter used during the first campaign is extracted in 15 ml deionized water and sonicaton for 50 min. Both extracts are micro-filtered and analyzed by ion chromatography (IC) (Saliba and Chamseddine, 2012). During the 2013 sampling campaign, denuder extraction followed the same procedure. Each size resolved filter was extracted in 20ml Deionized water and sonicated for 50min then analyzed using ion chromatography model Metrohm 850 professional IC AnCat with 858 Professional Sample Processor.

## Gas Monitoring Station

The monitoring station is mounted at the same sampling location. It is equipped with Thermo Environmental analyzers used to nitrogen oxides (Model 42i, Chemiluminescence Principle) and sulfur dioxide (Model 43i, Pulsed Fluorescence Principle). The analyzers are calibrated using the Thermo Environmental Multigas Calibrator (Model 146i) for both zero and span concentrations. Zero air is provided from the Thermo Zero Air Generators (Model 111) connected to the Thermo Dual Reactor (Model 1150). Span gases are provided from standard gas bottles for NO, and $SO_2$. The Met One instruments (http://www.metone.com/meteorology.php) were used to setup the weather at a logging interval of 1 min. It is placed on a pole that was lifted about 5 m above the monitoring station at the AUB-Chemistry roof top.

*2) Missing Data*

*Since HONO formation is typically explained by NO2 reactions (see also the discussion of the present study), measurements of this most important precursor are missing. Thus, any discussion on potential NO2 mechanisms is highly speculative.*

As per the reviewer recommendations that the $NO_2$ data makes the backbone of the manuscript; we introduced the 2013 campaign which contains the $NO_2$ and $SO_2$ data as shown in Table 2.

Table 2. Concentrations of $NO_2$ and $SO_2$ during the sampling days of the 2013 field campaign

| Date | $NO_2$ (µg/m$^3$) | $SO_2$(µg/m$^3$) |
|---|---|---|
| | **Non Dusty** | |
| 23-Jul-13 | 39.41 | 6.07 |
| 29-Jul-13 | 17.88 | 3.95 |
| 22-Aug-13 | 37.10 | 7.71 |
| 4-Sep-13 | 29.12 | 4.20 |
| 10-Sep-13 | 35.86 | 12.03 |
| | **Dusty** | |
| 23-Oct-13 | 60.66 | 15.94 |
| 5-Nov-13 | 41.19 | 11.77 |
| 7-Nov-13 | 60.62 | 13.65 |
| 12-Nov-13 | 43.03 | 7.32 |
| 19-Nov-13 | 61.18 | 15.90 |

*Mechanisms discussed besides several errors on potential mechanisms in the introduction (see specific comments), there is not sufficient experimental data to propose the two source reactions of HONO.*

The introduction is revised to include all the comments raised by the two reviewers. See specific comments below.

The point raised by the reviewer is well taken and the discussion has been revised accordingly. First the evidences deduced from the two field campaigns are presented in bullet points. Following, a paragraph summarizing the analysis of the results will be considered the basis of the proposed mechanism that will be shown in the manuscript. It is important to note that due to the scarcity of field measurements for HONO formation during dust storms, we relied on mechanism of HONO formation from laboratory studies. The formation of HONO on dust particles is well documented in literature (Grassian and coworkers). In a paper published in ACP 2011 by Broske et al, the authors discussed that the enrichment of sulfate is favored on dust enriched with calcium and in a previous study in our lab (Saliba and Chamseddine, 2012) we showed that indeed the Arabian dust storms are enriched with calcium.

A. Gas Phase

- There is a burst of HONO during dusty days (Figure A)
- There is an increase in $HNO_3$ and $H_2SO_4$ levels during dusty days (Figure B & C)
- An increase in $NO_2$ and $SO_2$ gas levels is observed for the 2013 experimental data (Figures D)
- There is a high correlation of HONO with RH in non-dusty days ($R^2 = 0.95$ in the 2013 field campaign and $R^2 = 0.41$ in the 2009 campaign) (Figure E)
- In the 2013 campaign, HONO correlates with $HNO_3$ during non-dusty ($R^2 = 0.6$) but does not correlate with $HNO_3$ during Arabian dusty days ($R^2 = 0.08$) (Figure F)
- The HONO/$NO_2$ doubles during dusty days despite the increase in $NO_2$ levels (0.03 during non-dusty to 0.06 during dusty)
- During dusty days $SO_2$ highly correlates with $H_2SO_4$ ($R^2 = 0.6$, $p < 0.05$), and anti-correlates with HONO ($R^2 = 0.85$, $p < 0.05$). In non-dusty days, these correlations are poor ($SO_2$ and $H_2SO_4$ ($R^2 = 0.14$), and $SO_2$ and HONO ($R^2 = 0.10$))(Figure G)
- During dusty days HONO/$H_2SO_4$ shows an increase over non-dusty days despite the increase in both concentrations

*Conclusions from the presented observations*: During dusty days, a burst of HONO was measured, where in the present sets of data, more than a twofold increase of HONO levels was observed during Arabian dust storms in comparison to non-dusty days. Also, $HNO_3$ and $H_2SO_4$ levels exhibit a clear increase during dusty days. Concomitantly, an increase in $NO_2$ and $SO_2$ gas levels is observed for the 2013 experimental data (Figure 2). During dusty days, the $NO_2$ increase might be explained by the accumulation of locally emitted $NO_2$ pollutants in the stagnant atmospheric environment. Although $NO_2$ and its precursor, NO, could be considered a source of HONO, the trend does not explain the two-fold increase of HONO. In fact, the HONO/$NO_2$ doubles (from an average of 0.03 during non-dusty to 0.06 during dusty days) during dusty days despite the increase in $NO_2$ levels. The higher value of HONO/$NO_2$ of 0.06 remains typical of urban environments (Stutz et al., 2004). Also, the HONO/$HNO_3$ ratio goes up from 1.3 in non-dusty to 1.9 during Arabian dusty days. Similar trend for HONO/$HNO_3$ is observed in 2009 data, where the ratio increases from 0.7 in non-dusty to 1.0 in dusty days. The increase in both ratios (HONO/$NO_2$ and HONO/$HNO_3$) during dusty days indicates that HONO production is due to sources other than $NO_2$. Furthermore, it is important to note that HONO does not correlate with RH during Arabian dusty days while it highly correlates with RH during non-dusty days ($R^2 = 0.4$ in 2009 and $R^2 = 0.9$ in 2013) suggesting that $NO_2$ heterogeneous conversion which leads to HONO and $HNO_3$ is a possible mechanism during non-dusty days (Stutz et al., 2004) as illustrated in equations (R2)-(R4).

$$2NO_2\ (g) \xleftrightarrow{surface} N_2O_4\ (surface) \qquad (R2)$$

$$N_2O_4\ (surface) \rightarrow ONONO_2\ (surface) \rightarrow NO^+NO_3^-\ (surface) \qquad (R3)$$

$$NO^+NO_3^- \xrightarrow{H2O} HONO\ (g) + H^+ + NO_3^- \qquad (R4)$$

The increase in $H_2SO_4$ and $SO_2$ alongside HONO and $NO_2$, during dusty days, could be due to similar or independent factors. In fact, a poor correlation between $SO_2$ and $NO_2$ ($R^2 = 0.4$) during non-dusty days suggests the two gases could have similar sources. However, the enhancement of this correlation during dusty days (correlation between $SO_2$ and $NO_2$ ($R^2 = 0.7$)) and the high correlations between $SO_2$ and $H_2SO_4$ ($R^2 = 0.6$) and $SO_2$ and HONO ($R^2 = 0.85$, descending) suggests that $SO_2$ plays a role in the formation of HONO during dust. One possible explanation is the synergistic mechanism of adsorption and reaction between $NO_2$ and $SO_2$ that could be enhanced by dust particles; mainly mineral oxides according to (R5).

$$SO_2 + NO_2 + 2H_2O \xrightarrow{H2O} HONO\ (g) + H_2SO_{4\ (g,\ particle)} \qquad (R5)$$

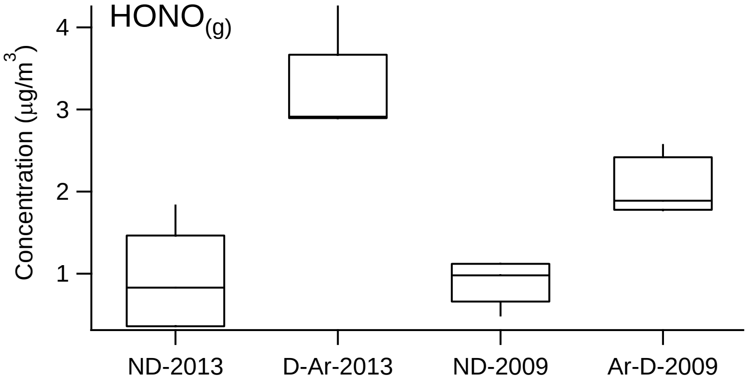

Figure A Box plots of concentrations of acid gas HONO during non-dusty (ND) and Arabian dusty (Ar-D) days in 2013 and 2009.

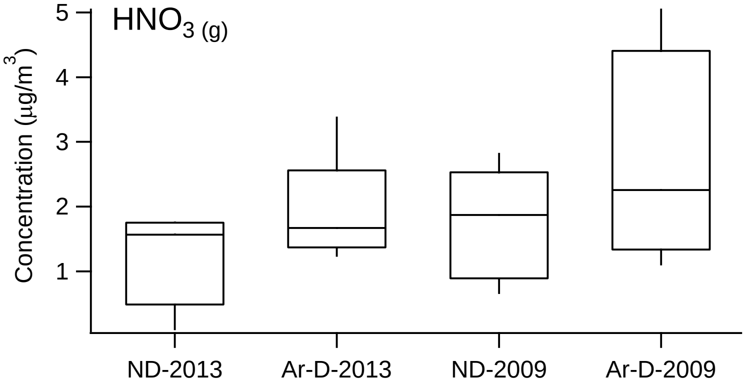

Figure B Box plots of concentrations of acid gas $HNO_3$ during non-dusty (ND) and Arabian dusty (Ar-D) days in 2013 and 2009..

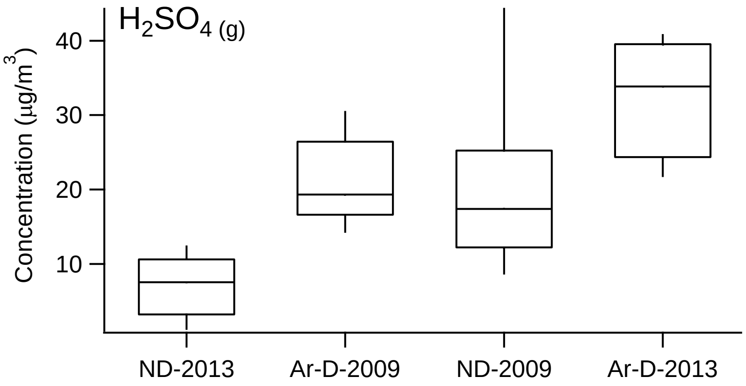

Figure C Box plots of concentrations of acid gas $H_2SO_4$ during non-dusty (ND) and Arabian dusty (Ar-D) days in 2013 and 2009.

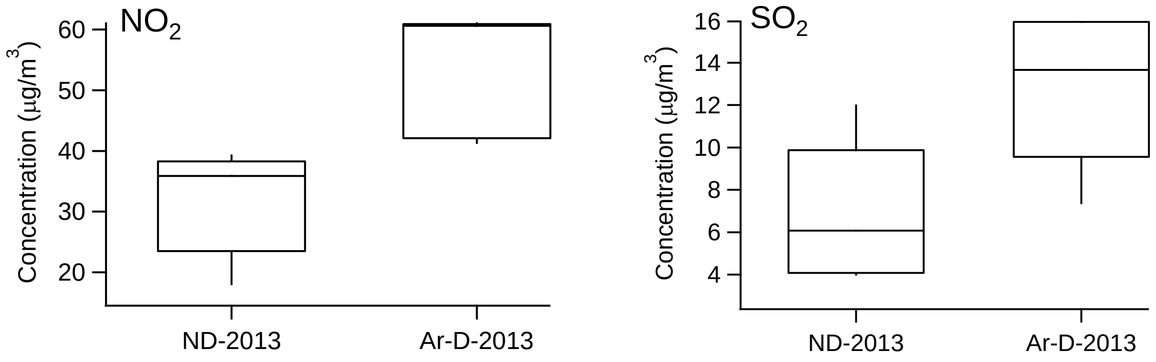

Figure D Box plots of concentration of $NO_2$ and $SO_2$ in the 2013 campaign during non-dusty (ND) and Arabian dusty (Ar-D) days.

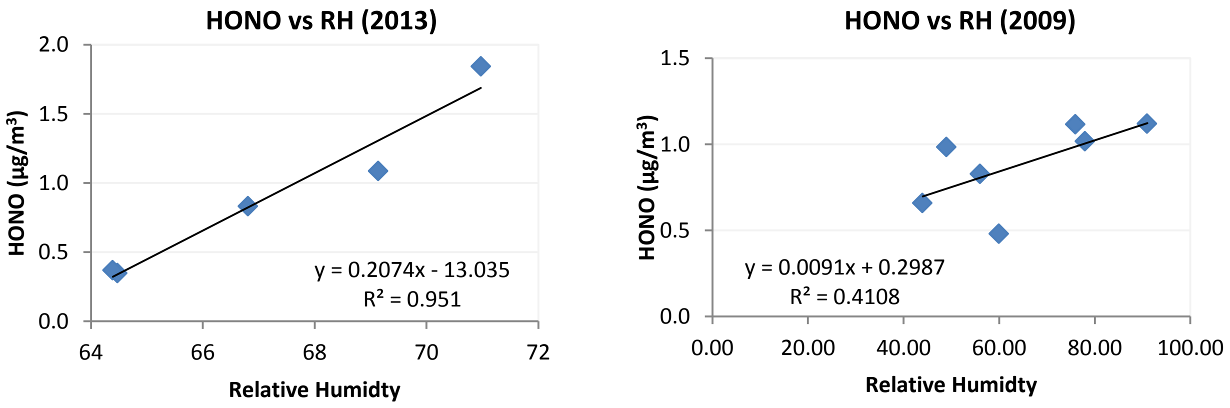

Figure E Correlation between concentration of HONO (µg/m$^3$) and RH during non-dusty days of the 2013 and 2009 sampling campaigns.

