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Short communication

Strong HONO formation in a suburban site during snowy days



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H I G H L I G H T S

- We measured HONO concentrations during a winter field campaign in a suburban site.
- We compared calculations with measurements and found missing source of HONO.
- Much higher HONO missing source is found when snow was present at ground.
- This evidences the existence of a large HONO formation in presence of snow.
- These findings may significantly affect the photochemistry in urban winter atmosphere.

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Nitrous acid measurements were carried out during the MEGAPOLI (Megacities: Emissions, urban, regional and Global Atmospheric POLLution and climate effects, and Integrated tools for assessment and mitigation) winter field campaign at the SIRTa observatory in Paris surroundings from the 20th of January to the 15th of February 2010. At the end of the campaign, significant snow events occurred leading to snow accumulation at the sampling site during the last days. These specific conditions gave the opportunity to examine the HONO budget with and without the presence of snow at ground. Much higher HONO sources were found for the days when the site was covered by snow. This provides evidence for the existence of a large snowpack source of HONO in mid-latitude polluted regions that needs to be investigated for a better understanding of wintertime photochemistry.

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1. Introduction

The hydroxyl (OH) radical is the main oxidant of the troposphere under sunlight conditions. Nowadays, numerous studies recognize HONO photolysis as a major daytime source of OH (Stone et al., 2012 as a review; Michoud et al., 2012 for the same measurement site). The contribution of HONO photolysis to the radical budget is even larger during winter (Aumont et al., 2003). Despite its obvious importance for tropospheric chemistry, there are still uncertainties

concerning HONO formation processes.

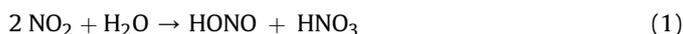
In Polar Regions, following the pioneering experiments conducted by Zhou et al. (2001) numerous studies found unexpectedly high HONO levels (see Villena et al. (2011) and references therein). Though certain measurements of low levels encountered in these regions may have suffered from interferences (Kleffmann et al., 2006), HONO production from the snow surface is suspected (see Grannas et al. (2007) as a review). Flux studies conducted over the snowpack have shown that HONO is sometimes released into the overlying atmospheric boundary layer (Zhou et al., 2001; Honrath et al., 2002) but sometimes not (Beine et al., 2005, 2006). The hypothesis of a photochemical snow source of HONO is also supported by investigations of HONO mixing ratios present in snowpack interstitial air and its change during shading experiments (Dibb

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et al., 2002). Finally, laboratory experiments conducted by irradiating natural (Beine et al., 2008; Legrand et al., 2014) or artificial (Bartels-Rausch et al., 2010) snow layers tend to support the importance of snow as a source of HONO. While it is well established that the photolysis of nitrate present in snow is the major source of released NO_x (via its major channel: $\text{NO}_3^- + h\nu \rightarrow \text{NO}_2 + \text{O}^-$), for HONO it is still unclear if either the nitrate photolysis directly produces HONO from hydrolysis of NO_2 produced by its second channel ($\text{NO}_3^- + h\nu \rightarrow \text{NO}_2^- + \text{O}$) or if HONO is formed as a secondary product from NO_2 (Villena et al., 2011). Among possible secondary production pathways it is generally accepted that the reduction of NO_2 on photo-sensitized organic material like humic acid (Bartels-Rausch et al., 2010 and references therein) would proceed more efficiently than the disproportionation reaction of NO_2 :



Until now, very little work has been performed to evaluate the impact of an urban snowpack on atmospheric chemistry of the overlying boundary layer. So far, this feedback has mainly been considered as affecting the energy balance and hence air mass dynamics over cities (Lemonsu et al., 2010). More recently, the study of ozone production in oil and gas extraction regions of Western US received increasing attention. An apparent paradox has been detected as the highest ozone events were observed in winter when snow was covering the ground while neither an increase of the albedo in a box model nor a doubling of the HCHO and HONO snowpack emissions could fully reproduce the measurements (Edwards et al., 2013).

At places where the snowpack is permanent, the quantification of the snow contribution to HONO budget is limited to flux studies. At places with intermittent snow layers a direct analysis of the atmospheric HONO variability would permit examination of the significance of emissions from the snowpack. Such an approach is followed in this paper by using the HONO record obtained during the MEGAPOLI winter campaign in the Paris area (Michoud et al., 2014), when ground was covered by snow during several days at the end of the campaign.

2. Experimental

Ambient measurements were conducted at the SIRTa observatory (48.718°N, 2.207°E), located 14 km south west of Paris (France) in a semi-urban environment (Haefelin et al., 2005), during the MEGAPOLI winter campaign. This campaign took place from 15th of January to the 15th of February 2010. Nitrous acid (HONO) was measured by deploying a device (NitroMAC) based on wet chemical derivatization and HPLC detection as described in Michoud et al. (2014). During the winter campaign, ancillary measurements were performed including NO , NO_2 , O_3 , photolysis frequencies ($J(\text{NO}_2)$ and $J(\text{HONO})$) and relative humidity (RH), temperature, pressure, wind speed and direction as well as boundary layer height and albedo. A full description of the campaign can be found in Michoud et al. (2014). At the end of the campaign, significant snow events occurred, on the 10th and 11th of February leading to the accumulation of snow at the sampling site followed by a slow decrease of the snowpack until total disappearance on the 15th of February.

