Interactive comment on

# “Emission of nitrous acid from soil and biological soil crusts represents a dominant source of HONO in the remote atmosphere in Cyprus”

by Hannah Meusel et al.

## Anonymous Referee #3

**Summary:**

*Soil samples used in this work are from soils collected from the field, manipulated in a controlled lab environment, and then measured fluxes extrapolated to compare with the missing HONO source calculated for the CYPHEX field campaign in the same location. Soils were collected and categorized from a gridded sampling scheme. HONO and NO fluxes were measured from the soils in replicates in order to quantify which surface soil community members, if any, were responsible for the majority of the HONO fluxes observed. The authors performed nice controlled experiments in the lab and found some interesting conclusions, counter to previous findings in similar soils by this group. The manuscript may be acceptable for publication in Atmospheric Chemistry and Physics, subject to a number of concerns being addressed.*

**Comment:**

*There is no experimental control of soils devoid of microbial activity for each soil type. One would think it necessary to fumigate (or otherwise kill) soil samples of each type to control for biotic versus abiotic HONO and NO emissions, yet this is not presented. If possible, the authors should consider acquiring this data and adding it to the manuscript for comparison and correction of the dataset.*

**Response:**

The main purpose of this study is to investigate if Cyprus soil and representative biocrust covers are indeed an important source for HONO, as was assumed from atmospheric observations in an earlier paper by Meusel et al. (2016). The role of biological activities versus physical emission was not focus of the present study, but was proven in earlier studies. As shown by Oswald et al. (2013), natural soils emit much more HONO and NO than sterilized samples, and also Weber et al. (2015) found strongly decreased emission upon sterilization, pointing to a biological emission process.

We add the following note into the introduction of the manuscript: “It was found that sterilized soil emit lower amounts of reactive nitrogen than natural soil (Oswald et al., 2013; Weber et al., 2015).”

**Comment:**

*The consideration of the effects of the measured soil pH on HONO release using the method of the Su et al. (2011) work is not considered in the interpretation of the data. What proportion of the emissions measured in each case can be ascribed to simple partitioning? What effect does this have on comparisons between soil types considered in this work when abiotic exchange is estimated versus measured (see comment above) in the experimentally measured fluxes? A major concern is that if abiotic partitioning from dead soils is not favored by calculation from bulk pH measurements and nutrient loadings (i.e. soil pH » pKa HONO) then another emission mechanism is active and should be considered/discussed.*

**Response:**

Following the suggestion by the referee, [HONO]* was calculated according to Su et al. (2011) for 2 different $NO_2^-$ contents in the given range of observed $NO_2^-$ content and their observed mean pH-value. In this calculation the absolute amount of nitrite was assumed to be constant, i.e., with lower soil water content the liquid phase nitrite concentration increases (please note that we did not find significant differences between nitrite concentrations before and after the chamber trace gas exchange experiments).

As expected, the calculated equilibrium concentration [HONO]* shows a positive dependence on nitrite concentration (compare dashed lines in Fig. R3) and pH (compare dashed red and orange lines in Fig. R3). At the optimum soil water content of 10-20 % (mass $H_2O$/mass soil) or 25-35% whc, respectively, the calculated [HONO]* (at pH = 7) is only about 5-10% of the one observed by chamber measurements. For slightly lower pH the calculated [HONO]* increase, and contribute about 17% to the measured.

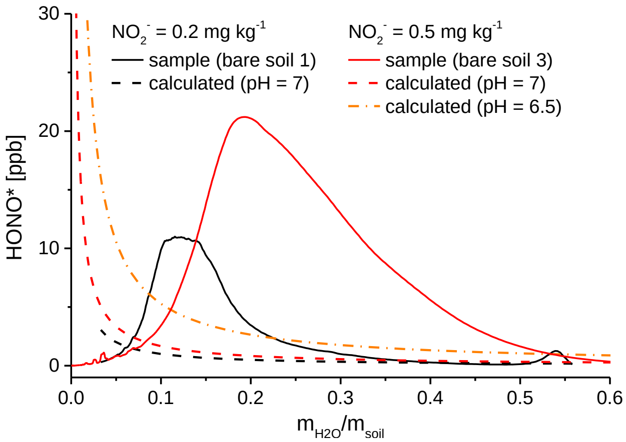


Fig. R4 (S3): Calculated [HONO]* for two different $NO_2^-$ concentrations at pH 7 and pH 6.5 (dashed lines) in comparison with measured [HONO]* for two samples with similar $NO_2^-$ content (solid lines) vs the gravimetric soil water content.