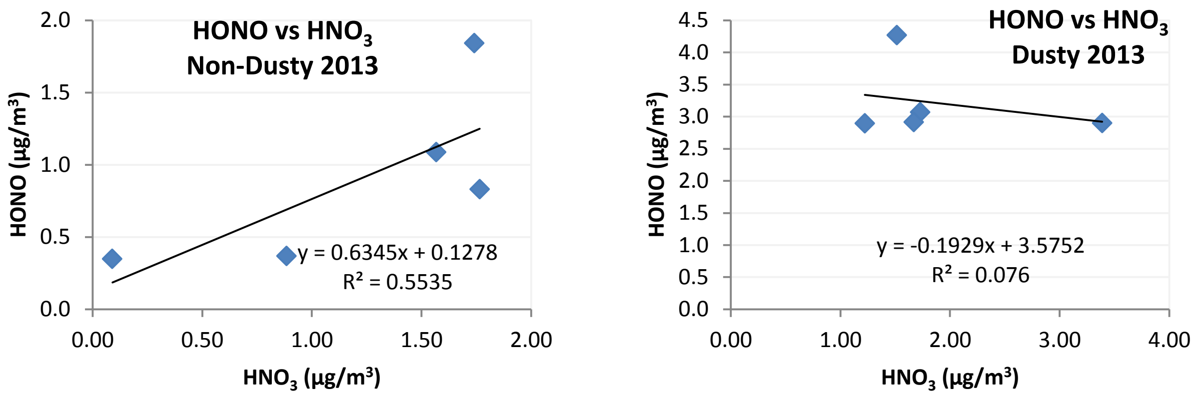

Figure F Correlation between HONO and $HNO_3$ during non-dusty and dusty days in the 2013 campaign

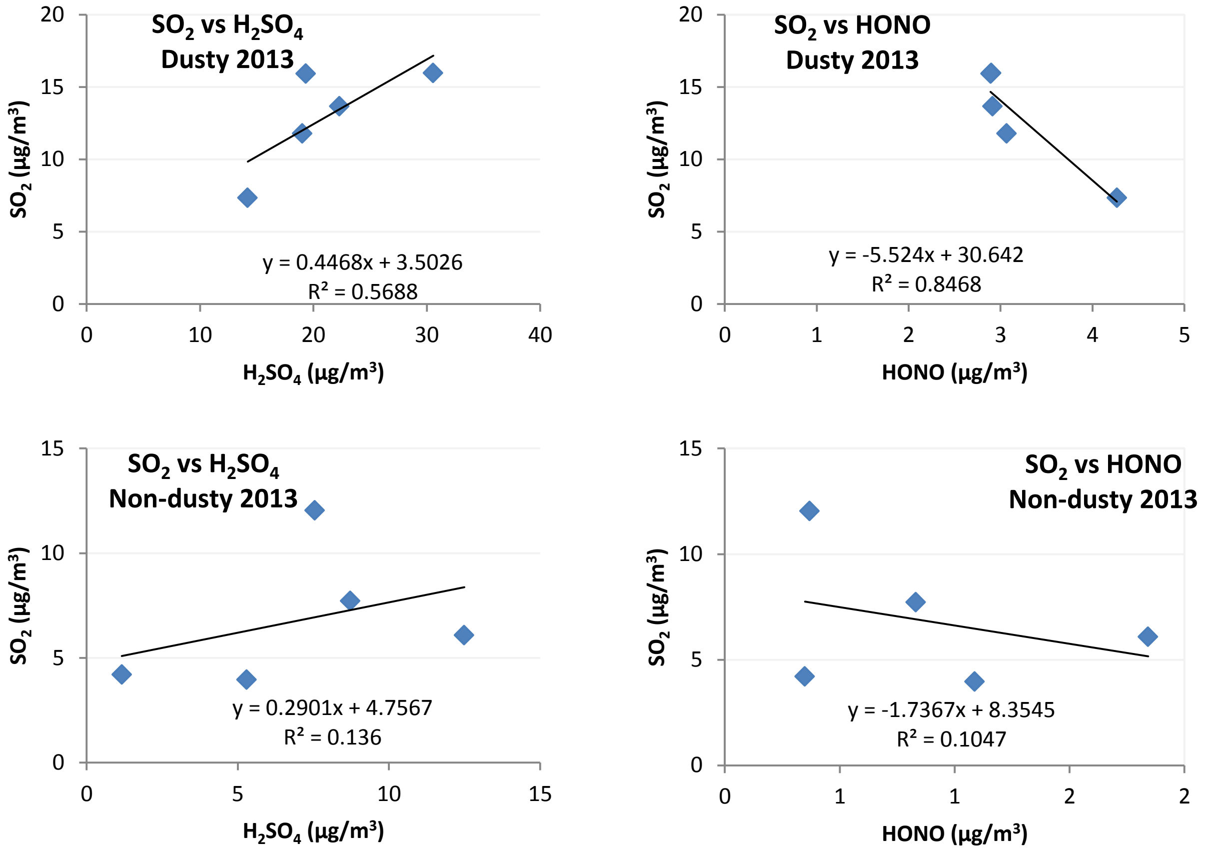

Figure G Correlations of $SO_2$ with $H_2SO_4$ and HONO during dusty and non-dusty days in the 2013 sampling campaign

## B. Particle Phase

- There is an increase in the nitrates and sulfates in $PM_{10}$. However, when considering the ultrafine and accumulation modes of the 2013 data, it is observed that higher levels of nitrates and sulfates are mostly found in the accumulation mode (Figure H).
- Increased acidity during dusty days is mostly noticed in the accumulation and coarse modes with no variation in the UF mode (Table 3). Acidity is calculated (Kerminen et al., 2001;Schwab et al., 2004)

  $$[H^+] = [SO_4^{2-}] + [NO_3^-] - [NH_4^+]$$

  It is important to note that both campaigns showed increased in acidity.
- The extent to which acidic aerosol is neutralized is approximated as per Stevens et al., 1980 by:

  $$f = \frac{[H^+]}{[H^+] + [{NH_4}^+]}$$

  It is considered that when $f = 0$, there is full neutralization by $NH_4^+$, if $f = 1$, no neutralization has occurred. At $f = 0.5$, the bulk aerosol is a mixture of chemical species of properties similar to $NH_4HSO_4$; at $f = 0.25$, the mixture is similar to letovicite ($(NH_4)_3H(SO_4)_2$)(Stevens et al., 1980)
- Considering the different PM sizes: UF, ACC and Coarse, which were sampled in the 2013 campaign it is found that:
  a. There is a high correlation between PM-ACC and HONO ($R^2 = 0.8$, $p < 0.05$) during non-dusty days that. In dusty days (Arabian), HONO anti-correlates with PM-UF ($R^2 = 0.8$, $p < 0.05$) (Figure I).
  b. HONO correlates highly with NO3-ACC during non-dusty days ($R^2 = 0.96$, $p < 0.3$) and with $NO_3^-$-ACC ($R^2 = 0.65$, $p < 0.05$) and NO3—UF ($R^2 = 0.86$, $p < 0.05$) during dusty days (Figure J).
- Ammonium poor medium and f value > 0.5 indicates that there is no neutralization of the anions mainly $NO_3^-$ and $SO_4^{2-}$ (Table 3).

*Conclusions from the presented observations*: The study of the particle phase composition emphasizes the aforementioned observations and conclusions. In particles, there was a clear increase in the levels of nitrates and sulfates which were mostly found in the accumulation mode when examining the 2013 field measurements (Figure H). This was accompanied by an increase in the ammonium levels. During non-dusty days, the correlations of HONO with PM-ACC ($R^2 = 0.80$ for the 2013 field measurements), $NO_3^-$-ACC ($R^2 = 0.96$ for the 2013 field measurements) and $NO_3^-$ - PM10 ($R^2 = 0.4$ for the 2009 field measurements) indicate either HONO and PM-ACC and $NO_3^-$ originate from similar sources or HONO is the result of a secondary reaction involving PM and leading to nitrate; i.e. $NO_2$ heterogeneous hydrolysis. The same behavior was not observed during dusty days.

A drop in the neutralization factor of the 2013 field campaign (drop from 0.7 to 0.5) (Table 3), mostly noticed in the ACC mode, was counterfeited by an increase in the aerosol acidity (calculated as $[H^+] = [SO_4^{2-}] + [NO_3^-] - [NH_4^+]$)(Kerminen et al., 2001;Schwab et al., 2004). This increase was observed in both the 2009 and 2013-$PM_{10}$ field measurements (Table 3). As a result of that, the particle-gas conversion and hence the increase in acid gases during dusty days becomes enhanced. Another source of HONO would be the heterogeneous reaction of $NO_2$ with semi-volatile organics which have been shown to account for 75% of the HONO formation in Mexico City (Li et al., 2010). Recent studies in our laboratory have shown dusty episodes exhibiting an increase of 33 % over non-dusty episodes in the organic matter of the fine fraction.

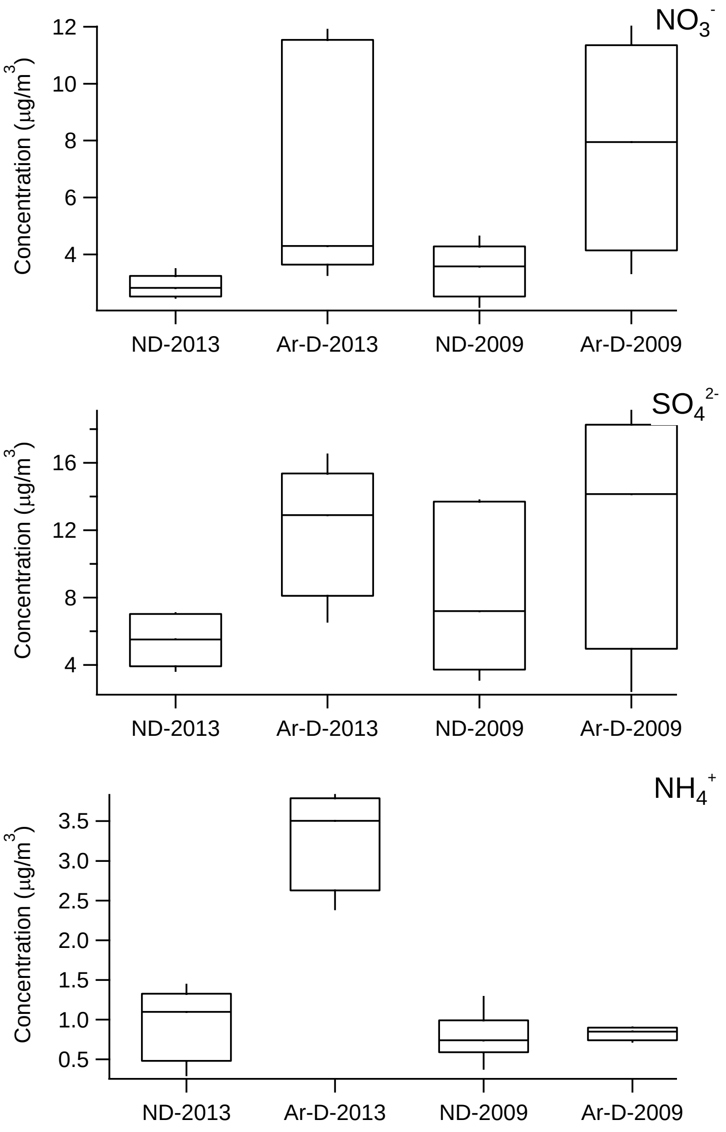

Figure H. Concentrations of $NO_3^-$, $SO_4^{2-}$ and $NH_4^+$ in µg/m$^3$ during non-dusty (ND) Arabian dusty (Ar-D) and days of the 2009 and 2013 field campaigns