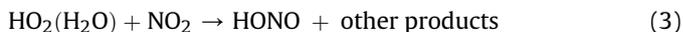
3. Results and discussion

HONO measurements were conducted from the 20th of January to the 15th of February 2010. During the whole measurement period HONO concentrations were highly variable ranging from

few pptv to a maximum of 4 ppbv on the 13th of February (mean 24 h averaged mixing ratio of 600 pptv, see supplementary material S1).

A discussion of observed HONO levels, in particular a comparison of the observations with HONO levels calculated by Photo-Stationary State (PSS) approximation have been conducted for the first period of this campaign (i.e. between the 20th of January and the 6th of February) in Michoud et al. (2014). This was done by considering homogeneous formation of HONO (reaction $\text{OH} + \text{NO}$) using simulated OH levels regarding the lack of such measurements during the campaign, heterogeneous conversion of NO_2 into HONO and direct emission of HONO (so called PSS₂ in Michoud et al., 2014). It was found that observed levels generally exceeded the calculated ones suggesting a missing source. An additional photo-lytic process has been proposed to explain these discrepancies. However, it is worth noting that the PSS approach can be problematic for species such as HONO with lifetime during the day of tens of minutes (typically 10–20 min). This is even truer in environments close to emission sources (Lee et al., 2013). Nevertheless, this approach is commonly used (Kleffmann, 2007 and references therein) and allows studying the HONO budget while keeping in mind its limits.

In this study, we extend the analysis conducted for the first part of the campaign to the second part where snow covered the measurement site (i.e. from February 10 to February 14, see the measured surface albedo in supplementary material S2). In comparison to the analysis we performed in Michoud et al., 2014, we also consider another gas-phase source of HONO as recently proposed by Li et al. (2014) via reaction of $\text{HO}_2(\text{H}_2\text{O})$ complex with NO_2 :



Calculated HONO concentrations sometimes underestimate measured HONO concentrations (top panel of Fig. 1). This underestimation indicates that the sources included in the calculations are insufficient to explain encountered HONO levels. It is thus possible to calculate a missing source needed to reconcile measurements and calculations (Michoud et al., 2014). Including the new source from Li et al., 2014 has led to a better agreement between calculation and measurement for some days, but led also to an overestimation of the measured HONO concentration for some other days (especially the 2nd and 3rd of February) which is not likely since the major sinks are included in the calculation and only sources should be missing. Thus, further studies should be done to confirm or disconfirm this new source. That HONO source was finally excluded in the quantitative analyses performed hereafter.

The calculated missing source for the whole campaign is shown in Fig. 1 (bottom panel). Underestimation of the calculation clearly increased when snow was present on the ground leading to a rise of the missing HONO source. Indeed, before snow period, the maxima of the missing HONO source ranged between 0.04 and 1.25 ppbv h^{-1} , while during this period, the maxima ranged between 1.1 and 4.5 ppbv h^{-1} . This suggests that an additional specific process might be involved in the additional formation of HONO during this period. The fact that the increase of the missing HONO source coincides with the presence of snow at the measurement site suggests a HONO formation process occurring on snow grain surface. Compared to the snow-free and warmer first period, no significant changes in physical and chemical parameters (Relative Humidity, NO_x concentrations, photolysis frequencies, boundary layer height) have been found during the second snow and colder period. This strengthens the assumption that the increase of the

