

Manuscript Number:

Title: Contribution of Airborne Dust Particles to HONO Sources

Keywords: particle sulfate, NO₂ hydrolysis, synergistic NO₂ and SO₂ reaction, HONO, dust aerosols, acidity

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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 NO₂ 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, HNO₃ and H₂SO₄ 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 NO₂ hydrolysis occurs whereas during Ar-D days, where the air is relatively dry, a synergistic mechanism of adsorption and reaction between NO₂ and SO₂ on dust particles to produce HONO and sulfate in the particle phase is suggested. Other possible mechanisms are attributed to the heterogeneous reaction of NO₂ 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.

To: Editor in Chief

Re: Research Article "*Contribution of Airborne Dust Particles to HONO Sources*".

Dear Editor in Chief,

Kindly consider the revised version of the article entitled: "*Contribution of Airborne Dust Particles to HONO Sources*".

The manuscript has been revised and modified to include all the suggestions requested by the reviewers.

Should you need any further 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 PM_{10} are listed for the 2009 field campaign.

2013	<i>RH</i>	<i>UF</i>	<i>ACC</i>	<i>CPM</i>	<i>PM</i>
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	<i>RH</i>	<i>UF</i>	<i>ACC</i>	<i>CPM</i>	<i>PM</i>
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

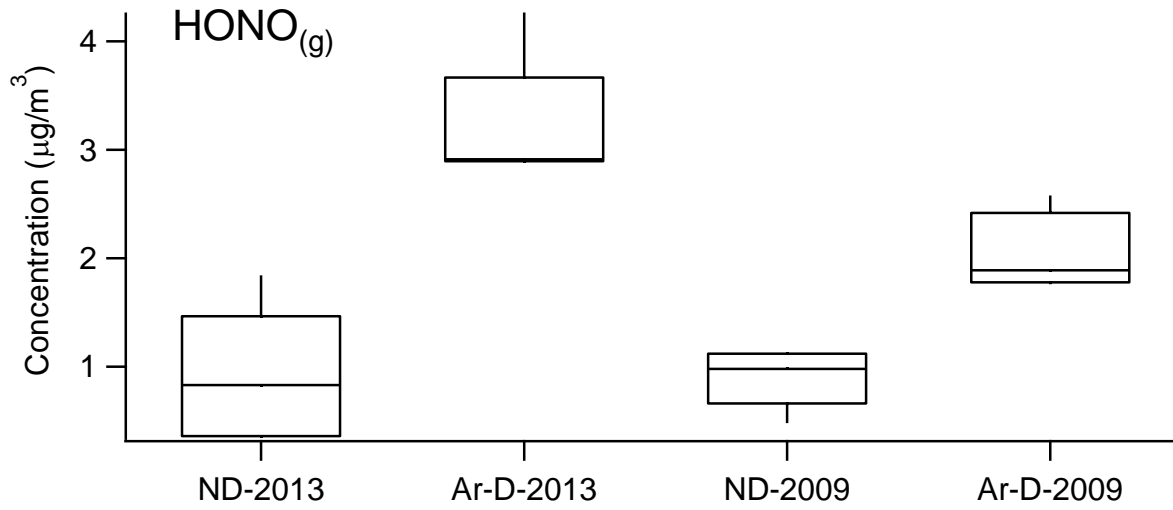


Figure 1 Box plots of concentrations of acid gas HONO during Arabian dusty and non-dusty days. Where ND stands for non-dusty and Ar-D stands for Arabian dusty days

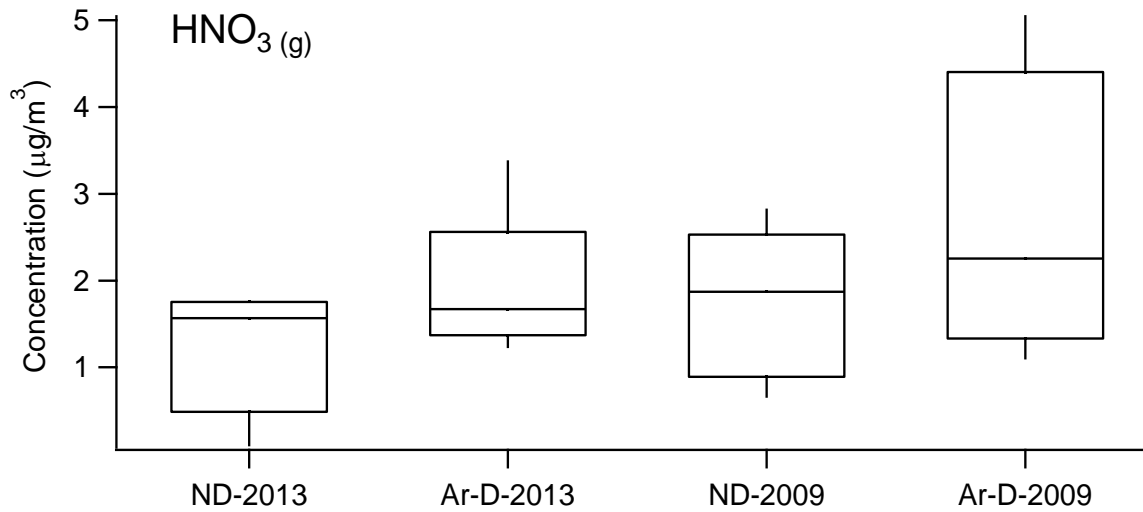


Figure 2 Box plots of concentrations of acid gas HNO₃ during Arabian dusty and non-dusty days. Where ND stands for non-dusty and Ar-D stands for Arabian dusty days

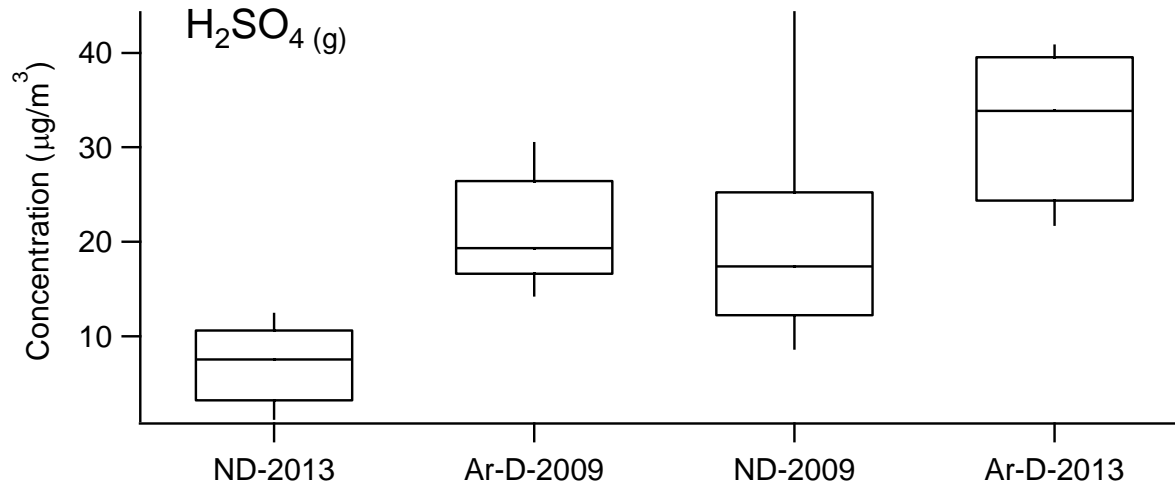


Figure 3 Box plots of concentrations of acid gas H_2SO_4 during Arabian dusty and non-dusty days. Where ND stands for non-dusty and Ar-D stands for Arabian dusty days

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 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 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.