Table 3 Acidity and neutralization factor (*f*) of size-segregated aerosols (UF (ultrafine particles), ACC (Accumulation) and CPM (coarse particulate matter) during dusty and non-dusty days

| Date | [H$^+$] (mol/m$^3$) | | | | *f* (mol/m$^3$) | | | | Date | [H$^+$] (mol/m$^3$) | *f* (mol/m$^3$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | UF | Acc | CPM | Total PM | UF | Acc | CPM | Total PM | | | |
| | | | | **2013** | | | | | | **2009** | |
| | | | | **Non-dusty** | | | | | | | |
| 23-Jul-13 | 0.04 | 0.05 | 0.03 | **0.12** | 0.49 | 0.7 | 0.65 | **0.61** | 6-Sep-09 | **0.28** | **0.80** |
| 29-Jul-13 | 0.04 | 0.01 | 0.04 | **0.09** | 0.62 | 0.7 | 0.85 | **0.71** | 24-Sep-09 | **0.10** | **0.83** |
| 22-Aug-13 | 0.05 | 0.03 | 0.04 | **0.12** | 0.45 | 0.88 | 0.89 | **0.65** | 30-Sep-09 | **0.17** | **0.80** |
| 4-Sep-13 | 0.02 | 0.09 | 0.03 | **0.14** | 0.79 | 0.94 | 0.85 | **0.9** | 6-Oct-09 | **0.18** | **0.84** |
| 10-Sep-13 | 0.01 | 0.01 | 0.04 | **0.06** | 0.22 | 0.3 | 0.79 | **0.5** | 12-Oct-09 | **0.21** | **0.80** |
| | | | | | | | | | 30-Oct-09 | **0.06** | **0.61** |
| | | | | | | | | | 29-Nov-09 | **0.28** | **0.83** |
| **Dusty** | | | | **Dusty** | | | | | | | |
| 5-Nov-13 | 0.03 | 0.09 | 0.17 | **0.29** | 0.51 | 0.37 | 0.97 | **0.61** | 18-Oct-09 | **0.39** | **0.91** |
| 7-Nov-13 | 0.03 | 0.11 | 0.18 | **0.32** | 0.45 | 0.4 | 0.97 | **0.6** | 24-Oct-09 | **0.37** | **0.89** |
| 12-Nov-13 | 0.03 | 0.1 | 0.01 | **0.13** | 0.57 | 0.36 | 0.43 | **0.39** | 11-Nov-09 | **0.54** | **0.91** |
| 19-Nov-13 | 0.05 | 0.04 | 0.03 | **0.12** | 0.38 | 0.52 | 0.7 | **0.48** | 23-Nov-09 | **0.06** | **0.53** |

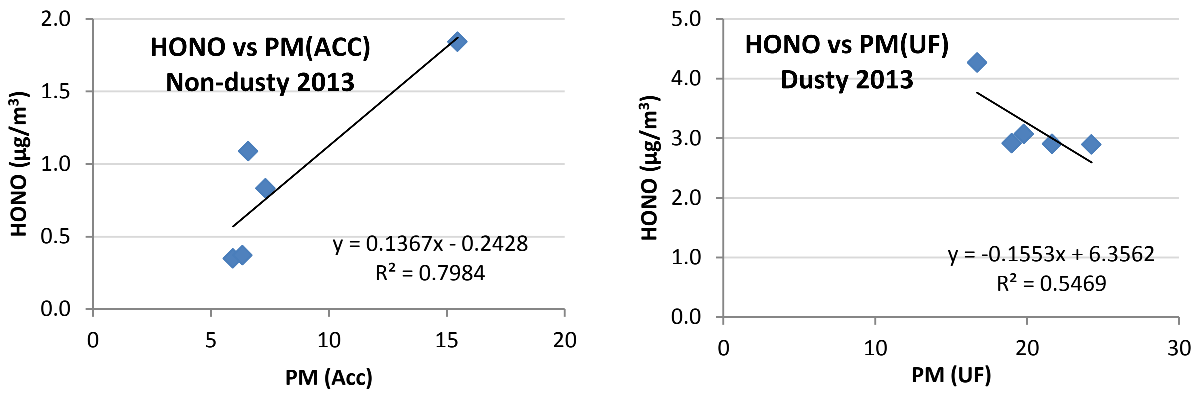

Figure I Correlations of HONO with PM (Acc) during non-dusty days and with PM(UF)during dusty days in the 2013 sampling campaign, where PM is particulate matter, Acc stands for accumulation and UF stands for ultrafine.

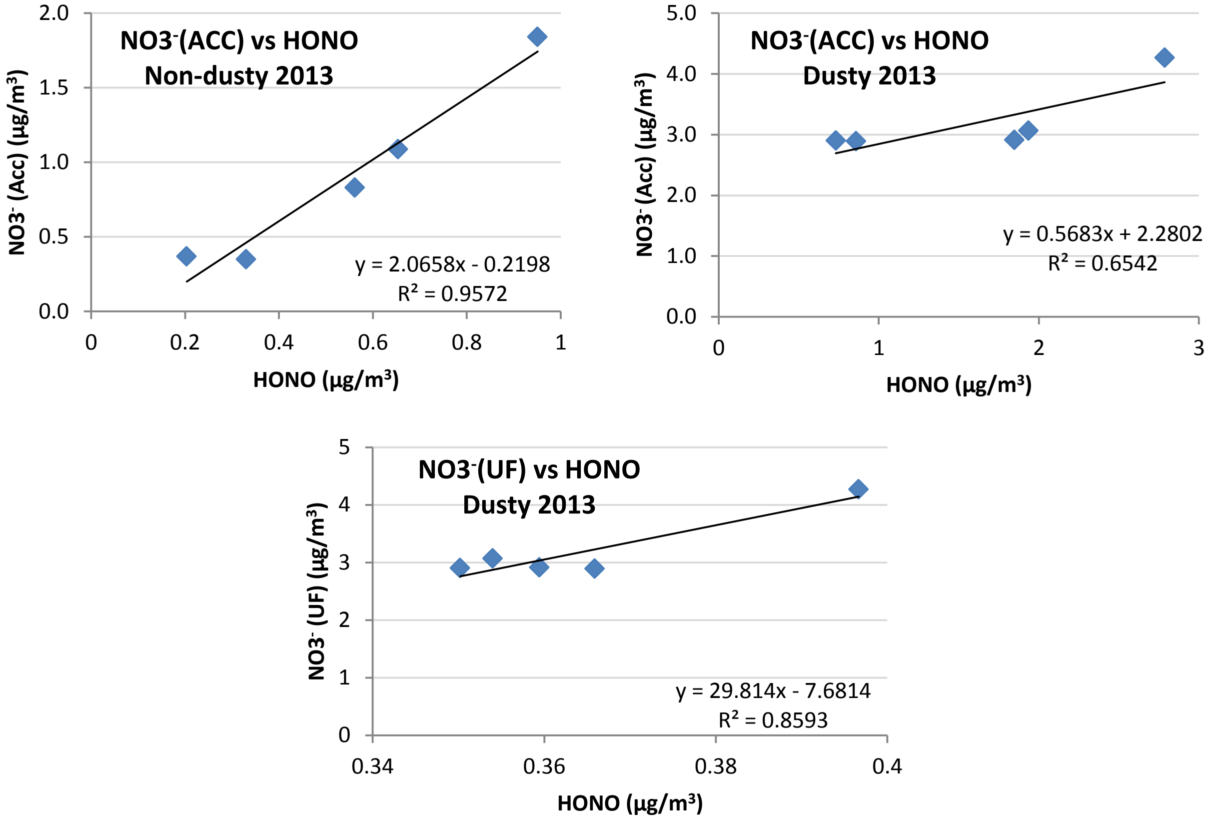

Figure J Correlations of HONO with Nitrate (Acc) during non-dusty days and suring dusty days and with Nitrate (UF)during dusty days in the 2013 sampling campaign, where PM is particulate matter, Acc stands for accumulation and UF stands for ultrafine.

Based on the presented evidences and discussions, the paragraph reads as:

*Gas phase composition: The average gas phase HONO, $HNO_3$, and $H_2SO_4$ (sum of $SO_2$ and $H_2SO_4$ captured by the denuders and represented thereafter by $H_2SO_4$) levels for the sampling periods are shown in Figure 1. During dusty days, a burst of HONO was measured where more than a twofold increase of HONO levels was observed during Ar-D days in comparison to non-dusty days. Also, $HNO_3$ and $H_2SO_4$ levels exhibit a clear increase during dusty days. Concomitantly, an increase in $NO_2$ and $SO_2$ gas levels is observed for the 2013 experimental data (Figure 2). During dusty days, the $NO_2$ increase might be explained by the accumulation of local emission due to stagnant wind. Although $NO_2$ and its precursor, NO, could be considered a source of HONO, the trend does not explain the two-fold increase of HONO. In fact, the HONO/$NO_2$ doubles (from an average of 0.03 to 0.06) during dusty days despite the increase in $NO_2$ levels. The higher value of HONO/$NO_2$ of 0.06 remains typical of urban environments (Stutz et al., 2004). Also, the HONO/$HNO_3$ ratio goes up from 1.3 in non-dusty to 1.9 during Arabian dusty days. Similar trend for HONO/$HNO_3$ is observed in 2009 data, where the ratio increases from 0.7 to 1.0 in in* non-dusty and dusty days, respectively. The increase in both ratios ($HONO/NO_2$ and $HONO/HNO_3$) during dusty days indicates that HONO production is due to sources other than $NO_2$. Furthermore, it is important to note that HONO does not correlate with RH during Arabian dusty days while it highly correlates with RH during non-dusty days ($R^2$ = 0.4 in 2009 and $R^2$ = 0.9 in 2013) suggesting that $NO_2$ heterogeneous conversion which leads to HONO and $HNO_3$ is a possible mechanism at relatively higher RH, during non-dusty days (Stutz et al., 2004) as illustrated in equations (R2)-(R4).

$2NO_2$ (g) $\xleftrightarrow{surface}$ $N_2O_4$ (surface) (R2)

$N_2O_4$ (surface) → $ONONO_2$ (surface) →$NO^+NO_3^-$ (surface) (R3)

$NO^+NO_3^-$ $\xrightarrow{H_2O}$ HONO (g) + $H^+$ + $NO_3^-$ (R4)

The increase in $H_2SO_4$ and $SO_2$ alongside HONO and $NO_2$, during dusty days, could be due to similar or independent factors. In fact, a poor correlation between $SO_2$ and $NO_2$ ($R^2$ = 0.4) during non-dusty days indicates that the two gases have a low probability to originate from similar sources. However, the enhancement of this correlation during dusty days (correlation between $SO_2$ and $NO_2$ ($R^2$ = 0.7)) and the high correlations between $SO_2$ and $H_2SO_4$ ($R^2$ = 0.6) and $SO_2$ and HONO ($R^2$ = 0.85, descending) suggests that $SO_2$ plays a role in the formation of HONO. One possible explanation is the synergistic mechanism of adsorption and reaction between $NO_2$ and $SO_2$ enhanced by dust particles; mainly mineral oxides according to (R5).

$SO_2$ + $NO_2$ + $2H_2O$ $\xrightarrow{H_2O}$ HONO (g) + $H_2SO_4$(g, particle) (R5)

Such effect has been shown to exist in laboratory experiments. For instance, Ma et al. (2008)(Ma et al., 2008) showed that adsorption of $NO_2$ on alumnia was altered in the presence of $SO_2$. In similar studies, co-adsorption of $SO_2$ and $NO_2$ showed that the intermediate $N_2O_4$ leads to nitrates and sulfates in pathways different than the formation of $NO^+NO_3^-$ on the surface (Liu et al., 2012).

Particle phase composition: The study of the particle phase composition emphasizes the aforementioned observations and conclusions. In particles, there was a clear increase in the levels of nitrates and sulfates which were mostly found in the accumulation mode when examining the 2013 field measurements (Figure 3). This was accompanied by an increase in the ammonium levels as shown in Figure 4. During non-dusty days, the correlations of HONO with PM-ACC (Accumulation) ($R^2$ = 0.80 in 2013), $NO_3^-$-ACC ($R^2$ = 0.96 in 2013) and $NO_3^-$ - $PM_{10}$ ($R^2$ = 0.4 in 2009) indicate either HONO and PM-ACC and $NO_3^-$ originate from similar sources or HONO is the result of a secondary reaction involving PM and leading to nitrate; i.e. $NO_2$ heterogeneous hydrolysis. The same behavior was not observed during dusty days.

The extent to which the increase in ammonium (during the 2013 field campaign only), nitrate and sulfate affect the neutralization of aerosols is approximated as per Stevens et al., 1980:

$$f = \frac{[H^+]}{[H^+] + [{NH_4}^+]}$$

When 0 < f < 1= 0, the bulk aerosol is a mixture of chemical species of properties similar to $NH_4HSO_4$. At f = 0, a full neutralization by $NH_4^+$ in the particle is considered whereas no *neutralization is assumed when f = 1. A drop in the neutralization factor of the 2013 field campaign (from 0.7 to 0.5) (Table 3), mostly noticed in the ACC mode, was counterfeited by an increase in the aerosol acidity (calculated as* $[H^+] = [SO_4^{2-}] + [NO_3^-] - [NH_4^+]$*) (Kerminen et al. 2001; Schwab et al. 2004). This increase was observed in both the 2009 and 2013-*$PM_{10}$ *field measurements (Table 3). As a result of that, the particle-gas conversion and hence the increase in acid gases during dusty days becomes enhanced. Another source of HONO would be the heterogeneous reaction of* $NO_2$ *with semi-volatile organics which have been shown to account for 75% of the HONO formation in Mexico City (Li et al, 2010). Recent studies in our laboratory have shown dusty episodes exhibiting an increase of 33 % over non-dusty episodes in the organic matter of the fine fraction (Jaafar et al. 2004). The uptake of pollutants by mineral dust particles is well documented and has been shown to take place around the world. (Erel et al. 2006, and references therein). In the Eastern Mediterranean region, a study by Erel et al. 2006, shows, based on the assessment of element composition, organic species, and Pb isotope ratios in suspended dust samples, substantial contamination of dust particles by both local and long range transport anthropogenic emission. An enhancement of the non-mineral composition of particles during similar episodes emphasized the anthropogenic contribution and the higher atmospheric pollution during these dusty episodes (Kalderon-Asael et al. 2009).*

*In brief, dust episodes are accompanied by an increase in* $NO_2$ *and* $SO_2$ *levels; a high indication of the increase in local and long range transported pollutants. This is accompanied by an increase in the local emission of acid gases like HONO,* $HNO_3$ *and* $H_2SO_4$ *due to several possible mechanisms. These include the increase in the acidity of particles, the synergistic reaction of* $NO_2$ *and* $SO_2$ *on mineral dust surfaces to produce HONO and* $H_2SO_4$ *and the heterogeneous reaction of* $NO_2$ *with organic materials.*

*Here, HONO formation by reactions on particle surfaces is proposed, which is in contrast to most recent studies. Since the uptake kinetics of NO2 is not very different for ground and particle surfaces, if the same material is considered (e.g. silicates), near ground surface (I again assume that, no details specified) HONO data will be mainly influenced by the formation on ground surfaces, caused by the smaller S/V ratio of particles compared to the ground in any assumed mixing layer and caused by the lifetime of HONO.*

Recent studies have shown that HONO formation is more enhanced on soot particles, however some studies have shown that the HONO formation can happen on other particles but the extent of its formation varies depends on the composition of the particle (Broske et al., 2003). We agree with the reviewer that, near ground surface () HONO data will be mainly influenced by the formation on ground surfaces, caused by the smaller S/V ratio of particles compared to the ground in any assumed mixing layer and caused by the lifetime of HONO however, sampling occurred at the same location so given the fact that near ground surface contribution to HONO formation is the same in the presence and absence of dust storms, the increase in HONO levels during dust storms can only be explained by the additional mineral dust particles formed. There is body of literature on the formation of HONO on dust particles (Grassian and coworkers ), the goal of this study was to investigate that dust particles are contributing to an increase in HONO concentration which is shown in the aforementioned data.