Indeed, as stated in Su et al. (2011) the calculated [HONO]* based on nitrite partitioning may deviate from the measured values due to the non-ideal solution behavior (adsorption, Kelvin and solute interaction effects on gas/liquid partitioning). Thus the agreement between simple models (based on ideal solution assumption) and measurements cannot be used to discriminate the physical and biological processes. We also want to clarify that the soil emission proposed by Su et al. (2011) is not an abiotic processes. Their conclusion is that biogenic nitrite in soil can be emitted to the atmosphere, of which the transport or partitioning is also subject to other physio-chemical processes like other nitrogen containing gases (e.g., NO, see fig. R4).

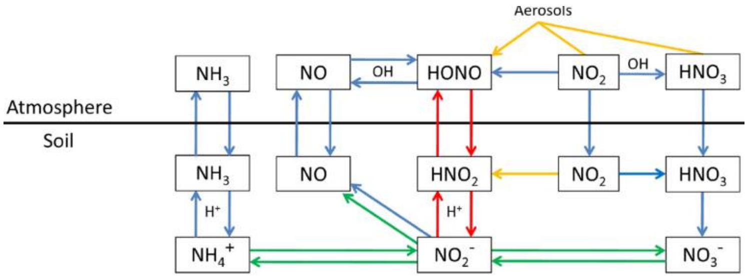


Fig. R5 (Fig 1 of Su et al., 2011): Coupling of atmospheric HONO with soil nitrite. Red arrows represent the multiphase processes linking gaseous HONO and soil nitrite (acid-base reaction and phase partitioning), green arrows represent biological processes, orange arrows represent heterogeneous chemical reactions converting $NO_2$ and $HNO_3$ into HONO, and blue arrows represent other related physicochemical processes in the N cycle.

This consideration is now also added to the revised version of the manuscript (end of chapter 3.3):
"Since most of the samples were slightly alkaline and only moss samples were slightly acidic, no effect of pH could be observed. But in general it is expected that with higher nutrient and lower pH values HONO emission is increased by simple partitioning processes (Su et al., 2011). The simulated equilibrium concentration at soil surface [HONO]* (equation see Su et al., 2011) is much lower than the measured one (see supplement Fig. S3). This deviation is probably based on the non-ideal behavior of the soil samples (adsorption, Kelvin and solute interaction effects on gas/liquid partitioning). But this method does not allow differentiation between physical or biological nitrite production processes."

**Comment:**
*Scaling to atmospheric relevance for the field campaign is very interesting, but inappropriate to include in the title of the manuscript. The linkage between microbial activity and HONO and NO emissions is of growing importance to constrain and these lab-based measurements help to do so. However, the uncertainty in the*

*extrapolation of the data to the field campaign observations of the missing daytime HONO source covers an order of magnitude range, which means at the low end of the estimate these processes account for < 10 % of the daytime HONO source. The authors do not discuss this limitation and should do so. The title of the manuscript should also remove the HONO budget closure implications due to this significant uncertainty. An important consideration here is one that has been reported and discussed much in the atmospheric community over the past 5 years and that is the vertical structure of HONO, and by proxy, the daytime HONO source strength near the ground surface. Using soil HONO emissions to scale to measurements made nearly 6 m above the ground may add additional error in the budget closure calculation as the perceived missing source changes with height. This topic and the relevant references would be a worthwhile addition to this component of the discussion as there are several reports on vertical structure of HONO in arid agricultural and rural regions in the US.*

**Response:**

The title doesn´t really imply a HONO budget closure, it only indicates that soil emission can be a dominant source. Nevertheless, following the reviewer's suggestion, we now tuned the title reading "… represents an important source…".

Indeed, the range of HONO production given in the original manuscript had a high uncertainty, spanning an order of magnitude (based on the lowermost and uppermost fluxes observed in the lab). According to the suggestion of referee #1, we now give a more detailed best estimate, including more site-specific input variables (diel trend of temperature and soil water content). This confines the estimated source strength to $6x10^4$-$1.1x10^6$ $cm^{-3}$ $s^{-1}$.

Anyhow, in agreement to the referee’s objection we now better emphasize the uncertainty of the newly calculated HONO emissions in the discussion section of the revised version of the manuscript, like “… the emissions at 25°C and a swc of 10% whc would span a wide range between $1.1x10^5$ and $9.6x10^5$ $cm^{-3}$ $s^{-1}$, covering 9 to 73% of the missing mean source of $1.3x10^6$ $cm^{-3}$ $s^{-1}$ observed in the field (Meusel et al., 2016)…” (see also the response of referee #1).