Date	[H ⁺] (mol/m ³)				<i>f</i>				Date	[H ⁺] (mol/m ³)		<i>f</i>
	UF	Acc	CPM	PM ₁₀	UF	Acc	CPM	PM ₁₀		PM ₁₀	PM ₁₀	
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												
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 NO₂ 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 NO₂ which leads to the formation of HONO and HNO₃. If it is a simple physisorption 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 N₂ 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 HNO₃ 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 SO₂ and HNO₃ (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, HNO₃ and H₂SO₄) were sampled for 24hr using a diffusion denuder system; where the reported H₂SO₄ is a combination of converted SO₂ and atmospheric H₂SO₄. The system is based on two Honey Comb denuders (HC) coated with 1% NaCO₃ 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 PM₁₀ 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 PM₁₀ 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 PM₁₀ 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 sonicated 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 SO₂.

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 (Figure S1) 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. The occurrence of a dust storm was 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.

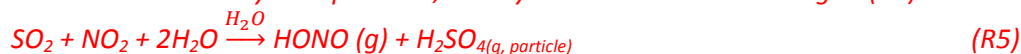
p. 4832-4833: The authors note that gas phase HONO is correlated with gas phase H₂SO₄ during an Arabian dust storm accompanied by dry air. They suggest that the correlation indicates a synergistic mechanism of adsorption and reaction between NO₂ and SO₂ on dust surfaces. I think it is fine to discuss 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, 2002). In a paper published by 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/NO₂ data increased by 100% during dusty days. Based on the SO₂ and NO₂ data and analysis the paragraph has been modified as:

“Gas phase composition: The average gas phase HONO, HNO₃, and H₂SO₄ (sum of SO₂ and H₂SO₄ 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, HNO₃ and H₂SO₄ levels exhibit a clear increase during dusty days. Concomitantly, an increase in NO₂ and SO₂ gas levels is observed for the 2013 experimental data (Figure 2). During dusty days, the NO₂ increase might be explained by the accumulation of locally emitted NO₂ pollutants in the stagnant atmospheric environment. Although NO₂ 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/NO₂ doubles (from an average of 0.03 during non-dusty to 0.06 during dusty days) during dusty days despite the increase in NO₂ levels. The higher value of HONO/NO₂ of 0.06 remains typical of urban environments (Stutz et al., 2004). Also, the HONO/HNO₃ ratio goes up from 1.3 in non-dusty to 1.9 during Arabian dusty days. Similar trend for HONO/HNO₃ 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/NO₂ and HONO/HNO₃) during dusty days indicates that HONO production is due to sources other than NO₂. 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 (R² = 0.4 in 2009 and R² = 0.9 in 2013) suggesting that NO₂ heterogeneous conversion which leads to HONO and HNO₃ is a possible mechanism during non-dusty days (Stutz et al., 2004) as illustrated in equations (R2)-(R4).



The increase in H₂SO₄ and SO₂ alongside HONO and NO₂, during dusty days, could be due to similar or independent factors. In fact, a poor correlation between SO₂ and NO₂ (R² = 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 SO₂ and NO₂ (R² = 0.7)) and the high correlations between SO₂ and H₂SO₄ (R² = 0.6) and SO₂ and HONO (R² = 0.85, descending) suggests that SO₂ plays a role in the formation of HONO during dust. One possible explanation is the synergistic mechanism of adsorption and reaction between NO₂ and SO₂ that could be enhanced by dust particles; mainly mineral oxides according to (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 NO₂ on alumina was altered in the presence of SO₂. In similar studies, co-adsorption of SO₂ and NO₂ showed that the intermediate N₂O₄ leads to nitrates and sulfates in pathways different than the formation of NO⁺NO₃⁻ 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.

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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, NO₂ and SO₂ 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 N₂ 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 HNO₃ 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 SO₂ and HNO₃ (Spurny, 1999)(and references therein).

As for the sulfuric acid part, I agree with the reviewer that SO₂ is collected as H₂SO₄, yet this is only the case when the denuders are extracted with H₂O₂ solution which aids the complete conversion of SO₂ 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 H₂O₂ oxidizing agent and therefore the collected acidic gases represent the sum of converted SO₂ and original gas phase H₂SO₄. Hydrogen peroxide was not added to the extraction solution, as its presence leads to the oxidation of HONO into HNO₃, leading to an underestimation and overestimation of the latter, respectively. From here on, the collected SO₂ and H₂SO₄ on denuders will be referred to as H₂SO₄ (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					
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. The occurrence of a dust storm was 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, HNO₃ and H₂SO₄) were sampled for 24hr using a diffusion denuder system. The system is based on two Honey Comb denuders (HC) coated with 1% NaCO₃ 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 PM₁₀ 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 PM₁₀ 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 sonicated 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 SO₂. 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 NO₂ data makes the backbone of the manuscript; we introduced the 2013 campaign which contains the NO₂ and SO₂ data as shown in Table 2.

Table 2. Concentrations of NO₂ and SO₂ 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.

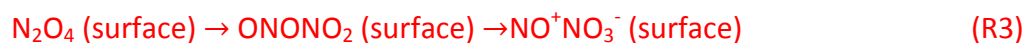
The point raised by the reviewer is well taken and the discussion has been revised accordingly. First the evidences deduced from the two field campaigns are presented in bullet points. Following, a paragraph summarizing the analysis of the results will be considered the basis of the proposed mechanism 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 HNO₃ and H₂SO₄ levels during dusty days (Figure B & C)
- An increase in NO₂ and SO₂ gas levels is observed for the 2013 experimental data (Figures D)
- There is a high correlation of HONO with RH in non-dusty days (R² = 0.95 in the 2013 field campaign and R² = 0.41 in the 2009 campaign) (Figure E)
- In the 2013 campaign, HONO correlates with HNO₃ during non-dusty (R² = 0.6) but does not correlate with HNO₃ during Arabian dusty days (R² = 0.08) (Figure F)
- The HONO/NO₂ doubles during dusty days despite the increase in NO₂ levels (0.03 during non-dusty to 0.06 during dusty)
- During dusty days SO₂ highly correlates with H₂SO₄ (R² = 0.6, p < 0.05), and anti-correlates with HONO (R² = 0.85, p < 0.05). In non-dusty days, these correlations are poor (SO₂ and H₂SO₄ (R² = 0.14), and SO₂ and HONO (R² = 0.10))(Figure G)
- During dusty days HONO/H₂SO₄ 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, HNO₃ and H₂SO₄ levels exhibit a clear increase during dusty days. Concomitantly, an increase in NO₂ and SO₂ gas levels is observed for the 2013 experimental data (Figure 2). During dusty days, the NO₂ increase might be explained by the accumulation of locally emitted NO₂ pollutants in the stagnant atmospheric environment. Although NO₂ 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/NO₂ doubles (from an average of 0.03 during non-dusty to 0.06 during dusty days) during dusty days despite the increase in NO₂ levels. The higher value of HONO/NO₂ of 0.06 remains typical of urban environments (Stutz et al., 2004). Also, the HONO/HNO₃ ratio goes up from 1.3 in non-dusty to 1.9 during Arabian dusty days. Similar trend for HONO/HNO₃ 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/NO₂ and HONO/HNO₃) during dusty days indicates that HONO production is due to sources other than NO₂. 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 (R² = 0.4 in 2009 and R² = 0.9 in 2013) suggesting that NO₂ heterogeneous conversion which leads to HONO and HNO₃ is a possible mechanism during non-dusty days (Stutz et al., 2004) as illustrated in equations (R2)-(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).