The importance of the study lies on the fact that there are so many laboratory studies and few field studies. It is evident that more field studies are needed and better characterization of dust particles to ensure what is the best mechanism for HONO formation.

*This may be confirmed by the experimental data from the present study. If I take the HNO3 data as an indicator for the urban pollution (and NO2 precursor) concentration, than the HONO/HNO3 ratio is exactly the same for the non-dusty and dusty days (27/28%, see supplement tables S1/2). This is in contrast to the proposed mechanism of the present study. Here correlations of HONO/NO2 ratios against particle surface area would be more helpful. However, even such evaluations could be influenced by the common dilution of any near ground surface sources, even without any necessary chemical link. E.g. HONO correlates nicely with Radon*

In the 2013 data we showed that the HONO/$NO_2$ data increased by 100% during dusty days. This will solve the issue of extrapolating the data of $HNO_3$ to deduce the contribution of $NO_2$ in the process.

Specific comments:
The following comments are listed in the order how they appear in the manuscript.

Page 4828, line 3:
Here and also below (page 4829, line 1-10) different source reactions of HONO are mixed. The heterogeneous "hydrolysis" of NO2 (i.e. 2 NO2+H2O, disproportionation, max. HONO yield 50 %) is different to the reaction of NO2+soot (redox reaction, soot oxidized, max. HONO yield 100%). Also the reaction of NO2+TiO2 follows a different mechanism (photocatalysis), whereas R1 is clearly not photoenhanced (Ramzan et al.). Here more thoroughly discussion is necessary. In addition, many (more important) HONO source reactions are missing and no differences between night-time and daytime source is discussed, although the integrated rate of HONO formation of the daytime sources is more important compared to the night-time sources, for which R1 will not represent the most important reaction (see below).

We thank the reviewer for his comments, the introduction was modified to include daytime and nighttime sources of HONO and it reads:

*" It is proposed that in the absence of sunlight, the heterogeneous hydrolysis of hydrolysis of NO2 on wet surfaces (R1) is the main route of HONO formation in the troposphere(Finlayson-Pitts and Pitts, 2000) (and references therein).*

$NO_2 + H_2O \xrightarrow{surface} HONO\ (g) + HNO3\ (particle)$ (R1)

*The heterogeneous reaction of $NO_2$ has been studied on several underlying substrates such as soot, glass, mineral oxides and aerosol surfaces (Finlayson-Pitts et al., 2003;Ullerstam et al., 2003;Underwood et al., 1999;Underwood et al., 2001;Yu et al., 2009;Kalberer et al., 1999;Gutzwiller, 2002). However, discrepancies between daytime measured HONO concentrations and models suggest that a daytime source of HONO exists of which the mechanism is still unclear and R1 is not the main source of HONO in the troposphere (George et al., 2005;Gustafsson et al., 2006). Recent studies have shown that there is an enhancement of NO2 uptake on organic surface in the presence of UV light which can be an important potential daytime source of HONO(Ndour et al., 2008b;Gustafsson et al., 2006;George et al., 2005;Stemmler et al., 2007;Stemmler et al., 2006).*

*The heterogeneous reaction of $NO_2$ on different mineral dust surfaces ($SiO_2$, $Al_2O_3$, $TiO_2$, CaO, MgO) has been studied extensively in the absence (Underwood et al., 2001;Zhang et al., 2012;Goodman et al., 1998;Usher et al., 2003;Wang et al., 2012;Ma et al., 2013) and the presence of sunlight (Ndour et al., 2008a;Gustafsson et al., 2006;Kebede et al., 2013;Ndour et al., 2009;Ma et al., 2013) and in both cases, it is considered to be a major source for HONO formation. As an example, $TiO_2$ nanoparticles which have been used in self-cleaning window glass, building materials, and on roads in Europe, Japan and the USA (Beaumont et al., 2009;Langridge et al., 2009) are considered a source for HONO and $H_2O_2$ from $NO_2$ and $H_2O$. $TiO_2$ in dust was also shown to be a contributor to the formation of HONO in the dark (Ma et al., 2013)"*

Page 4828, line 23-25:
R1 is by far not the "main source of HONO in the troposphere" by several reasons. First in the whole troposphere (up to 10 km) NO+OH will be the most important source (most probably the author's wanted to consider the lower boundary layer?). Second, if you consider the lower boundary layer (where the measurements were performed) the absolute integrated daytime sources are typically much more important than the integrated night-time sources (see many studied on the daytime production of HONO). However, R1 is not photoenhanced (see above), so cannot explain this larger fraction. Third, the uptake coefficients of NO2 for R1 are of the order of 10ˆ-7 – 10ˆ-8 (please convert numbers summarized in Finlayson-Pitts et al., 2003), whereas uptake coefficients measured at the ppb level on atmospheric surfaces (not only water adsorbed) is typically 10ˆ-6. Thus, even for the smaller night-time formation only ca. 10 % may be explained by R1. Here the authors ignored studies on other HONO sources, e.g. by NO2 conversion on adsorbed organics (both dark and photoenhanced).

This sentence has been added in the introduction" *The reaction of OH with NO in the gas phase is the main source of HONO, however this reaction fails to explain high levels of HONO formed during nighttime(Finlayson-Pitts and Pitts, 2000;Li et al., 2010).* We modified the introduction based on the reviewer's comments. Please see our response above.

Page 4830, section 2.1/2.2:

Please add details to the methods used including careful discussion on the limitations (see major concern 1). Please add also some information on the measurement site.

The sampling site and procedure has been modified in the manuscript as per our response above.

Page 4830, line 8:
Exchange frozen by stored at –x _C (a liquid is frozen).

As per the reviewer's comment the sentence in the sampling procedure has been modified as follows "*Following collection and gravimetric calculation of PM concentrations, the filters are cut into four equal pieces that are stored at 4°C until ready for chemical analysis."*

Page 4830, line 19:
If the extraction is done by H2O2, how can nitrite be determined? Will be oxidized to Nitrate.
The extraction of denuders did not include any $H_2O_2$. The exact denuder coating and extraction procedure are modified in the manuscript. Please see our response above.

Page 4830, line 29:
What is the threshold for dusty/non dusty day? Should be specified by any dust components (silicates/carbonates etc.). Or is that simply the 80 micro gram/mˆ3?

Dusty days are predicted and confirmed by following the backward air mass trajectories by NOAA-HYSPLIT model and BSC Dream forecast. Please see sampling section. Also, samples collected in Lebanon have shown that $PM_{10}$ yearly averages are around 54 µg/$m^3$(Saliba and Massoud, 2011) .

Page 4831, line 4 (and others):
Exchange H2SO4 by SO2, see above.
I agree with the reviewer that some of the $SO_2$ is oxidized into $H_2SO_4$ on denuder surfaces, yet by looking at the concentrations of $H_2SO_4$ and $SO_2$, we see that the concentration of $H_2SO_4$ is around double that of $SO_2$ in both dusty and non-days which signifies that the denuders collect gas phase $H_2SO_4$.

Page 4831, line 9:
I cannot see any threefold increase in the figure. The average non-dusty HONO levels are 1.09 (see table S1) and for African and Arabian dusty day I estimated ca. 2.0 and 2.15 from Figure 1.

Upon the introduction of the 2013 campaign, the modification of the 2009 campaign and the removal of the 2011 campaign, the graphs were modified. More than a two-fold increase of HONO during both campaigns is evident. The text has been modified to read "During dusty days, a burst of HONO was measured, where in the present sets of data, more than a twofold increase of HONO levels was observed during Arabian dust storms in comparison to non-dusty days."

Page 4831, lines 15-17:
If water shields the active sites, why does R1 show a positive humidity dependence?

We understand the confusion this sentence might have caused to the reviewer. What we meant was that presence of water shields the metal site and the competitive adsorption of $NO_2$ and $SO_2$ is less important, hence HONO formation, during non-dusty days proceeds via reaction R1 which is humidity dependent. In Arabian dust storms and due to minimal amount of water the mechanism for HONO formation is affected by the presence of the metal site. The mechanism of gas-surface interaction was removed since enough evidence was not presented. Please refer to the modifications shown above or to the manuscript.

Page 4831, line 27:
In Bröske et al. (see also typo) no photochemical source was studied.

Broske et al has been removed as a reference for this sentence

Page 4832, R2-5:
Although quite often cited in the literature, the mechanism postulated by Finlayson-Pitts et al., 2003 cannot explain laboratory (and field) experiments at low (atmospheric) ppb NO2 levels. Typically, uptake coefficients of NO2 on different materials are 10ˆ-6 up to 10ˆ-7 at low ppb levels (do not consider most of the ppm experiments cited in the study mentioned above). If you consider the equilibrium constant of 2NO2=N2O4 and 1 ppb NO2, the concentration of N2O4 is 0.007 ppq (: : :) at 298 K. To get a measured
uptake of NO2 of even only 10ˆ-7, the uptake coefficient of N2O4 needs to be higher than one, which is impossible by definition

While we understand this fact, we mentioned this mechanism because Ma et al has shown that the $NO_2$ hydrolysis on alumina proceed via dimerization of $N_2O_4$ and then autoionizes to form $NO^+NO_3^-$ which will further react with water to then generate HONO + $HNO_3$. We modified the mechanism as such:

$2NO_2\ (g) \xleftrightarrow{surface} N_2O_4\ (surface)$ (R2)

$N_2O_4\ (surface) \rightarrow ONONO_2\ (surface) \rightarrow NO^+NO_3^-\ (surface)$ (R3)

$NO^+NO_3^- \xrightarrow{H2O} HONO\ (g) + H^+ + NO_3^-$ (R4)

Page 4832, line 20:
In their reaction 2, Ma et al. proposed the formation of MNO2 and MNO3, which is different to R6 from the present study? How should this reaction proceed, any oxidation of the dust surface (NO2: oxidation state IV, HNO3(particle): oxidation state V)?

While it would be interesting to know the exact mechanism of how $HNO_3$ is being formed in our ambient samples however, it is hard to infer this from IC. The reaction most likely to be due to redox reactions happening on the surface where $NO_2$ gets adsorbed and oxidized to form loosely bound $MNO_3$ which in the presence of $H^+$ on the surface can lead to the formation of $HNO_3$ in the particle phase. Based on studies by Grassian et al loosely bound nitrate can form on dust surfaces. Definitely more surface characterization studies are needed and so the mechanism of gas-surface interaction was removed. Please refer to the modifications shown above or to the manuscript.

Page 4832, line 25-26:
The absolute majority (>99.99%) is in the form of NO2, see above: : :
References (please check all again, here only examples):

Page 4834, line 12: ChemPhysChem

Page 4835, line 1: Wingen, L.M.

Page 4835, line 14: Cox, R. A.

Page 4835, line 23: Liu, Y.

Page 4835, line 26: Liu, Y.

Fig. 1:
Please add error bars. Most probably the differences between African/Arabian are not significant: : : In addition, it would be less confusing, if simply the gas phase species were mentioned. (NO2- = HONO, etc: : :).

Supplement Figure S-1:
In the figure HNO3 against HNO2, most probably one data point is missing (see regression line extending the data)?

As per the reviewer's comments the references have been revised. Also, upon the modification of the sampling campaigns, the figures have been modified: bar graphs were replaced by box plots, and gases are reported as HONO, $HNO_3$, and $H_2SO_4$.

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# Contribution of Airborne Dust Particles to HONO Sources

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## Abstract

HONO is a major precursor for OH radicals in early mornings. In addition to the reaction of NO and OH to produce HONO, its formation has been attributed to the heterogeneous hydrolysis of $NO_2$ on surfaces such as soot, glass, mineral oxides and aerosol surfaces. In particular, dust events which are loaded with mineral oxide aerosols have been associated with higher HONO concentrations in the gas phase. In order to understand the mechanism of reactions related to this process, samples during dusty and non-dusty days were collected during two campaigns in the fall and summer of 2009 and 2013. Data are divided between dusty days based on wind trajectories originating from Arabian deserts and non-dusty days. In this study, an increase of HONO, $HNO_3$ and $H_2SO_4$ levels is observed during dusty days. The increase in the acidic gas concentrations is accompanied by an increase in the PM nitrate and sulfate ion concentrations. During high relative humidity (non-dusty days), it is proposed that the mechanism of $NO_2$ hydrolysis occurs whereas during Ar-D days, where the air is relatively dry, a synergistic mechanism of adsorption and reaction between $NO_2$ and $SO_2$ on dust particles to produce HONO and sulfate in the particle phase is suggested. Other possible mechanisms are attributed to the heterogeneous reaction of $NO_2$ with organic aerosols and the enhanced particle-gas conversion resulting from the increased acidity of particles. This study implies that enhanced $NO_x$ conversion during dust events leads to a higher mixing level of HONO, which could then photolyze to produce OH radicals.