It is true that there is a gradient in HONO concentration in the atmosphere with higher concentration near the ground. Our estimate does not include a respective chemistry-transport model (accounting for vertical gradients of atmospheric sinks and sources), nor accounts for the existence of a vertical profile of concentrations. The ground-based source was calculated for a boundary layer height of 300 m above ground level, found typical for Cyprus during the campaign 2014 (for details please see Meusel et al., 2016). The method is according to, e.g., Stemmler et al. (2006), who used homogeneous mixed air columns between 150 and 430 m for their calculations of a surface-based HONO source. A recent study calculated the height over a rural basin in Utah, USA, at which the influence of HONO surface fluxes on the total HONO column becomes negligible. At a height of 273 m the impact of the surface flux to the HONO budget was less than 1 ppt (Tsai et al., 2017).

We now discuss it in the manuscript:

“Field observations (VandenBoer et al., 2013; Zhang et al., 2009; Tsai et al. 2017) as well as model results (Wong et al., 2013) showed that HONO concentrations typically decrease exponentially from the surface upwards. Eq. 7 does not include a chemistry-transport model, nor accounts for the existence of a vertical profile of concentrations, which may bias the calculation on HONO source strength. But the method for predicting the ground source using homogeneous mixed air columns is consistent with other recent studies (Stemmler et al., 2006; Tsai et al., 2017). Tsai et al. (2017) clearly showed the presence of an important ground source of daytime HONO at a rural basin in Utah, during wintertime (no snow, low temperatures). They inferred that ground surface fluxes may account for 63±32% of the unidentified HONO daytime source throughout the day. HONO fluxes of up to 7.4 ng $m^{-2}$ $s^{-1}$ (Fig. 8, lower panel) determined in this study are comparable to HONO fluxes found in other regions, e.g., 2.7 ng $m^{-2}$ $s^{-1}$ reported for the northern Michigan forest canopy (Zhang et al., 2009; Zhou et al., 2011), the average daytime HONO flux of 7.0 ng $m^{-2}$ $s^{-1}$ measured over an agricultural field in Bakersfield (Ren et al., 2011), and the average HONO flux of about 11.6 ng $m^{-2}$ $s^{-1}$) measured by Tsai et al. (2017). In contrast to the present study, the latter concluded that, under the prevailing high NOx conditions, the respective HONO formation was related to solar radiation and $NO_2$ mixing ratios, such as photo-enhanced conversion of $NO_2$ or nitrate photolysis on the ground. This can be ruled out in this study, as pure air (no $NO_2$) was used to purge the chambers and no light was applied. “

**Comment:**

*The quality of the nutrient data cannot be determined as no accuracy, precision, or detection limit values are presented. The data table in the supplement reports measurements of zero, which should be represented by '< LOD' and the detection limits determined by the experimental runs calculated (do not use the instrument manufacturer's stated values). My concern is that some of the measurements made on the samples are near the detection limits and therefore highly uncertain, which may confound the comparisons made throughout the manuscript. The authors should also be more cautious in their reported values from these measurements. Are these analytically certain to so many significant digits?*

**Response:**

Agreed, the reported data in the supplement table on nutrient levels close to 0 are now changed to "<LOD". The detection limits were checked again and were 0.012, 0.051, and 0.015 mg $L^{-1}$ for $NO_2^-$, $NO_3^-$ and $NH_4^+$, respectively. Transforming the unit to mg $kg^{-1}$ results in detection limits of 0.014, 0.046 and 0.047 mg $kg^{-1}$ for $NO_2^-$ -N, $NO_3^-$ - N, and $NH_4^+$ - N. Most of the nutrient levels are well above these levels, no concerns from your side.