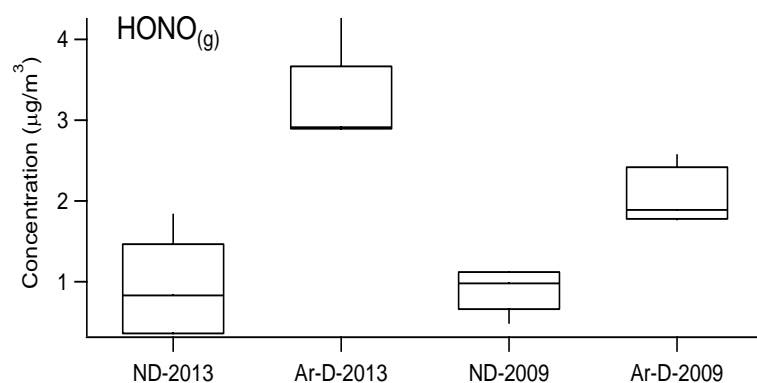
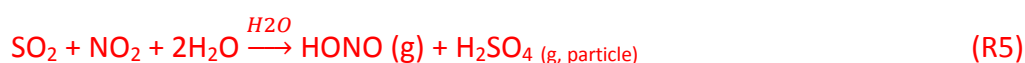


Figure A Box plots of concentrations of acid gas HONO during non-dusty (ND) and Arabian dusty (Ar-D) days in 2013 and 2009.

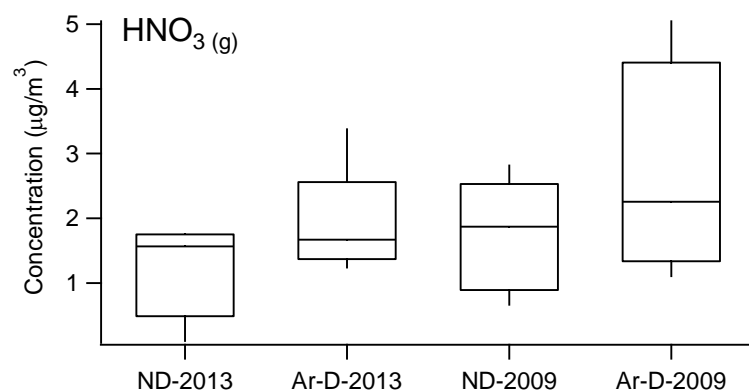


Figure B Box plots of concentrations of acid gas HNO₃ during non-dusty (ND) and Arabian dusty (Ar-D) days in 2013 and 2009.

days in 2013 and 2009..

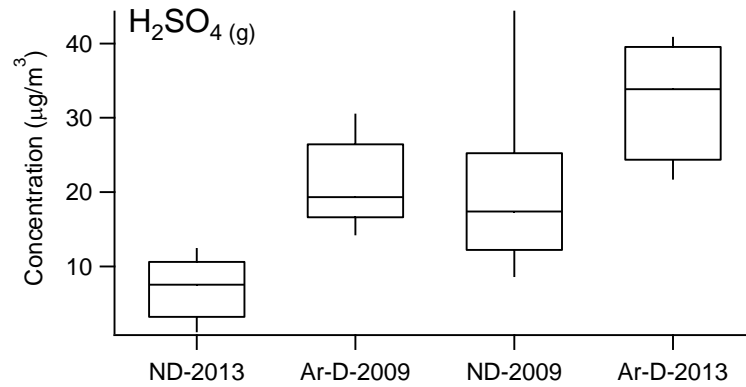


Figure C Box plots of concentrations of acid gas H_2SO_4 during non-dusty (ND) and Arabian dusty (Ar-D) days in 2013 and 2009.

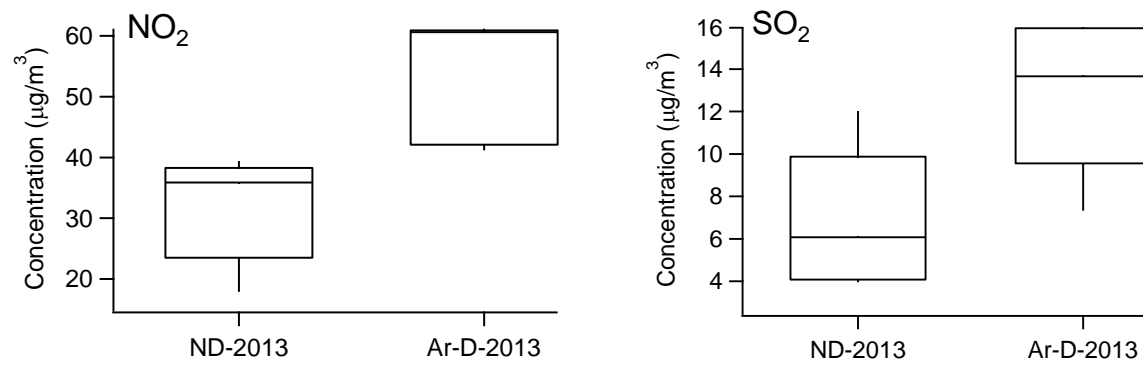


Figure D Box plots of concentration of NO_2 and SO_2 in the 2013 campaign during non-dusty (ND) and Arabian dusty (Ar-D) days.

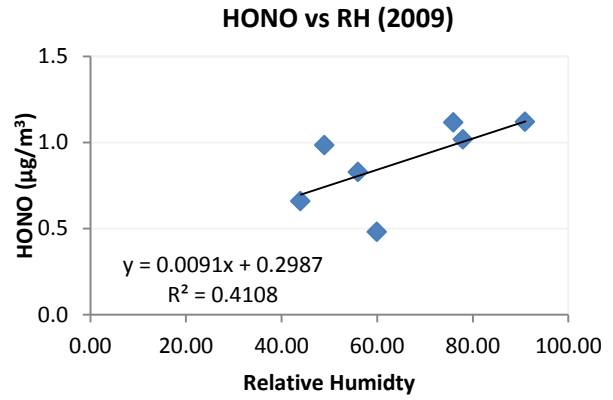
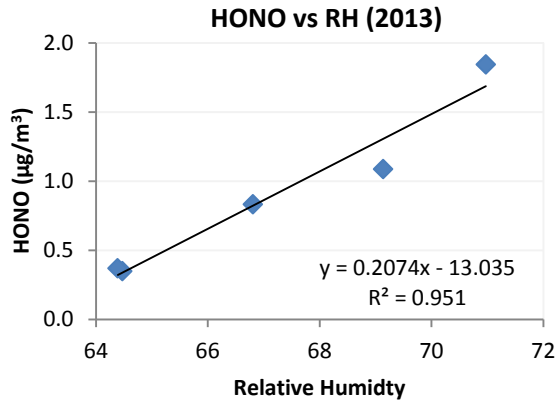


Figure E Correlation between concentration of HONO ($\mu\text{g}/\text{m}^3$) and RH during non-dusty days of the 2013 and 2009 sampling campaigns.