*Keywords*: particle sulfate, $NO_2$ hydrolysis, synergistic $NO_2$ and $SO_2$ reaction, HONO, dust aerosols, acidity

## 1. Introduction

HONO is an important precursor for OH radicals in the atmosphere. Compared to ozone and formaldehyde, HONO photolysis is considered the major source of OH radicals in the early morning (Finlayson-Pitts and Pitts, 2000). The reaction of OH with NO in the gas phase is the main source of HONO; however this reaction fails to explain high levels of HONO formed during the nighttime (Finlayson-Pitts and Pitts, 2000;Wang et al., 2010). It is proposed that in the absence of sunlight, the heterogeneous hydrolysis of $NO_2$ on wet surfaces (R1) is a major route of HONO formation in the troposphere (Finlayson-Pitts and Pitts, 2000) (and references therein).

$$NO_2 + H_2O \xrightarrow{surface} HONO_{(g)} + HNO_{3\,(particle)} \qquad \text{(R1)}$$

The heterogeneous reaction of $NO_2$ has been studied on several underlying substrates such as soot, glass, mineral oxides and aerosol surfaces (Finlayson-Pitts et al., 2003;Ullerstam et al., 2003;Underwood et al., 1999;Underwood et al., 2001;Yu et al., 2009;Kalberer et al., 1999;Gutzwiller, 2002;Ma et al., 2013). However, discrepancies between daytime measured HONO concentrations and models suggest that a daytime source of HONO exists of which the mechanism is still unclear and (R1) is not the main source of HONO in the troposphere (George et al., 2005;Gustafsson et al., 2006). Recent studies have shown that there is an enhancement of $NO_2$ uptake on organic surfaces in the presence of UV light; a source that can be an important potential daytime source of HONO (Ndour et al., 2008a;Gustafsson et al., 2006;George et al., 2005;Stemmler et al., 2007;Stemmler et al., 2006).

The heterogeneous reaction of $NO_2$ on different mineral dust surfaces ($SiO_2$, $Al_2O_3$, $TiO_2$, CaO, MgO) has been studied extensively in the absence (Underwood et al., 2001;Zhang et al., 2012;Goodman et al., 1998;Usher et al., 2003b;Wang et al., 2012;Ma et al., 2013) and the presence of sunlight (Ndour et al., 2008b;Gustafsson et al., 2006;Kebede et al., 2013;Ndour et al., 2009;Ma et al., 2013) and in both cases, it is considered to be a major source for HONO formation. As an example, $TiO_2$ nanoparticles which have been used in self-cleaning window glass, building materials, and on roads in Europe, Japan and the USA (Beaumont et al., 2009;Langridge et al., 2009) are considered a source for HONO and $H_2O_2$ from $NO_2$ and $H_2O$. $TiO_2$ in dust was also shown to be a contributor to the formation of HONO in the dark (Gustafsson et al., 2006;Kebede et al., 2013;Ma et al., 2013) . Furthermore, modeling studies suggest that mineral aerosols surfaces account for 40% of nitrate formation and dust events create a favorable medium for the accumulation of nitrates (Dentener et al., 1996;Guo et al., 2011;Usher et al., 2003a). $SO_2$ can also be taken up by mineral oxide surfaces to undergo a two-step mechanism including the reversible adsorption of $SO_2$ on the surface followed by the oxidation to sulfate (Ullerstam et al., 2002). In the case where $SO_2$ is co-adsorbed with $NO_2$ on the surface, it is shown that the oxidant is gaseous $NO_2$ which reacts with adsorbed $SO_2$ to produce sulfate in the particle phase. The oxidant role of $NO_2$ leads to nitrate or contributes to the formation of sulfate on the surface (Borerisen et al., 2000;Phillips, 2013;Wu et al., 2013;Ma et al., 2013). In urban regions, the reaction of $NO_2$ on surfaces is well known to be dependent on relative humidity (Finlayson-Pitts et al., 2003)(and references therein) while the reactivity of the surface towards $NO_2$ is a function of other competing reactions such as the aforementioned reaction of $NO_2$ in the presence of $SO_2$ on mineral surfaces (Liu et al., 2012).

Given the reactivity of mineral oxide surfaces towards $NO_2$ and $SO_2$, some studies reported an increase of HONO levels during dust storms (Phillips, 2013;Wang et al., 2003;Wu et al., 2013;Zhu et al., 2010), however, the mechanism of HONO formation on airborne dust particles is still not understood. This study investigates the association between the increase of HONO levels in the gas phase and the increase in the inorganic components of aerosols during Arabian dust storms. Possible mechanisms involved in the formation of HONO are proposed.

## 2. Methods

### *2.1. Sampling Location*

Samples were collected on the roof-top of the Chemistry department at the American University of Beirut; North-West Beirut, Lebanon. The site is around 40 m above sea level. South of the site is the university's green belt of shrubbery and trees, and faces the

Mediterranean Sea from the North. The location is considered to be an urban background site affected mainly by sea breeze; it is far from any industrial pollution sources and the closest roadway is located around 150 m north-east. More description of the site is presented by Daher et al 2013 (Daher et al., 2013).

### *2.2. Collection techniques*

Soluble gases and size resolved aerosols were sampled at ambient level during Arabian dusty and during non-dusty days. Dusty days were predicted using the NOAA-Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model of 48h isobaric backward trajectories (Draxler and Rolph, 2013). HYSPLIT was run at three different altitudes between 1 and 10 km, the height of an average dust event. Arabian dust outbreaks have low initial heights (2 to 4 km) and show east and south-east trajectories (Notaro et al., 2013;Dada et al., 2013). Dust episodes were confirmed using BSC Dream Atmospheric Dust Forecast System (http://www.bsc.es/earth-sciences/mineral-dust-forecast-system/bsc-dream8b-forecast/). Wind speed and direction, local weather and visibility were used as other indications to the occurrence of dust-rich episodes.

The aerosol and gas samples are collected using a Rupprecht & Patashnick Partisol 2300. Sampling occurred between two different campaigns, between October 2009 and November 2009, and between July 2013 and November 2013. Soluble acidic gases (HONO, $HNO_3$ and $H_2SO_4$) were sampled for 24hr using a diffusion denuder system. The system is based on two Honey Comb denuders (HC) coated with 1% $NaCO_3$ and 1% glycerol in 50:50 water: methanol solution and placed in series in Rupprecht & Patashnick (R&P) Chemcomb™ cartridges. Sampling and analysis of trace gases is fully described in Saliba and Chamseddine (Saliba and Chamseddine, 2012).

During the first sampling campaign (2009), aerosol collection extended over 24 hours using pre-weighed 37mm Teflon filter that is housed between two Teflon meshes downstream the gas collecting denuders in $PM_{10}$ inlets Harvard cartridges. The flow rate was set at 10 l/min. Following collection and gravimetric calculation of PM concentrations, the filters are cut into four equal pieces that are stored at 4°C until ready for chemical analysis (Kouyoumdjian and Saliba, 2006;Saliba et al., 2009;Saliba et al., 2010).

During the second campaign (2013), sampling followed the procedure of Daher et al. (Daher et al., 2013). Aerosols were sampled for 24hr using Sioutas Personal Cascade Impactor Samplers (Sioutas PCIS, SKC Inc., Eighty Four, PA, USA) preceded by denuder containing $PM_{10}$ inlets and operating at 9 l/min. Dust particles were collected according to their size fractions; 10-2.5 $\mu$m (coarse particulate matter) and 2.5-0.25 $\mu$m (accumulation PM) were collected on 25mm Teflon filters and <0.25 $\mu$m (quasi-ultrafine PM) were collected on 37 mm Teflon filters.

### *2.3. Ion Chromatography*

Coated denuders are extracted by a 20mL of Deionized water. One quarter of each Teflon filter used during the first campaign is extracted in 15 ml deionized water and sonicaton for 50 min. Both extracts are micro-filtered and analyzed by ion chromatography (IC) (Saliba and Chamseddine, 2012). During the 2013 sampling campaign, denuder extraction followed the same procedure. Each size resolved filter was extracted in 20ml Deionized water and sonicated for 50min then analyzed using ion chromatography model Metrohm 850 professional IC AnCat with 858 Professional Sample Processor.

### *2.4. Gas Monitoring Station*

The monitoring station is mounted at the same sampling location. It is equipped with Thermo Environmental analyzers used to nitrogen oxides (Model 42i, Chemiluminescence Principle) and sulfur dioxide (Model 43i, Pulsed Fluorescence Principle). The analyzers are calibrated using the Thermo Environmental Multigas Calibrator (Model 146i) for both zero and span concentrations. Zero air is provided from the Thermo Zero Air Generators (Model 111) connected to the Thermo Dual Reactor (Model 1150). Span gases are provided from standard gas bottles for NO, and $SO_2$.

The Met One instruments (http://www.metone.com/meteorology.php) were used to setup the weather at a logging interval of 1 min. It is placed on a pole that was lifted about 5 m above the monitoring station at the AUB-Chemistry roof top.

## 3. Results and Discussion

Sampling campaigns occurred between September 2009 and November 2009, and between July 2013 and November 2013. Sampling data were divided into non-dusty (ND) and Arabian-Dusty (Ar-D) days (Table 1).

*Gas phase composition:* The average gas phase HONO, $HNO_3$, and $H_2SO_4$ (sum of $SO_2$ and $H_2SO_4$ captured by the denuders and represented thereafter by $H_2SO_4$) levels for the sampling periods are shown in Figure 1. During dusty days, a burst of HONO was measured where more than a twofold increase of HONO levels was observed during Ar-D days in comparison to ND days. Also, $HNO_3$ and $H_2SO_4$ levels exhibit a clear increase during Ar-D days. Concomitantly, an increase in $NO_2$ and $SO_2$ gas levels is observed for the 2013 experimental data (Figure 2). During Ar-D days, the $NO_2$ increase might be explained by the accumulation of local emission due to stagnant wind. Although $NO_2$ and its precursor, NO, could be considered a source of HONO, the trend does not explain the two-fold increase of HONO. In fact, the HONO/$NO_2$ doubles (from an average of 0.03 to 0.06) during Ar-D days despite the increase in $NO_2$ levels. The higher value of HONO/$NO_2$ of 0.06 remains typical of urban environments (Stutz et al., 2004). Also, the HONO/$HNO_3$ ratio goes up from 1.3 in ND to 1.9 during Ar-D days. Similar trend for HONO/$HNO_3$ is observed in 2009 data, where the ratio increases from 0.7 to 1.0 in in ND and Ar-D days, respectively. The increase in both ratios (HONO/$NO_2$ and HONO/$HNO_3$) during Ar-D days indicates that HONO production is due to sources other than $NO_2$. Furthermore, it is important to note that HONO does not correlate with RH during Ar-D days while it highly correlates with RH during ND days ($R^2$ = 0.4 in 2009 and $R^2$ = 0.9 in 2013) suggesting that $NO_2$ heterogeneous conversion which leads to HONO and $HNO_3$ is a possible mechanism at relatively higher RH, during ND days (Stutz et al., 2004) as illustrated in equations (R2)-(R4).

$2NO_2\ (g) \xleftrightarrow{surface} N_2O_4\ (surface)$ (R2)

$N_2O_4\ (surface) \rightarrow ONONO_2\ (surface) \rightarrow NO^+NO_3^-\ (surface)$ (R3)

$NO^+NO_3^- \xrightarrow{H_2O} HONO\ (g) + H^+ + NO_3^-$ (R4)

The increase in $H_2SO_4$ and $SO_2$ alongside HONO and $NO_2$, during Ar-D days, could be due to similar or independent factors. In fact, a poor correlation between $SO_2$ and $NO_2$ ($R^2$ = 0.4) during ND days indicates that the two gases have a low probability to originate from similar sources. However, the enhancement of this correlation during Ar-D days (correlation between $SO_2$ and $NO_2$ ($R^2$ = 0.7)) and the high correlations between $SO_2$ and $H_2SO_4$ ($R^2$ = 0.6) and $SO_2$ and HONO ($R^2$ = 0.85, descending) suggests that $SO_2$ plays a role in the formation of HONO. One possible explanation is the synergistic mechanism of adsorption and reaction between $NO_2$ and $SO_2$ enhanced by dust particles; mainly mineral oxides according to (R5).

$SO_2 + NO_2 + 2H_2O \xrightarrow{H_2O} HONO\ (g) + H_2SO_4(g, particle)$ (R5)

Such effect has been shown to exist in laboratory experiments. For instance, Ma et al. (2008)(Ma et al., 2008) showed that adsorption of $NO_2$ on alumnia was altered in the presence of $SO_2$. In similar studies, co-adsorption of $SO_2$ and $NO_2$ showed that the intermediate $N_2O_4$ leads to nitrates and sulfates in pathways different than the formation of $NO^+NO_3^-$ on the surface (Liu et al., 2012).