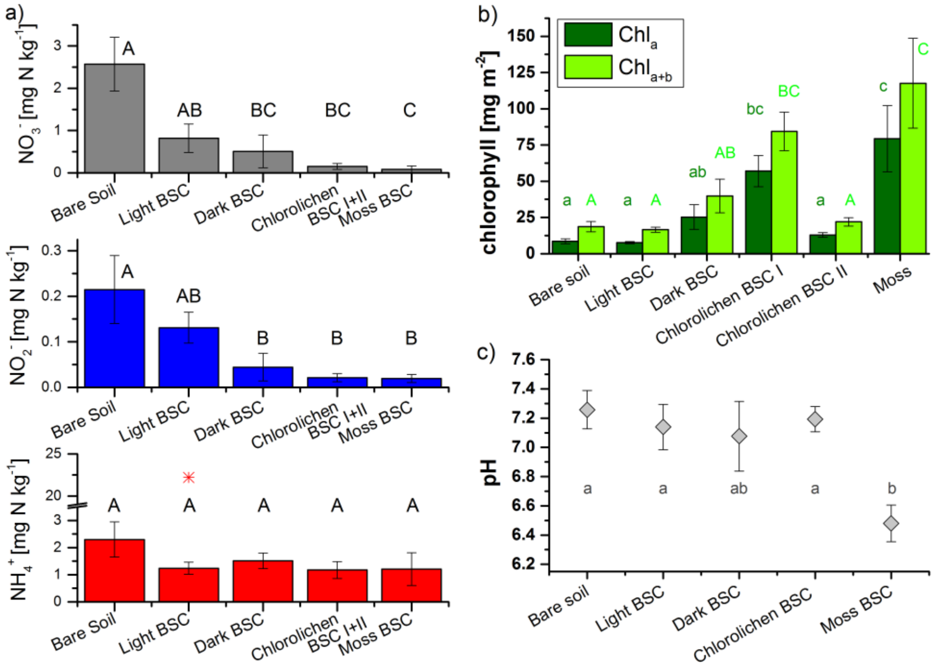
The detection limits are now added into the revised version of the manuscript: "The detection limits were 0.014, 0.046 and 0.047 mg kg-1 for $NO_2^-$-N, $NO_3^-$-N and $NH_4^+$-N."

**Comment:**

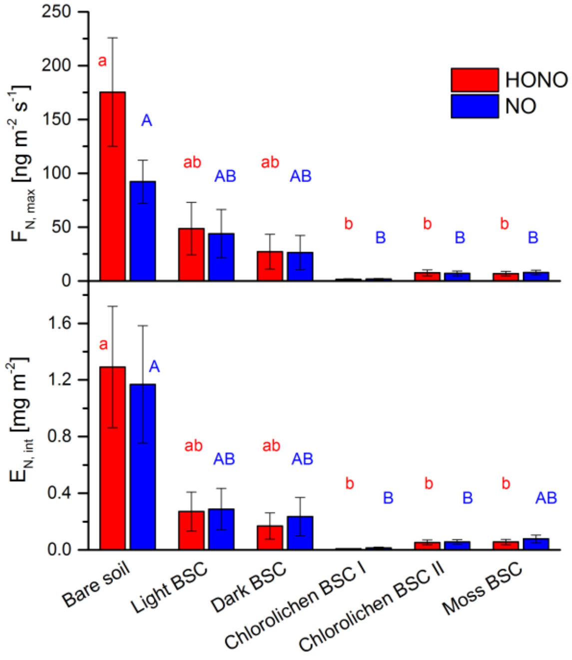
*The experiments performed on nutrient content before and after experiments (Figure 4) is good to have performed, but this data does not need to be presented in the figure and would help make this a cleaner plot. The data can be replaced with one sentence in the manuscript stating that the nutrient levels were not different in the soils by performing the flux experiments. To that end, this suggests that the full set of measurements of these nutrients could be pooled and improve the statistical analyses performed, as it would reduce the standard error in the measurements. Further to this point, where replicate measurements have been made, the authors should be presenting the standard error of the mean and not the standard deviation as it aids in connecting the reader to the statistical results. The results and discussion surrounding the purpose, method selection, and outcomes of these statistical tests needs to be improved either through clarity in existing sections or expansion of the text.*

**Response:**

Thanks for pointing out. The figures are modified accordingly. Figure 4a now shows the mean value of nutrient content of all samples and are not separated into samples without and after flux measurements. Error bars (in Fig 4a, b, c; 6) now indicate the standard error of the mean and not the standard deviation. Also in the text the standard deviation was changed to the standard error.



*New Fig 4 (revised manuscript, fig.3)*: a: nutrient content *for all samples*, star indicate outlier in $NH_4^+$ content (for light BSC), for a-c error bar indicate *standard error of the mean*, letters indicate significant difference (p=0.05, of log data).