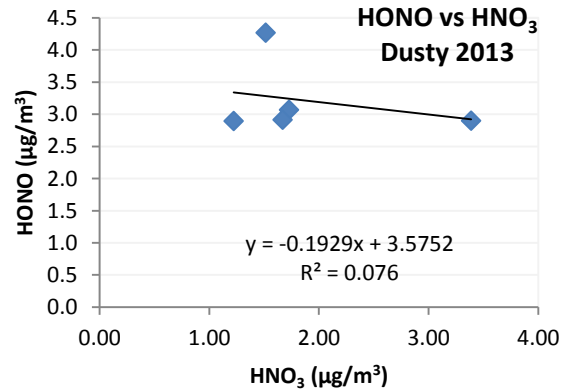
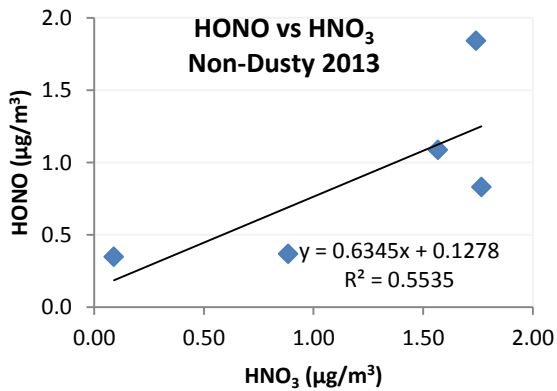
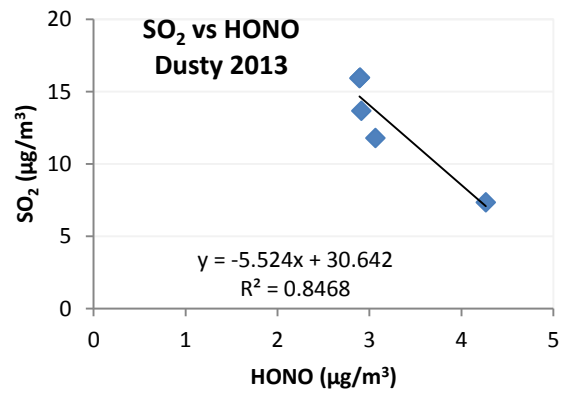
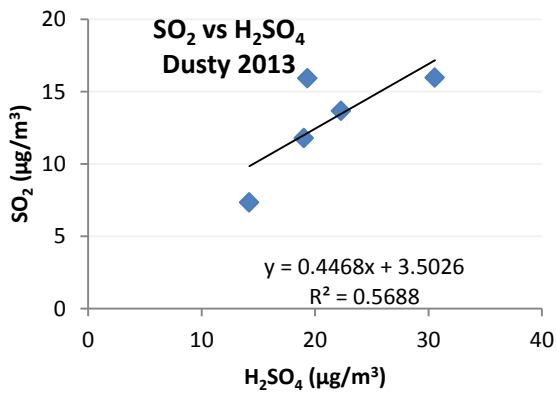


Figure F Correlation between HONO and HNO₃ during non-dusty and dusty days in the 2013 campaign



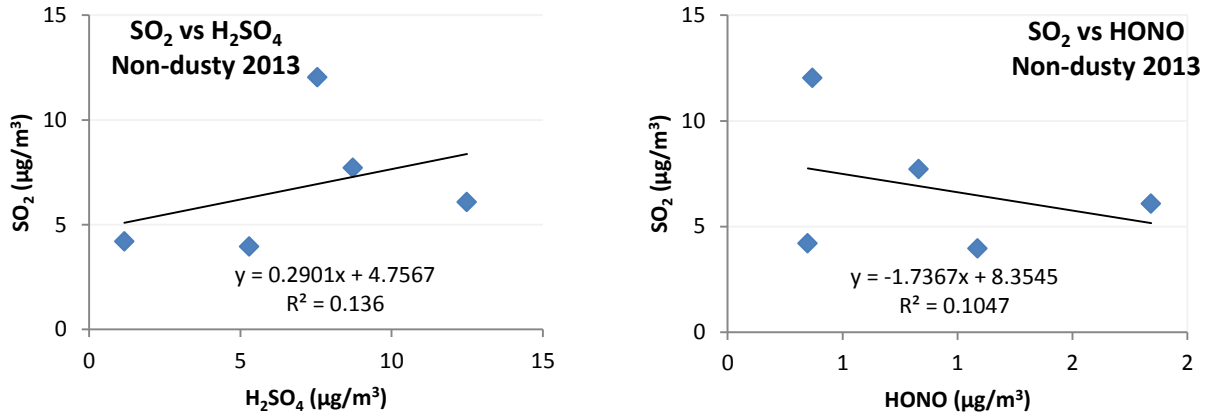


Figure G Correlations of SO₂ with H₂SO₄ and HONO during dusty and non-dusty days in the 2013 sampling campaign

B. Particle Phase

- There is an increase in the nitrates and sulfates in PM₁₀. 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:

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

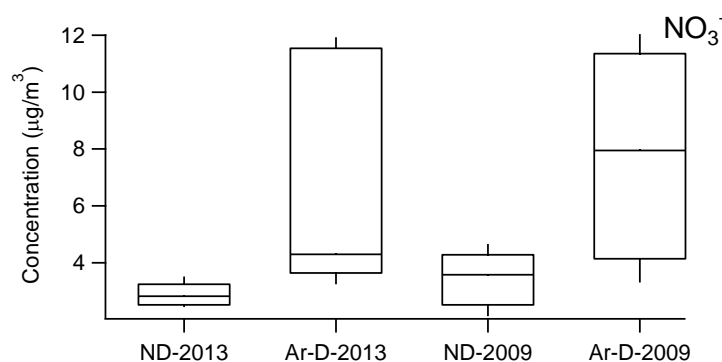
It is considered that when $f = 0$, there is full neutralization by NH₄⁺, if $f = 1$, no neutralization has occurred. At $f = 0.5$, the bulk aerosol is a mixture of properties similar to NH₄HSO₄; at $f = 0.25$, the mixture is similar to letovicite ((NH₄)₃H(SO₄)₂) (Stevens et al., 1980)

- 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 (R² = 0.8, p < 0.05) during non-dusty days that. In dusty days (Arabian), HONO anti-correlates with PM-UF (R² = 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 NO₃⁻-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 NO₃⁻ and SO₄²⁻ (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), NO₃⁻-ACC ($R^2 = 0.96$ for the 2013 field measurements) and NO₃⁻ · PM₁₀ ($R^2 = 0.4$ for the 2009 field measurements) indicate either HONO and PM-ACC and NO₃⁻ originate from similar sources or HONO is the result of a secondary reaction involving PM and leading to nitrate; i.e. NO₂ 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-PM₁₀ 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 NO₂ 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.



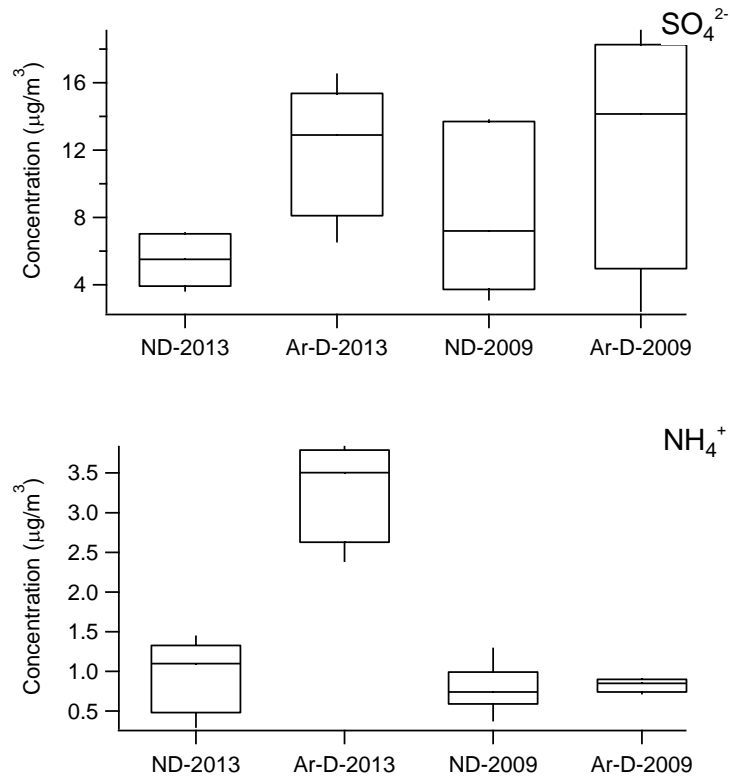


Figure H. Concentrations of NO_3^- , SO_4^{2-} and NH_4^+ in $\mu\text{g}/\text{m}^3$ during non-dusty (ND) Arabian dusty (Ar-D) and days of the 2009 and 2013 field campaigns

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	$[\text{H}^+]$ (mol/m^3)				f				Date	$[\text{H}^+]$ (mol/m^3)	F
	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