*Particle phase composition:* The study of the particle phase composition emphasizes the aforementioned observations and conclusions. In particles, there was a clear increase in the levels of nitrates and sulfates during the two campaigns. Increases were mostly found in the accumulation mode when examining the 2013 field measurements. This was accompanied by an increase in the ammonium levels as shown in Figure 3. During non-dusty days, the correlations of HONO with PM-ACC (Accumulation) ($R^2$ = 0.80 in 2013), $NO_3^-$-ACC ($R^2$ = 0.96 in 2013) and $NO_3^-$ - $PM_{10}$ ($R^2$ = 0.4 in 2009) indicate either HONO and PM-ACC and $NO_3^-$ originate from similar sources or HONO is the result of a secondary reaction involving PM and leading to nitrate; i.e. $NO_2$ heterogeneous hydrolysis. The same behavior was not observed during dusty days.

The extent to which the increase in ammonium (during the 2013 field campaign only), nitrate and sulfate affect the neutralization of aerosols is approximated as per Stevens et al., 1980:

$$f = \frac{[H^+]}{[H^+] + [{NH_4}^+]}$$

When 0 < $f$ < 1= 0, the bulk aerosol is a mixture of chemical species of properties similar to $NH_4HSO_4$. At $f$ = 0, a full neutralization by $NH_4^+$ in the particle is considered whereas no neutralization is assumed when $f$ = 1(Stevens et al., 1980). A drop in the neutralization factor of the 2013 field campaign (drop from 0.7 to 0.5) (Table 2), mostly noticed in the ACC mode, was counterfeited by an increase in the aerosol acidity (calculated as $[H^+] = [SO_4^{2-}] + [NO_3^-] - [NH_4^+]$) (Kerminen et al., 2001;Schwab et al., 2004). This increase was observed in both the 2009 and 2013-$PM_{10}$ field measurements (Table 2). As a result of that, the particle-gas conversion and hence the increase in acid gases during dusty days becomes enhanced. Another source of HONO would be the heterogeneous reaction of $NO_2$ with semi-volatile organics which have been shown to account for 75% of the HONO formation in Mexico City(Li et al., 2010). Recent studies in our laboratory have shown dusty episodes exhibiting an increase of 33 % over non-dusty episodes in the organic matter of the fine fraction(Jaafar et al., 2014). The uptake of pollutants by mineral dust particles is well documented and has been shown to take place around the world(Rashki et al., 2013;Sorek-Hamer et al., 2012;Lawrence et al., 2013;Gaetani and Pasqui, 2012;Gaetani et al., 2012;de Meij et al., 2012;Séguret et al., 2011). In the Eastern Mediterranean region, a study reported by Erel et al. shows, based on the assessment of element composition, organic species, and Pb isotope ratios in suspended dust samples, substantial contamination of dust particles by both local and long range transport anthropogenic emission(Erel et al., 2006). An enhancement of the non-mineral composition of particles during similar episodes emphasized the anthropogenic contribution and the higher atmospheric pollution during these dusty episodes (Kalderon-Asael et al., 2009).

In brief, dust episodes are accompanied by an increase in $NO_2$ and $SO_2$ levels; a high indication of the increase in local and long range transported pollutants. This is accompanied by an increase in the local emission of acid gases like HONO, $HNO_3$ and $H_2SO_4$ due to several possible mechanisms. These include the increase in the acidity of particles, the synergistic reaction of $NO_2$ and $SO_2$ on mineral dust surfaces to produce HONO and $H_2SO_4$ and the heterogeneous reaction of $NO_2$ with organic materials.

The missing source of HONO has several implications on the OH concentration and oxidative budget in the atmosphere. Furthermore, the simultaneous enhanced formation of sulfates and nitrates in particles impacts their optical and physical properties. A particle coated with sulfate and nitrate is hygroscopic and will take up water; it may therefore take up more $SO_2$ into this aqueous layer that would otherwise be formed (Zhang and Chan, 2002). Hence, it is likely that the mineral dust particles have a greater capacity for sulfate formation than suggested by the reactive uptake studies alone (Ullerstam et al., 2003).

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Table 1. PM and acid gas concentrations collected during Arabian dusty and non-dusty days in 2009 and 2013 field campaign measurements. Size segregated (UF (ultrafine), ACC (Accumulation), and CPM (Coarse particulate matter) concentrations are shown for the 2013 field campaign and values corresponding to measurements of PM10 are listed for the 2009 field campaign.

| **2013** | RH | UF | ACC | CPM | PM |
|---|---|---|---|---|---|
| **Non Dusty** | | | | | |
| **23-Jul-13** | 70.97 | 26.33 | 15.46 | 25.59 | **67.38** |
| **29-Jul-13** | 69.14 | 12.97 | 6.58 | 14.85 | **34.40** |
| **22-Aug-13** | 66.81 | 17.94 | 7.32 | 15.50 | **40.76** |
| **4-Sep-13** | 64.48 | 13.79 | 5.94 | 23.99 | **43.72** |
| **10-Sep-13** | 64.39 | 22.26 | 6.34 | 22.44 | **51.03** |
| **Arabian Dusty Days** | | | | | |
| **23-Oct-13** | 30.00 | 21.64 | 10.39 | 29.10 | **61.14** |
| **5-Nov-13** | 69.03 | 19.78 | 38.44 | 63.41 | **121.63** |
| **7-Nov-13** | 74.18 | 18.99 | 42.44 | 74.52 | **135.95** |
| **12-Nov-13** | 58.87 | 16.71 | 33.59 | 36.58 | **86.88** |
| **19-Nov-13** | 55.92 | 24.24 | 15.22 | 18.97 | **58.43** |

| **2009** | RH | UF | ACC | CPM | PM |
|---|---|---|---|---|---|
| **Non Dusty** | | | | | |
| 6-Sep-09 | 60.00 | | | | **46.15** |
| 24-Sep-09 | 49.00 | | | | **30.65** |
| 30-Sep-09 | 44.00 | | | | **44.54** |
| 6-Oct-09 | 78.00 | | | | **56.89** |
| 12-Oct-09 | 56.00 | | | | **42.66** |
| 30-Oct-09 | 91.00 | | | | **62.87** |
| 29-Nov-09 | 76.00 | | | | **37.08** |
| **Arabian Dusty Days** | | | | | |
| 18-Oct-09 | 12.00 | | | | **129.52** |
| 24-Oct-09 | 30.00 | | | | **83.55** |
| 11-Nov-09 | 43.00 | | | | **80.86** |
| 23-Nov-09 | 33.00 | | | | **77.47** |

Table 2. Acidity $[H^+]$ and neutralization factor (*f*) of size-segregated aerosols (UF (ultrafine particles), ACC (Accumulation) and CPM (coarse particulate matter) during dusty and non-dusty days PM for the 2013 field campaign and PM10 for the 2009 field campaign.

| | $[H^+]$ (mol/m$^3$) | | | | *f* (mol/m$^3$) | | | | | $[H^+]$ (mol/m$^3$) | *f* (mol/m$^3$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Date** | **UF** | **Acc** | **CPM** | **PM10** | **UF** | **Acc** | **CPM** | **PM10** | **Date** | **PM** | **PM** |
| | | | | **2013** | | | | | | **2009** | |
| | | | | **Non-dusty** | | | | | | | |
| 23-Jul-13 | 0.04 | 0.05 | 0.03 | **0.12** | 0.49 | 0.7 | 0.65 | **0.61** | 6-Sep-09 | **0.28** | **0.80** |
| 29-Jul-13 | 0.04 | 0.01 | 0.04 | **0.09** | 0.62 | 0.7 | 0.85 | **0.71** | 24-Sep-09 | **0.10** | **0.83** |
| 22-Aug-13 | 0.05 | 0.03 | 0.04 | **0.12** | 0.45 | 0.88 | 0.89 | **0.65** | 30-Sep-09 | **0.17** | **0.80** |
| 4-Sep-13 | 0.02 | 0.09 | 0.03 | **0.14** | 0.79 | 0.94 | 0.85 | **0.9** | 6-Oct-09 | **0.18** | **0.84** |
| 10-Sep-13 | 0.01 | 0.01 | 0.04 | **0.06** | 0.22 | 0.3 | 0.79 | **0.5** | 12-Oct-09 | **0.21** | **0.80** |
| | | | | | | | | | 30-Oct-09 | **0.06** | **0.61** |
| | | | | | | | | | 29-Nov-09 | **0.28** | **0.83** |
| **Dusty** | | | | **Dusty** | | | | | | | |
| 5-Nov-13 | 0.03 | 0.09 | 0.17 | **0.29** | 0.51 | 0.37 | 0.97 | **0.61** | 18-Oct-09 | **0.39** | **0.91** |
| 7-Nov-13 | 0.03 | 0.11 | 0.18 | **0.32** | 0.45 | 0.4 | 0.97 | **0.6** | 24-Oct-09 | **0.37** | **0.89** |
| 12-Nov-13 | 0.03 | 0.1 | 0.01 | **0.13** | 0.57 | 0.36 | 0.43 | **0.39** | 11-Nov-09 | **0.54** | **0.91** |
| 19-Nov-13 | 0.05 | 0.04 | 0.03 | **0.12** | 0.38 | 0.52 | 0.7 | **0.48** | 23-Nov-09 | **0.06** | **0.53** |

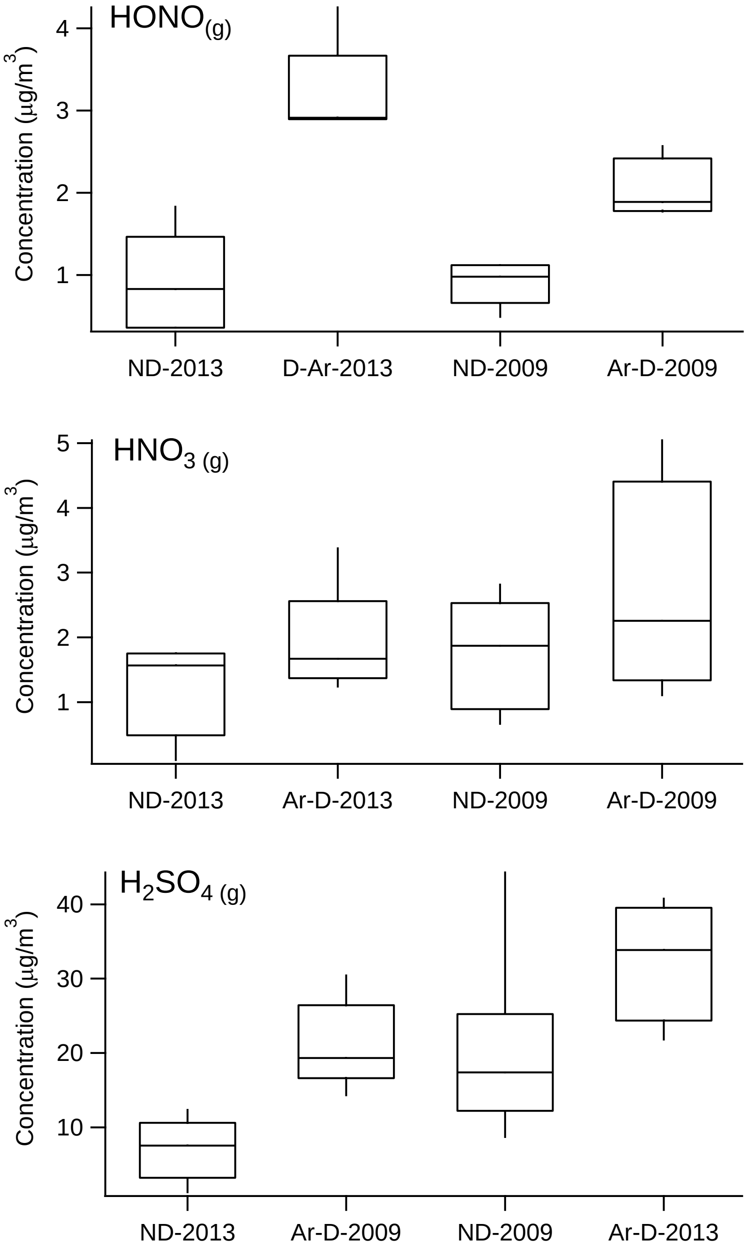

Figure 1. Concentrations of HONO, $HNO_3$ and $H_2SO_4$ in $\mu g/m^3$ during non-dusty (ND) Arabian dusty (Ar-D) and days of the 2009 and 2013 field campaigns

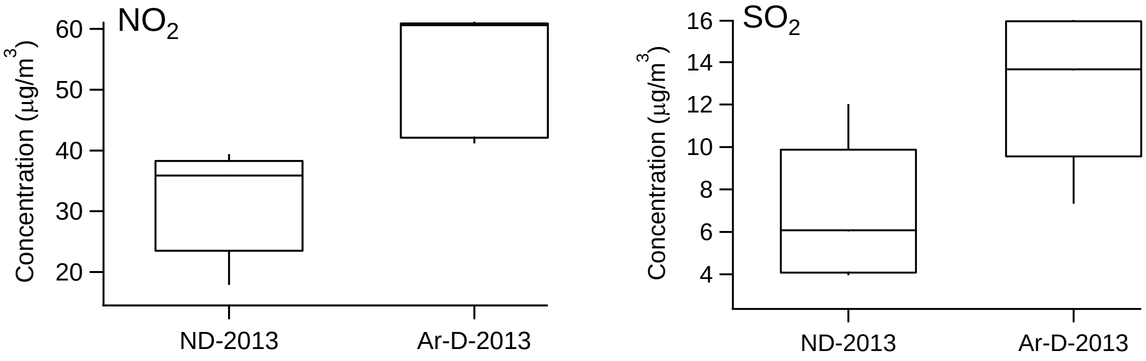

Figure 2. Concentrations of $NO_2$ and $SO_2$ in µg/$m^3$ during non-dusty (ND) Arabian dusty (Ar-D) and days of the 2013 field campaign

