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Atmospheric Chemistry and Physics
Discussions

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:

1) 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 ref-

erence, 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.

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.

3) 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. 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.

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. . .

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).

Page 4828, line 23-25:

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

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.

Page 4830, line 8:

Exchange frozen by stored at –x °C (a liquid is frozen . . .).

Page 4830, line 19:

If the extraction is done by H2O2, how can nitrite be determined? Will be oxidized to nitrate. . .

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/m^3?

Page 4831, line 4 (and others):

Exchange H2SO4 by SO2, see above.

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.

Page 4831, lines 15-17:

If water shields the active sites, why does R1 show a positive humidity dependence?

Page 4831, line 27:

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

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…

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)?

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)?

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