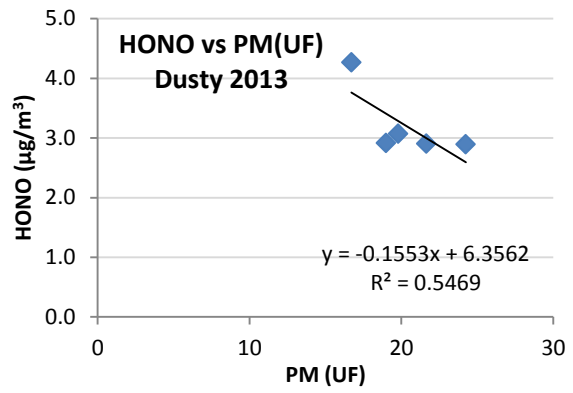
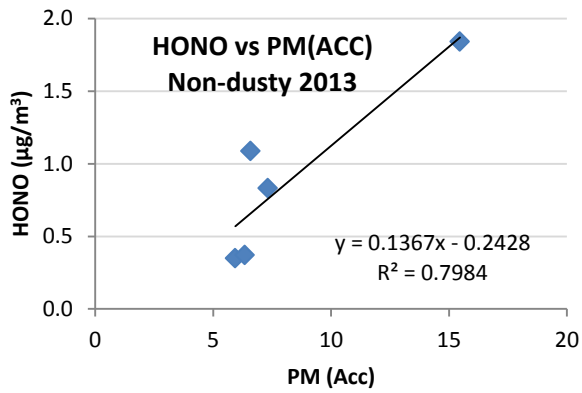
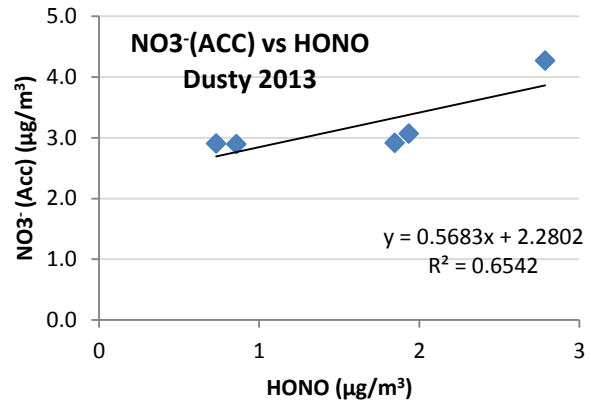
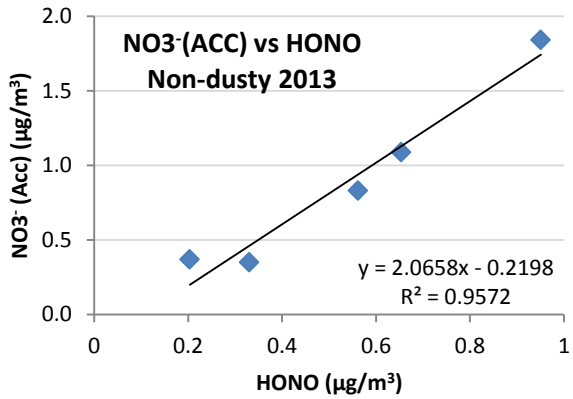


Figure I Correlations of HONO with PM (Acc) during non-dusty days and with PM(UF)during dusty days in the 2013 sampling campaign, where PM is particulate matter, Acc stands for accumulation and UF stands for ultrafine.



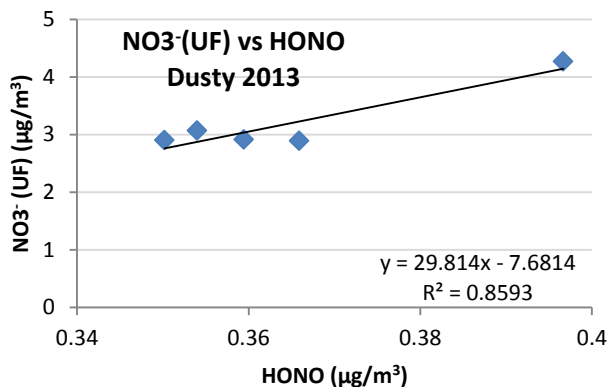
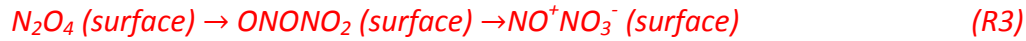


Figure J Correlations of HONO with Nitrate (Acc) during non-dusty days and during dusty days and with Nitrate (UF) during dusty days in the 2013 sampling campaign, where PM is particulate matter, Acc stands for accumulation and UF stands for ultrafine.

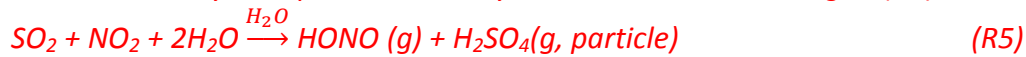
Based on the presented evidences and discussions, the paragraph reads as:

Gas phase composition: The average gas phase HONO, HNO₃, and H₂SO₄ (sum of SO₂ and H₂SO₄ captured by the denuders and represented thereafter by H₂SO₄) 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, HNO₃ and H₂SO₄ levels exhibit a clear increase during dusty days. Concomitantly, an increase in NO₂ and SO₂ gas levels is observed for the 2013 experimental data (Figure 2). During dusty days, the NO₂ increase might be explained by the accumulation of local emission due to stagnant wind. Although NO₂ 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/NO₂ doubles (from an average of 0.03 to 0.06) during dusty days despite the increase in NO₂ levels. The higher value of HONO/NO₂ of 0.06 remains typical of urban environments (Stutz et al., 2004). Also, the HONO/HNO₃ ratio goes up from 1.3 in non-dusty to 1.9 during Arabian dusty days. Similar trend for HONO/HNO₃ is observed in 2009 data, where the ratio increases from 0.7 to 1.0 in non-dusty and dusty days, respectively. The increase in both ratios (HONO/NO₂ and HONO/HNO₃) during dusty days indicates that HONO production is due to sources other than NO₂. 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 (R² = 0.4 in 2009 and R² = 0.9 in 2013) suggesting that NO₂ heterogeneous conversion which leads to HONO and HNO₃ is a possible mechanism at relatively higher RH, during non-dusty days (Stutz et al., 2004) as illustrated in equations (R2)-(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).



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 alumina 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 NO₂ and SO₂ 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, HNO₃ and H₂SO₄ due to several possible mechanisms. These include the increase in the acidity of particles, the synergistic reaction of NO₂ and SO₂ on mineral dust surfaces to produce HONO and H₂SO₄ and the heterogeneous reaction of NO₂ 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, 2002), 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/NO₂ data increased by 100% during dusty days. This will solve the issue of extrapolating the data of HNO₃ to deduce the contribution of NO₂ 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).



The heterogeneous reaction of NO₂ 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., 2008a; Gustafsson et al., 2006; George et al., 2005; Stemmler et al., 2007; Stemmler et al., 2006).

The heterogeneous reaction of NO₂ on different mineral dust surfaces (SiO₂, Al₂O₃, TiO₂, 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., 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, TiO₂ 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 H₂O₂ from NO₂ and H₂O. TiO₂ 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)”

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 10⁻⁷ – 10⁻⁸ (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 10⁻⁶. 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 H₂O₂. 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/m³?

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 PM₁₀ yearly averages are around 54 µg/m³ (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 SO₂ is oxidized into H₂SO₄ on denuder surfaces, yet by looking at the concentrations of H₂SO₄ and SO₂, we see that the concentration of H₂SO₄ is around double that of SO₂ in both dusty and non-days which signifies that the denuders collect gas phase H₂SO₄.

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 NO₂ and SO₂ 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:

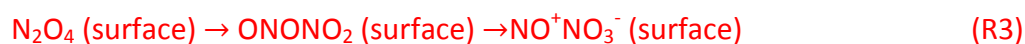
In Bröske et al. (see also typo) no photochemical source was studied.