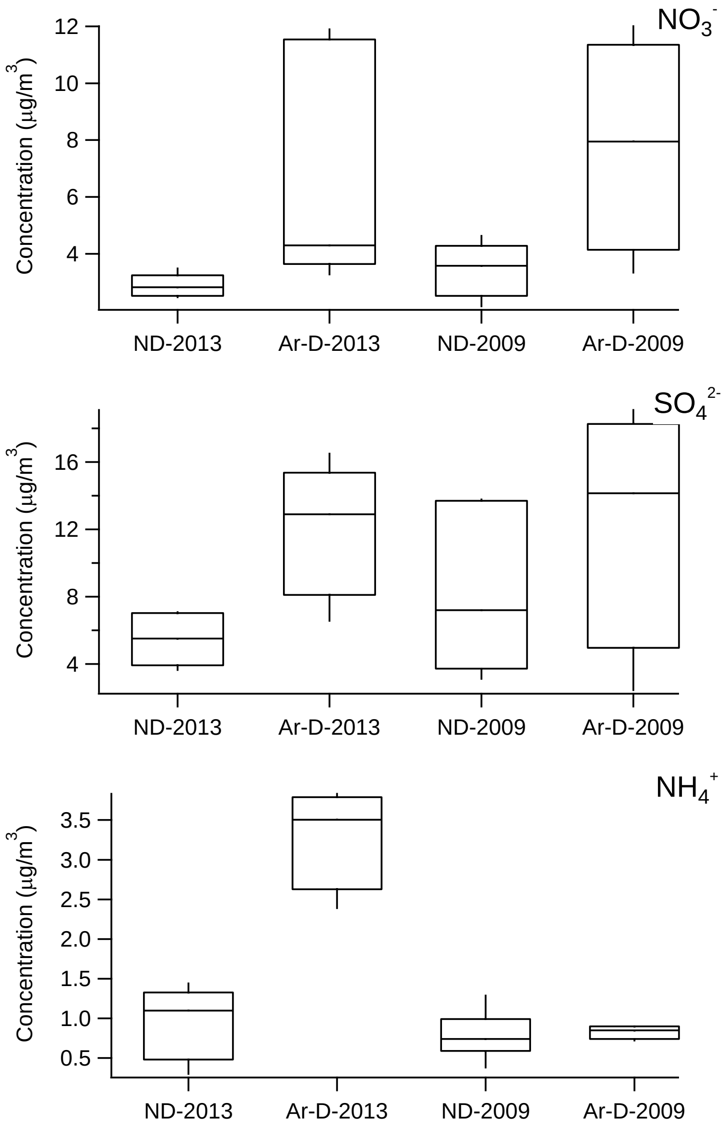

Figure 3. Concentrations of $NO_3^-$, $SO_4^{2-}$ and $NH_4^+$ in μg/m$^3$ during non-dusty (ND) Arabian dusty (Ar-D) and days of the 2009 and 2013 field campaigns

# Contribution of Airborne Dust Particles to HONO Sources

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M3H 5T4

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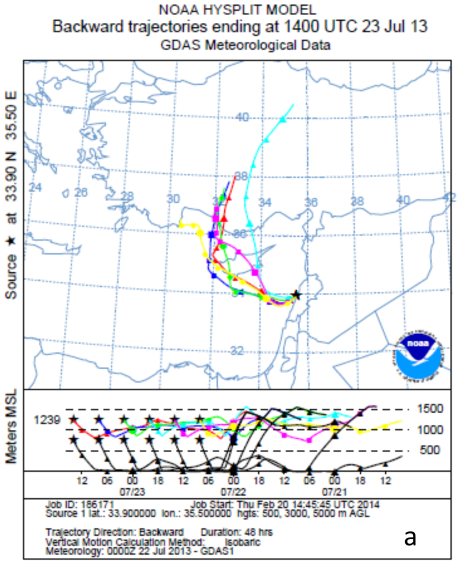
# Supplementary Information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42
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1000
500
12
06
00
18
12
06
00
18
12
06
00
18
12
07/23
07/22
07/21
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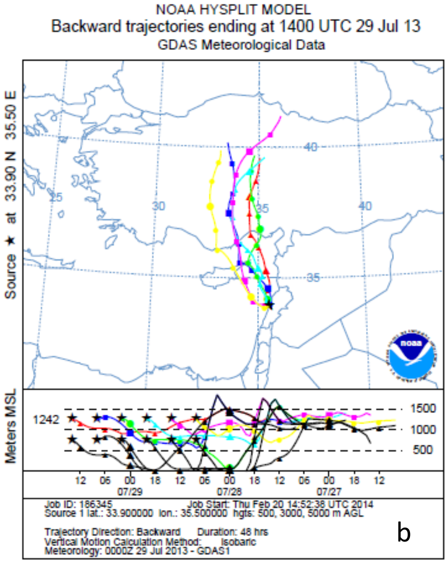
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12
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00
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06
00
18
12
07/29
07/28
07/27
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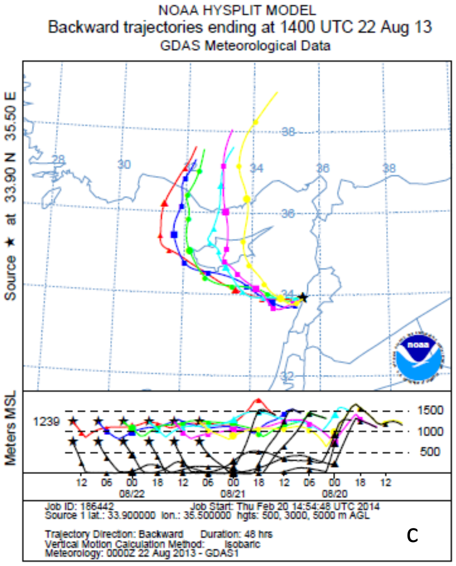
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Meters MSL
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1000
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12
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08/21
08/20
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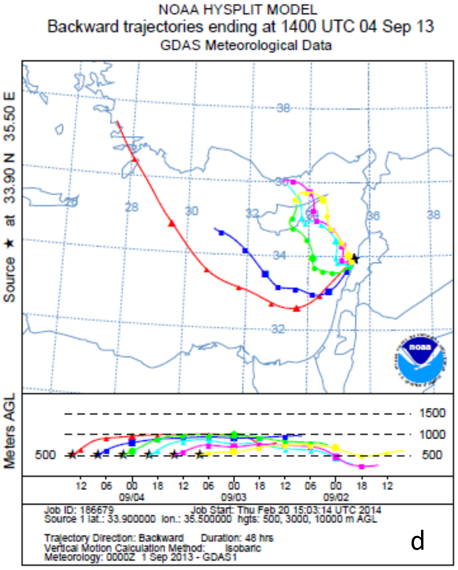
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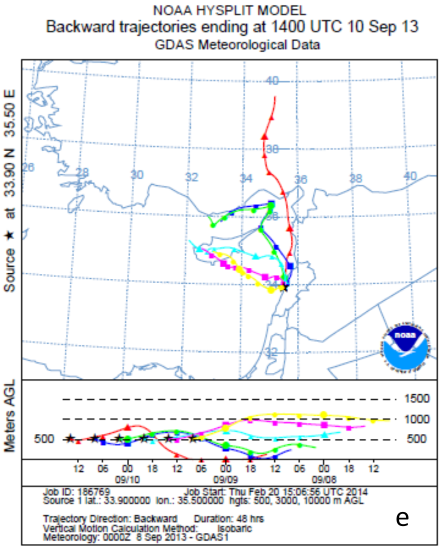
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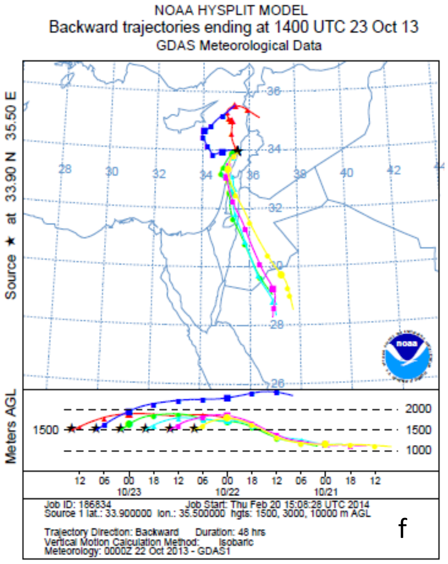
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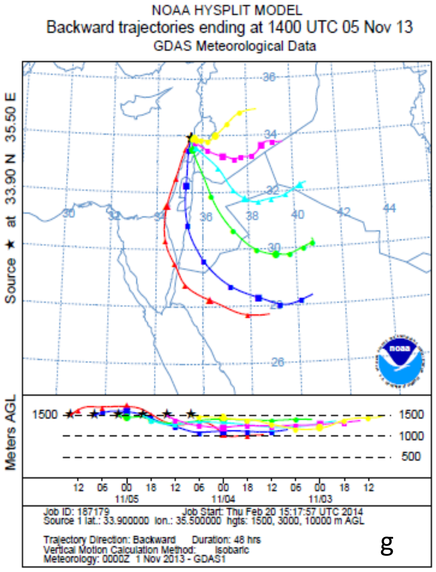
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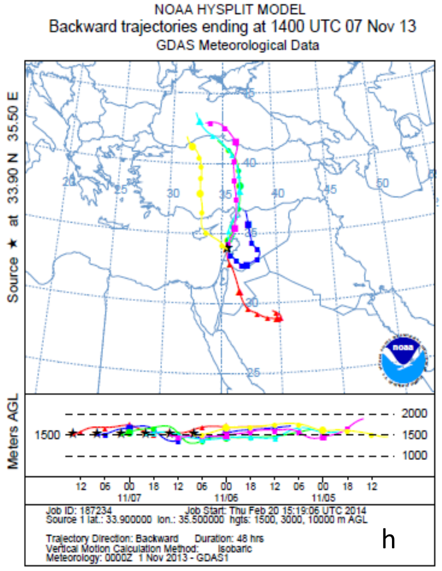
g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h

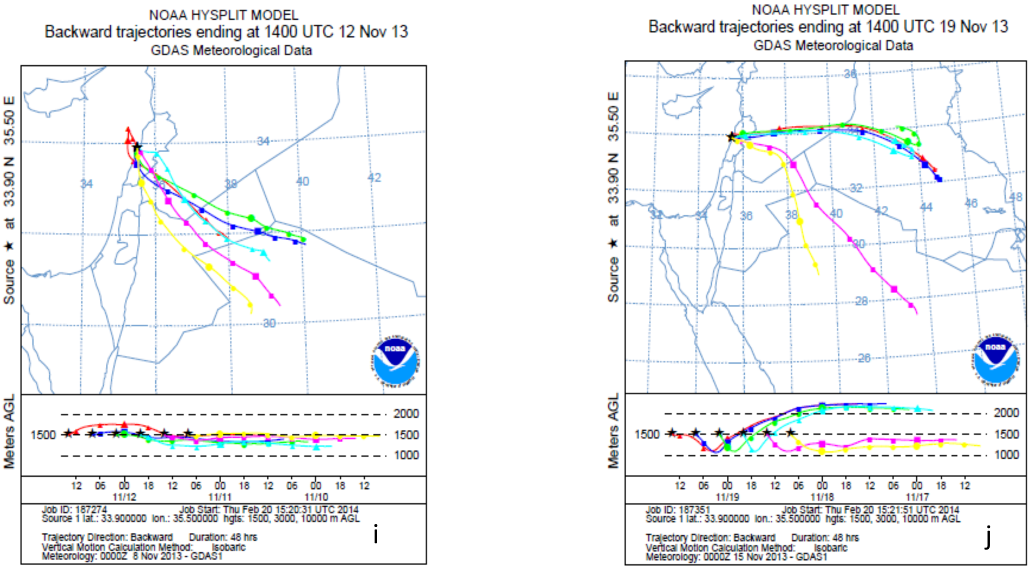


**Figure S1** NOAA-HYSPLIT air mass backwards trajectories showing: a-e) north and north west trajectories and f-j) east and south east trajectories indicative of wind originating from the Arabian Desert

.

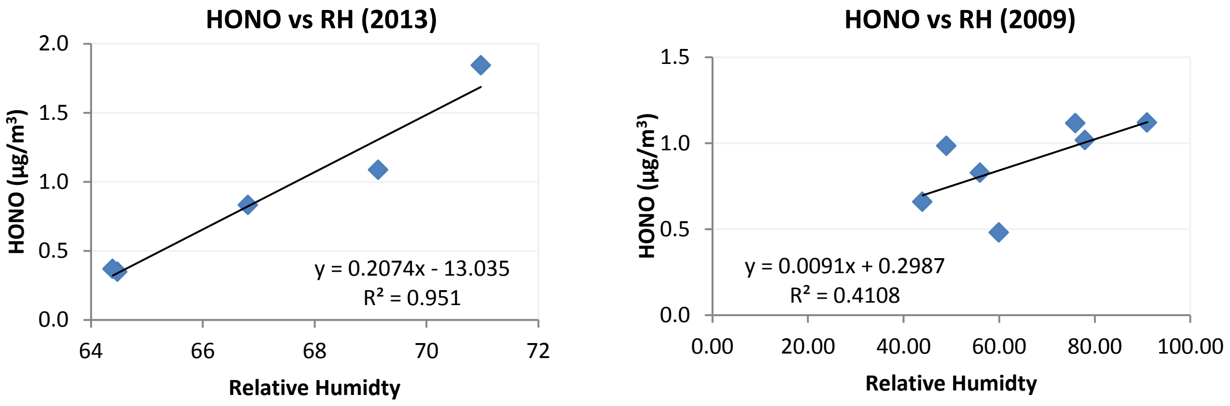


Figure S2 Correlation between concentration of HONO (µg/m$^3$) and RH during non-dusty days of the 2013 and 2009 sampling campaigns.

