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Interactive comment on "Contribution of airborne dust particles to HONO sources" *by* N. A. Saliba et al.

Anonymous Referee #1

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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 NO2 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, HNO3, and H2SO4), 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

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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. 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 HNO3 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.

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.”

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.

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.

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.

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.

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 suggests 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.

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.

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 4827, 2014.