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 10⁻⁶ up to 10⁻⁷ 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 10⁻⁷, 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 NO₂ hydrolysis on alumina proceed via dimerization of N₂O₄ and then autoionizes to form NO⁺NO₃⁻ which will further react with water to then generate HONO + HNO₃. We modified the mechanism as such:



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 HNO₃ 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 NO₂ gets adsorbed and oxidized to form loosely bound MNO₃ which in the presence of H⁺ on the surface can lead to the formation of HNO₃ 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, HNO₃, and H₂SO₄.

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Contribution of Airborne Dust Particles to HONO Sources

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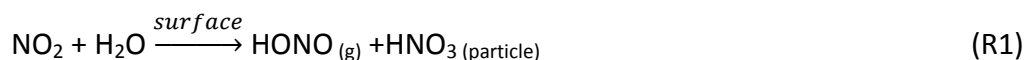
Abstract

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 NO₂ 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, HNO₃ and H₂SO₄ 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 NO₂ hydrolysis occurs whereas during Arabian dusty (Ar-D) days, where the air is relatively dry, a synergistic mechanism of adsorption and reaction between NO₂ and SO₂ on dust particles to produce HONO and sulfate in the particle phase is suggested. Other possible mechanisms are attributed to the heterogeneous reaction of NO₂ 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, NO₂ hydrolysis, synergistic NO₂ and SO₂ 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 NO₂ on wet surfaces (R1) is a major route of HONO formation in the troposphere (Finlayson-Pitts and Pitts, 2000) (and references therein).



The heterogeneous reaction of NO₂ 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 NO₂ 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 NO₂ on different mineral dust surfaces (SiO₂, Al₂O₃, TiO₂, 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, TiO₂ 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 H₂O₂ from NO₂ and H₂O. TiO₂ 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). SO₂ can also be taken up by mineral oxide surfaces to undergo a two-step mechanism including the reversible adsorption of SO₂ on the surface followed by the oxidation to sulfate (Ullerstam et al., 2002). In the case where SO₂ is co-adsorbed with NO₂ on the surface, it is shown that the oxidant is gaseous NO₂ which reacts with adsorbed SO₂ to produce sulfate in the particle phase. The oxidant role of NO₂ 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 NO₂ 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 NO₂ is a function of other competing reactions such as the aforementioned reaction of NO₂ in the presence of SO₂ on mineral surfaces (Liu et al., 2012).

Given the reactivity of mineral oxide surfaces towards NO₂ and SO₂, 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. The occurrence of a dust storm was 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, HNO₃ and H₂SO₄) were sampled for 24hr using a diffusion denuder system. The system is based on two Honey Comb denuders (HC) coated with 1% NaCO₃ 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 PM₁₀ 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 PM₁₀ inlets and operating at 9 l/min. Dust particles were collected according to their size fractions; 10-2.5 μ m (coarse particulate matter) and 2.5-0.25 μ m (accumulation PM) were collected on 25mm Teflon filters and <0.25 μ 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 sonicated 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*

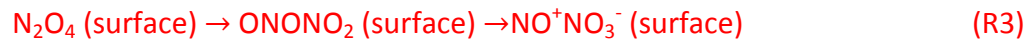
The monitoring station is mounted at the same sampling location. It is equipped with Thermo Environmental analyzers used to nitrogen oxides (Model 42i, Chemiluminescence Principle) and sulfur dioxide (Model 43i, Pulsed Fluorescence Principle). The analyzers are calibrated using the Thermo Environmental 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 SO₂.

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, HNO₃, and H₂SO₄ (sum of SO₂ and H₂SO₄ captured by the denuders and represented thereafter by H₂SO₄) 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, HNO₃ and H₂SO₄ levels exhibit a clear increase during Ar-D days. Concomitantly, an increase in NO₂ and SO₂ gas levels is observed for the 2013 experimental data (Figure 2). During Ar-D days, the NO₂ increase might be explained by the accumulation of local emission due to stagnant wind. Although NO₂ 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/NO₂ doubles (from an average of 0.03 to 0.06) during Ar-D days despite the increase in NO₂ levels. The higher value of HONO/NO₂ of 0.06 remains typical of urban environments (Stutz et al., 2004). Also, the HONO/HNO₃ ratio goes up from 1.3 in ND to 1.9 during Ar-D days. Similar trend for HONO/HNO₃ is observed in 2009 data, where the ratio increases from 0.7 to 1.0 in ND and Ar-D days, respectively. The increase in both ratios (HONO/NO₂ and HONO/HNO₃) during Ar-D days indicates that HONO production is due to sources other than NO₂. 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 NO₂ heterogeneous conversion which leads to HONO and HNO₃ is a possible mechanism at relatively higher RH, during ND days (Stutz et al., 2004) as illustrated in equations (R2)-(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) (Figure S4) 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).



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 alumina 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 $\text{NO}_3^- \cdot \text{PM}_{10}$ ($R^2 = 0.4$ 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. NO₂ 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 $0 < f < 1$, the bulk aerosol is a mixture of chemical species of properties similar to NH₄HSO₄. At $f = 0$, a full neutralization by NH₄⁺ 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-PM₁₀ 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 NO₂ 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.

Date	$[H^+]$ (mol/m ³)				f				Date	$[H^+]$	f
	UF	Acc	CPM	PM10	UF	Acc	CPM	PM10		(mol/m ³)	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											
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

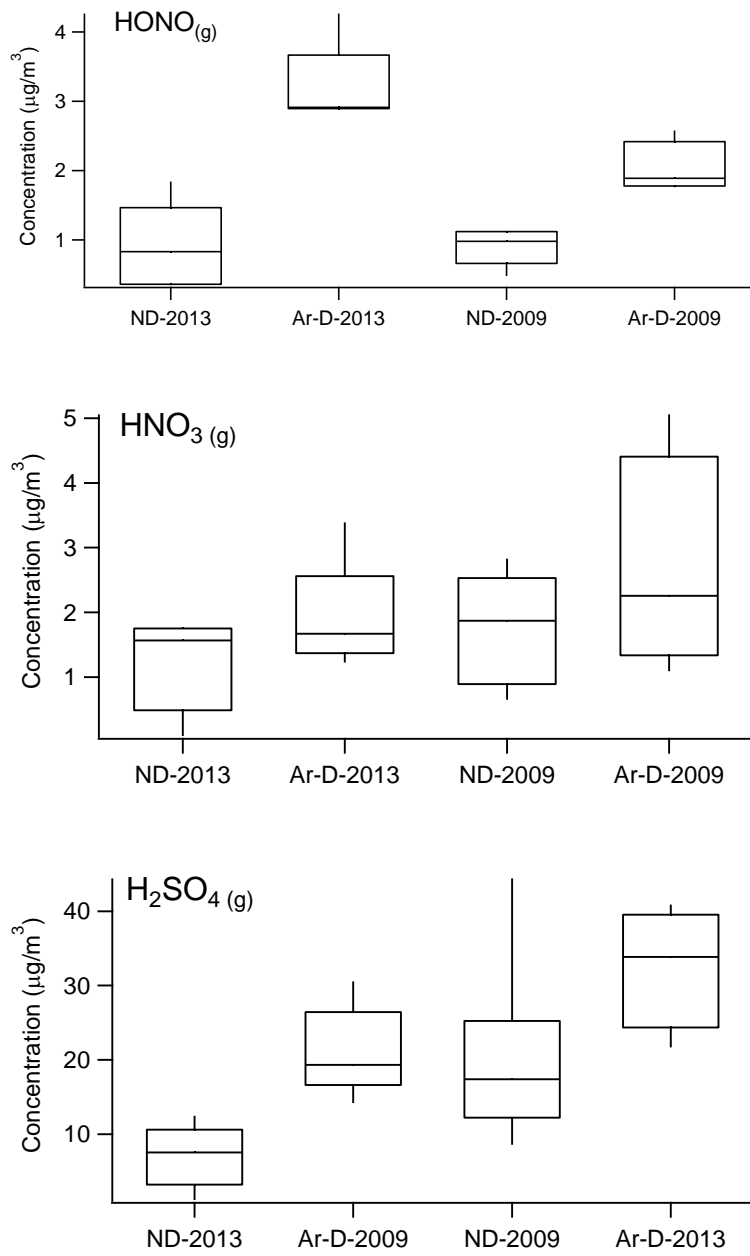


Figure 1. Concentrations of HONO, HNO₃ and H₂SO₄ in $\mu\text{g}/\text{m}^3$ during non-dusty (ND) and Arabian dusty (Ar-D) days of the 2009 and 2013 field campaigns