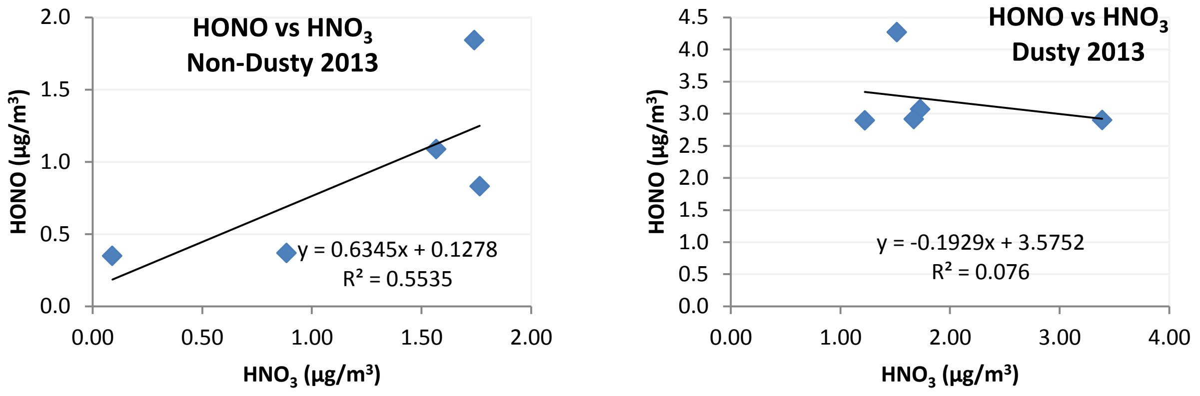
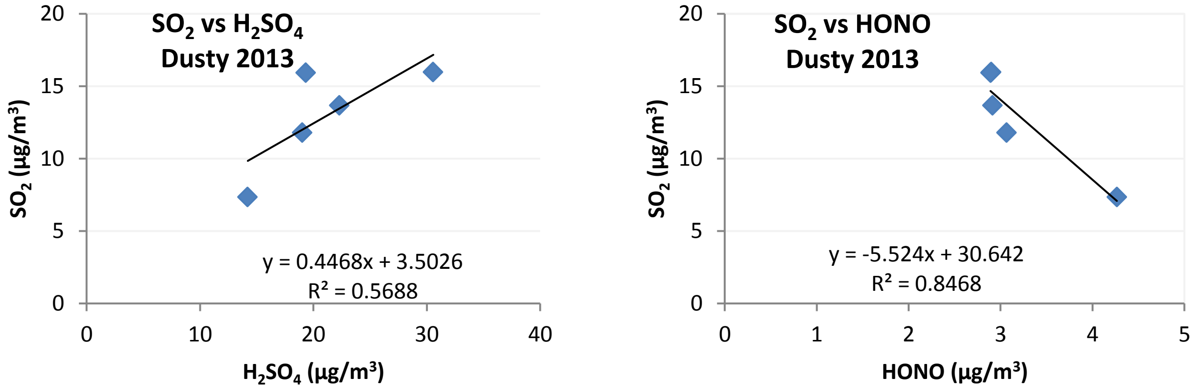


Figure S3 Correlation between HONO and $HNO_3$ during non-dusty and dusty days in the 2013 campaign



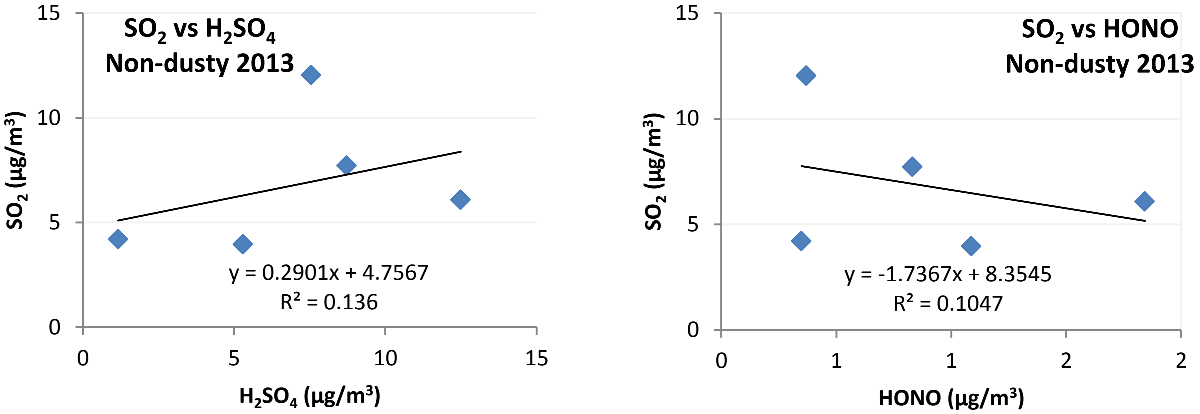


Figure S4 Correlations of $SO_2$ with $H_2SO_4$ and HONO during dusty and non-dusty days in the 2013 sampling campaign

Table S1. Correlation between gases and particle inorganic ions during non-dusty (ND-2009) and Arabian dusty (Ar-D-2009) days of the 2009 field campaign

| ND-2009 | **PM** | **HONO** | **$HNO_3$** | **$H_2SO_4$** | **$NO_3^-$** | **$SO_4^{2-}$** | **$Na^+$** | **$NH_4^+$** | **$K^+$** | **$Mg^{2+}$** | **$Ca^{2+}$** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **PM** | 1 | 0.14 | 0.05 | -0.29 | 0.03 | -0.29 | 0.48 | 0.02 | -0.20 | 0.36 | 0.52 |
| **HONO** | | 1 | -0.06 | -0.29 | -0.61 | -0.41 | -0.01 | -0.57 | 0.47 | -0.42 | 0.55 |
| **$HNO_3$** | | | 1 | 0.42 | -0.11 | -0.49 | -0.24 | -0.16 | -0.23 | -0.16 | 0.62 |
| **$H_2SO_4$** | | | | 1 | -0.18 | -0.30 | -0.13 | -0.29 | 0.17 | -0.34 | -0.16 |
| **$NO_3^-$** | | | | | 1 | 0.45 | -0.10 | 0.45 | -0.09 | 0.80 | -0.49 |
| **$SO_4^{2-}$** | | | | | | 1 | -0.53 | 0.87 | 0.21 | 0.00 | -0.67 |
| **$Na^+$** | | | | | | | 1 | -0.44 | -0.57 | 0.48 | 0.17 |
| **$NH_4^+$** | | | | | | | | 1 | -0.12 | 0.08 | -0.36 |
| **$K^+$** | | | | | | | | | 1 | -0.41 | -0.24 |
| **$Mg^{2+}$** | | | | | | | | | | 1 | -0.18 |
| **$Ca^{2+}$** | | | | | | | | | | | 1 |

| Ar-D-2009 | **PM** | **HONO** | **$HNO_3$** | **$H_2SO_4$** | **$NO_3^-$** | **$SO_4^{2-}$** | **$Na^+$** | **$NH_4^+$** | **$K^+$** | **$Mg^{2+}$** | **$Ca^{2+}$** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **PM** | 1 | 0.99 | 0.94 | -0.05 | -0.14 | 0.36 | -0.48 | -0.93 | -0.42 | 0.32 | 0.93 |
| **HONO** | | 1 | 0.87 | -0.21 | -0.03 | 0.47 | -0.42 | -0.86 | -0.28 | 0.39 | 0.96 |
| **$HNO_3$** | | | 1 | 0.27 | -0.38 | 0.08 | -0.59 | -1.00 | -0.66 | 0.19 | 0.79 |
| **$H_2SO_4$** | | | | 1 | -0.88 | -0.90 | -0.58 | -0.28 | -0.61 | -0.11 | -0.22 |
| **$NO_3^-$** | | | | | 1 | 0.87 | 0.89 | 0.35 | 0.34 | -0.38 | -0.12 |
| **$SO_4^{2-}$** | | | | | | 1 | 0.56 | -0.09 | 0.21 | -0.10 | 0.38 |
| **$Na^+$** | | | | | | | 1 | 0.55 | 0.18 | -0.69 | -0.55 |
| **$NH_4^+$** | | | | | | | | 1 | 0.70 | -0.12 | -0.76 |
| **$K^+$** | | | | | | | | | 1 | 0.54 | -0.07 |
| **$Mg^{2+}$** | | | | | | | | | | 1 | 0.62 |
| **$Ca^{2+}$** | | | | | | | | | | | 1 |

Table S2. Correlation between gases and particle inorganic ions during non-dusty (ND-2013) and Arabian dusty (Ar-D-2013) days of the 2009 field campaign

| ND-2013 | **PM** | **HONO** | **$HNO_3$** | **$H_2SO_4$** | **$NO_3^-$** | **$SO_4^{2-}$** | **$Na^+$** | **$NH_4^+$** | **$K^+$** | **$Mg^{2+}$** | **$Ca^{2+}$** | **$NO_2$** | **$SO_2$** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **PM** | 1 | 0.55 | 0.14 | 0.68 | 0.96 | 0.41 | 0.64 | 0.64 | -0.32 | -0.54 | 0.46 | 0.73 | 0.27 |
| **Ar-HONO** | | 1 | 0.74 | 0.74 | 0.61 | 0.57 | 0.63 | 0.61 | 0.60 | 0.38 | 0.91 | 0.16 | -0.32 |
| **$HNO_3$** | | | 1 | 0.80 | 0.36 | 0.40 | 0.77 | 0.75 | 0.77 | 0.53 | 0.93 | 0.15 | 0.03 |
| **$H_2SO_4$** | | | | 1 | 0.84 | 0.47 | 0.99 | 0.98 | 0.27 | -0.04 | 0.90 | 0.63 | 0.37 |
| **$NO_3^-$** | | | | | 1 | 0.51 | 0.81 | 0.82 | -0.19 | -0.47 | 0.62 | 0.82 | 0.36 |
| **$SO_4^{2-}$** | | | | | | 1 | 0.38 | 0.42 | 0.15 | -0.10 | 0.58 | 0.54 | -0.31 |
| **$Na^+$** | | | | | | | 1 | 1.00 | 0.20 | -0.10 | 0.83 | 0.67 | 0.51 |
| **$NH_4^+$** | | | | | | | | 1 | 0.17 | -0.14 | 0.82 | 0.71 | 0.52 |
| **$K^+$** | | | | | | | | | 1 | 0.94 | 0.63 | -0.49 | -0.47 |
| **$Mg^{2+}$** | | | | | | | | | | 1 | 0.35 | -0.75 | -0.56 |
| **$Ca^{2+}$** | | | | | | | | | | | 1 | 0.32 | -0.04 |
| **$NO_2$** | | | | | | | | | | | | 1 | 0.58 |
| **$SO_2$** | | | | | | | | | | | | | 1 |

| Ar-D-2013 | **PM** | **HONO** | **$HNO_3$** | **$H_2SO_4$** | **$NO_3^-$** | **$SO_4^{2-}$** | **$Na^+$** | **$NH_4^+$** | **$K^+$** | **$Mg^{2+}$** | **$Ca^{2+}$** | **$NO_2$** | **$SO_2$** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **PM** | 1 | -0.03 | -0.30 | -0.24 | 0.95 | 0.92 | 0.10 | 0.81 | 0.88 | 0.83 | 0.93 | -0.33 | -0.33 |
| **HONO** | | 1 | -0.28 | -0.67 | -0.31 | 0.18 | -0.95 | 0.37 | -0.23 | 0.37 | -0.47 | -0.66 | -0.92 |
| **$HNO_3$** | | | 1 | 0.19 | 0.87 | 0.90 | -0.05 | 0.84 | 0.94 | 0.92 | 0.87 | -0.49 | -0.38 |
| **$H_2SO_4$** | | | | 1 | -0.01 | -0.56 | 0.77 | -0.02 | 0.33 | -0.08 | 0.62 | 0.65 | 0.75 |
| **$NO_3^-$** | | | | | 1 | 0.79 | 0.37 | 0.61 | 0.91 | 0.65 | 0.99 | -0.19 | -0.06 |
| **$SO_4^{2-}$** | | | | | | 1 | -0.09 | 0.90 | 0.75 | 0.87 | 0.82 | -0.37 | -0.49 |
| **$Na^+$** | | | | | | | 1 | -0.50 | 0.27 | -0.44 | 0.43 | 0.41 | 0.87 |
| **$NH_4^+$** | | | | | | | | 1 | 0.59 | 0.97 | 0.55 | -0.36 | -0.61 |
| **$K^+$** | | | | | | | | | 1 | 0.72 | 0.94 | -0.46 | -0.14 |
| **$Mg^{2+}$** | | | | | | | | | | 1 | 0.62 | -0.55 | -0.66 |
| **$Ca^{2+}$** | | | | | | | | | | | 1 | -0.13 | 0.12 |
| **$NO_2$** | | | | | | | | | | | | 1 | 0.83 |
| **$SO_2$** | | | | | | | | | | | | | 1 |