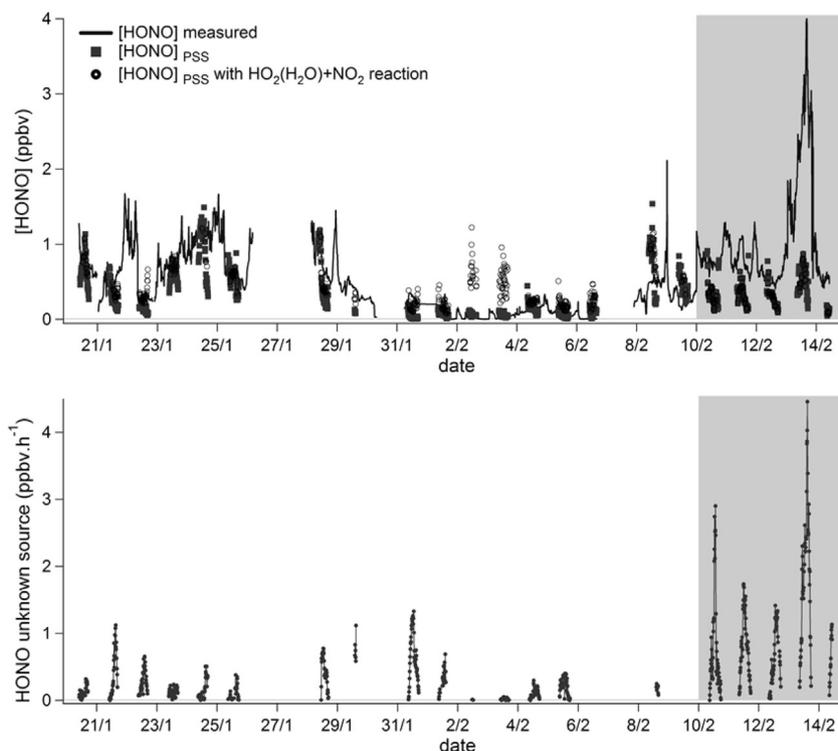


Fig. 1. Time series of HONO mixing ratios measured (solid line) and calculated with (open circles) or without (grey squares) the source proposed by Li et al. (2014) during the MEGAPOLI winter campaign (Top panel); and time series of the calculated unknown HONO source (without taking into account the source proposed by Li et al. (2014)) during the MEGAPOLI winter campaign (bottom panel). The grey shaded part of the graphs corresponds to the days when measurement sites were covered by snow.

HONO formation during the last snow period of the campaign is due to processes at the snow surface.

The correlation between the additional HONO source and the photolysis frequencies of NO_2 ($J(\text{NO}_2)$) is shown in Fig. 2. Other correlations have been made and are shown in supplementary material (Fig. S3 and Fig. S4). These correlations do not lead to clear relationship. Slopes for individual days between the missing HONO source and $J(\text{NO}_2)$ were clearly enhanced for most of the days when snow was present (see supplementary material S5). This means for a given $J(\text{NO}_2)$ much more HONO was produced for snowy days. This is particularly true for February 13 with a slope approximately four to ten times higher than for other days. This highlights a

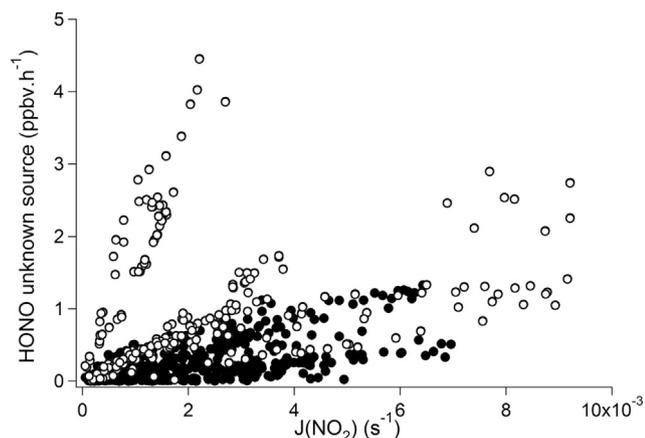


Fig. 2. Correlations between the calculated unknown HONO source (without taking into account the source proposed by Li et al. (2014)) and measured $J(\text{NO}_2)$. Open white circles correspond to days when snow was present at the site and solid black circles correspond to other days.

probable change in the processes involved in HONO formation between both periods. It is unclear why such differences are observed for February 13 compared to other days of the snow period. One can hypothesize that it might be due to an accumulation of HONO precursors within the snow layer during several days or to inherent physical properties of the snow.

During this campaign, no snow sampling had been performed and characterization of the snow layer was not possible. It is therefore difficult to elucidate the processes involved in the HONO formation during the snow period.

The fact that two contrasted situations were encountered during the campaign: one without snow and one with snow covering the ground, allowed us to highlight a potentially important role of the snowpack on air quality in urban/suburban environments. Indeed, if the impact of snowpack on the oxidizing capacity of the atmosphere in polar regions has received a considerable attention (Zhou et al., 2001; Amoroso et al., 2006), it is, to our best knowledge, the first time that such an effect is demonstrated in polluted area. In the absence of specific snow characterization, it can be assumed that snow in polluted area may contain high level of species expected to promote HONO formation such as nitrate ions, humic acids, photosensitizers or organic nitrate. A large HONO formation from snow surface combined with increased HONO photolysis frequencies due to enhanced albedo may significantly affect the OH budget in the urban winter atmosphere. As it has been demonstrated that HONO photolysis was the largest OH initiation source in winter in a large urban area as Paris (Michoud et al., 2014), this would lead to an increase in ozone production. Also secondary organic aerosol would be increased by the combined effect of enhanced OH and lower temperature.

Obviously, further studies on the processes involved in the HONO production by urban snowpack are required. They should combine HONO flux with snow composition/micro-physics

monitoring both in the field and in laboratory experiments. On a more general level, considering the intensity of the snow related source we have observed, it is clear that the effect of urban polluted snow on photo-oxidant level in the atmosphere deserves more interest.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2015.06.040>.

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