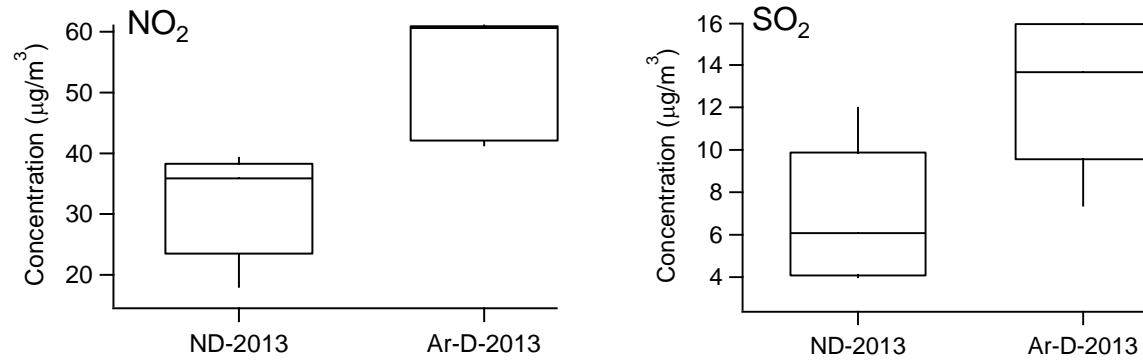


Figure 2. Concentrations of NO₂ and SO₂ in µg/m³ during non-dusty (ND) Arabian dusty (Ar-D) and days of the 2013 field campaign

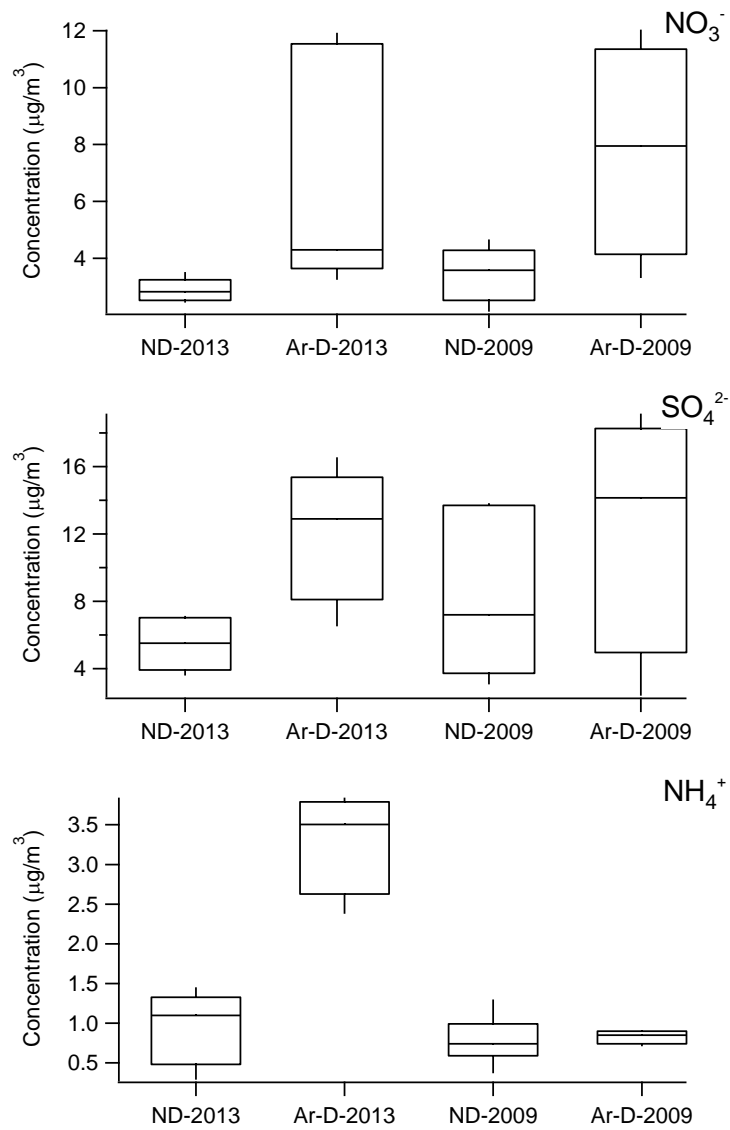


Figure 3. Concentrations of NO_3^- , SO_4^{2-} and NH_4^+ in $\mu\text{g}/\text{m}^3$ during non-dusty (ND) Arabian dusty (Ar-D) and days of the 2009 and 2013 field campaigns

Contribution of Airborne Dust Particles to HONO Sources

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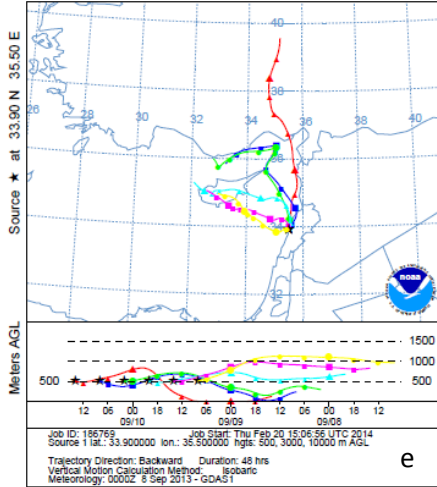
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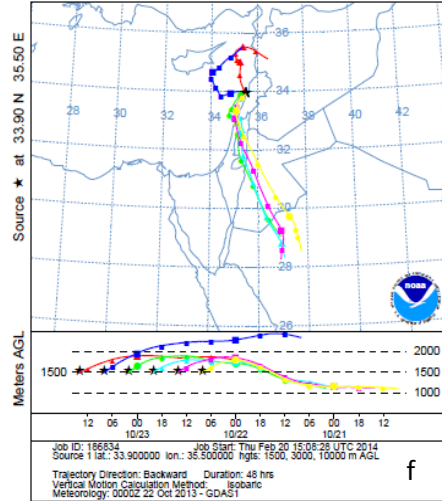
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Supplementary Information

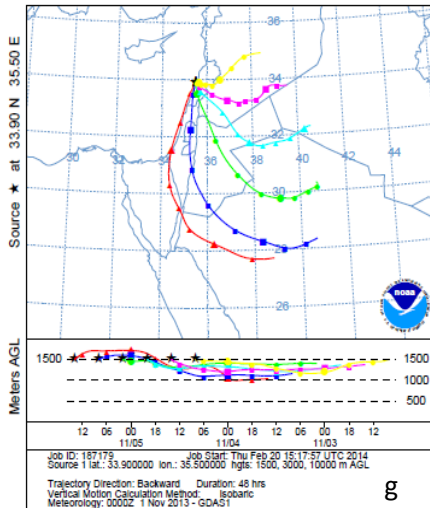
NOAA HYSPLIT MODEL
Backward trajectories ending at 1400 UTC 10 Sep 13
GDAS Meteorological Data



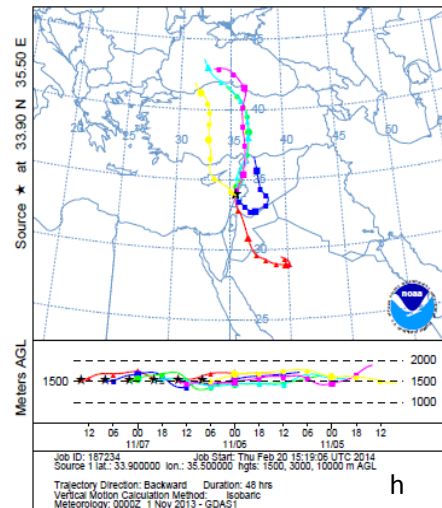
NOAA HYSPLIT MODEL
Backward trajectories ending at 1400 UTC 23 Oct 13
GDAS Meteorological Data



NOAA HYSPLIT MODEL
Backward trajectories ending at 1400 UTC 05 Nov 13
GDAS Meteorological Data



NOAA HYSPLIT MODEL
Backward trajectories ending at 1400 UTC 07 Nov 13
GDAS Meteorological Data



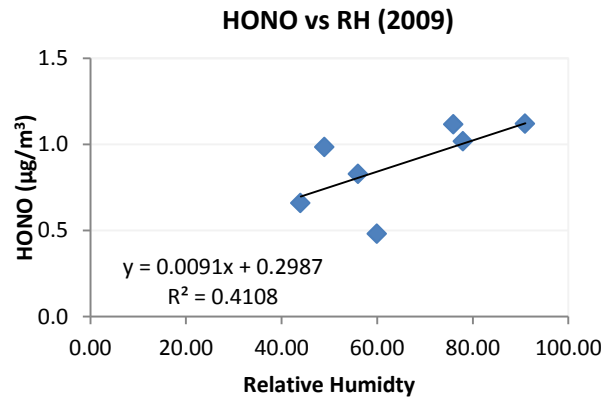
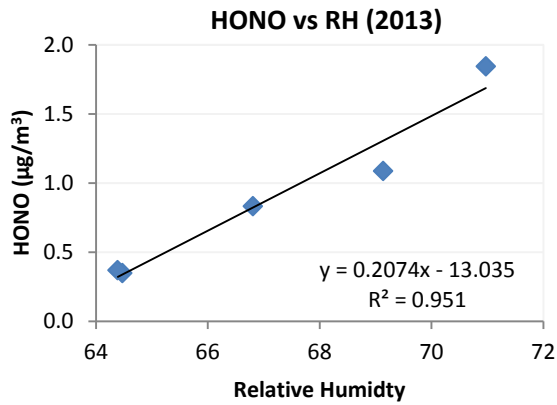


Figure S2 Correlation between concentration of HONO ($\mu\text{g}/\text{m}^3$) and RH during non-dusty days of the 2013 and 2009 sampling campaigns showing the dependence of HONO formation on relative humidity during non-dusty days.

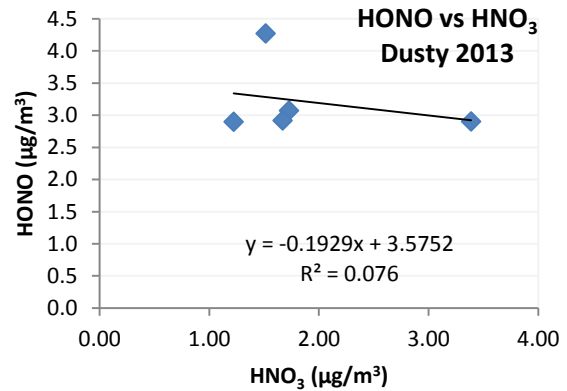
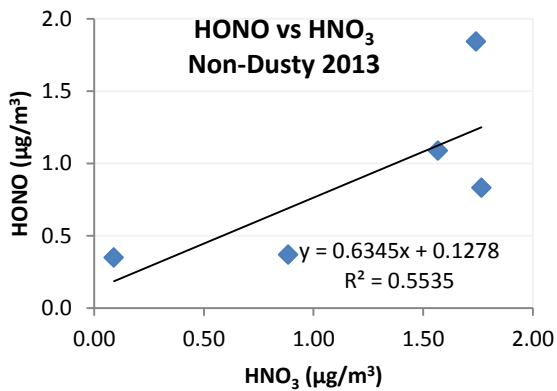


Figure S3 Correlation between HONO and HNO_3 during non-dusty (on the left) and dusty days (on the right) during the 2013 campaign. During non-dusty days HONO and HNO_3 show higher correlation than the one observed for Arabian dusty-days.

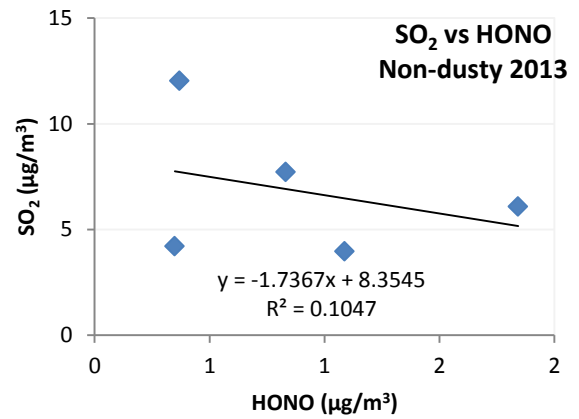
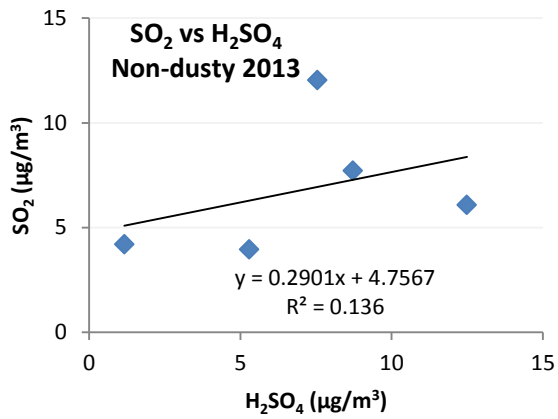
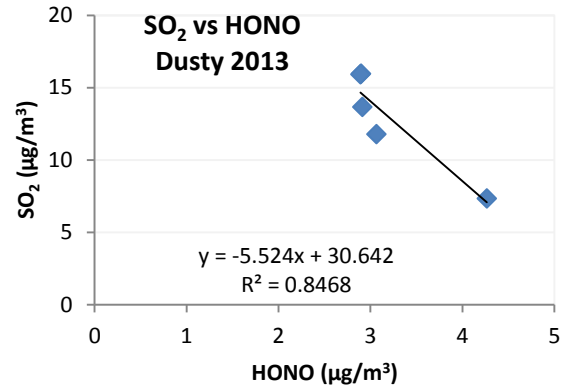
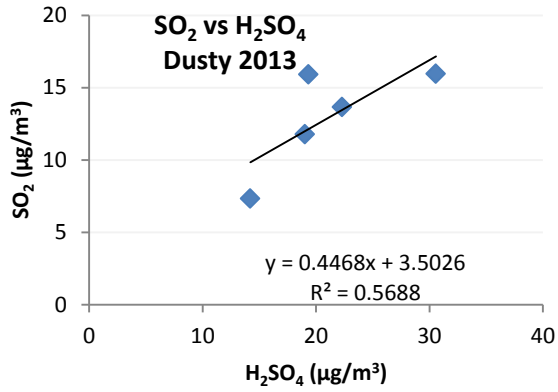


Figure S4 Correlations of SO₂ with H₂SO₄ and HONO during dusty and non-dusty days in the 2013 sampling campaign. The correlation is the highest for the dusty days of the 2013 field campaign. In the same episode, an anticorrelation is observed between SO₂ and HONO. No correlation between SO₂ and HONO and H₂SO₄ is noticed during non-dusty days.