*New Fig 6 (revised manuscript, fig. 5): …error bars indicate standard error of the mean…*

**Comment:**

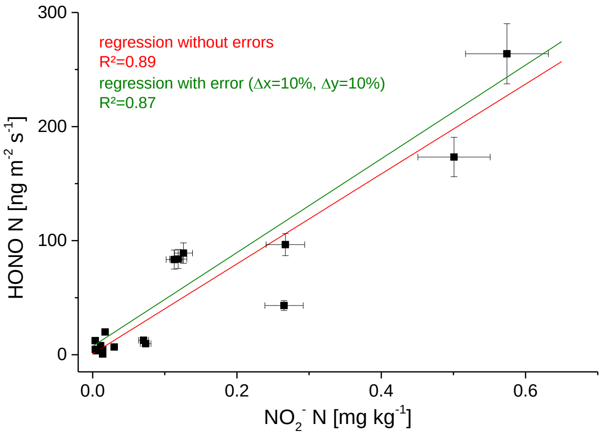
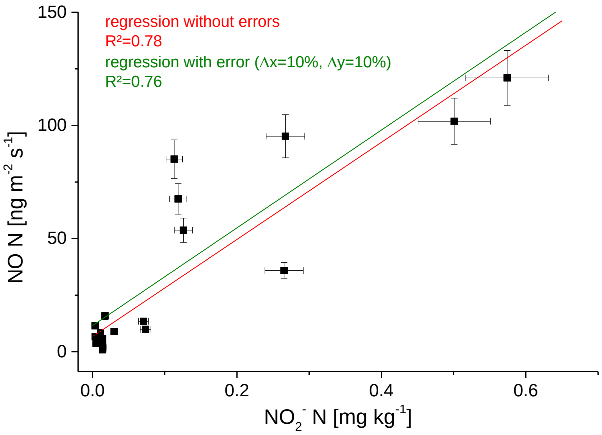
*Details on linear regression in Figure 7 needs to be presented. There is presumably large uncertainty in both measurements being compared and the appropriate considerations must be included prior to assessing the relationship between them, along with the associated uncertainty in the result. Building on this, the direction of* *the trend and also its associated uncertainty from the regression fit may be more telling towards whether the strength of the coefficient is truly robust or being limited by the sample size available.*

**Response:**

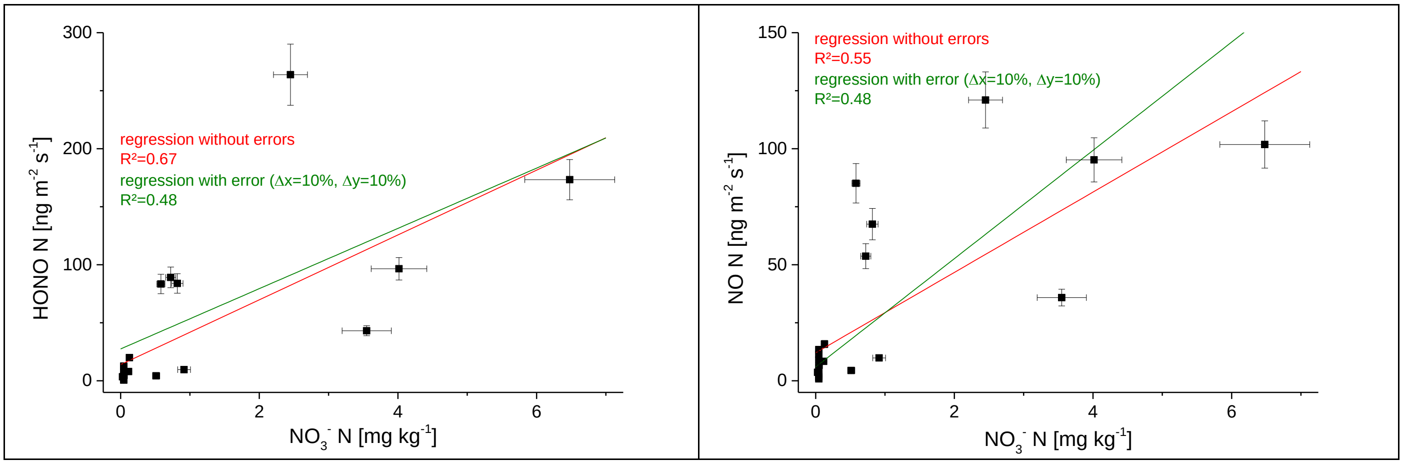
Regressions considering x-, and y- errors were performed as suggested by the referee. These were done by using the excel sheet for bivariate regressions provided by Cantrell, 2008. The errors were related to the uncertainties of the measurements (10%). In this method smaller values have smaller errors and therefore are weighted more. For nutrient levels < detection limit the value was set to the detection limit.

The coefficient of determination (R2) decreased slightly when errors are considered. But the correlation is still significant (see table below; error bars in the figures indicate the 10% uncertainty).

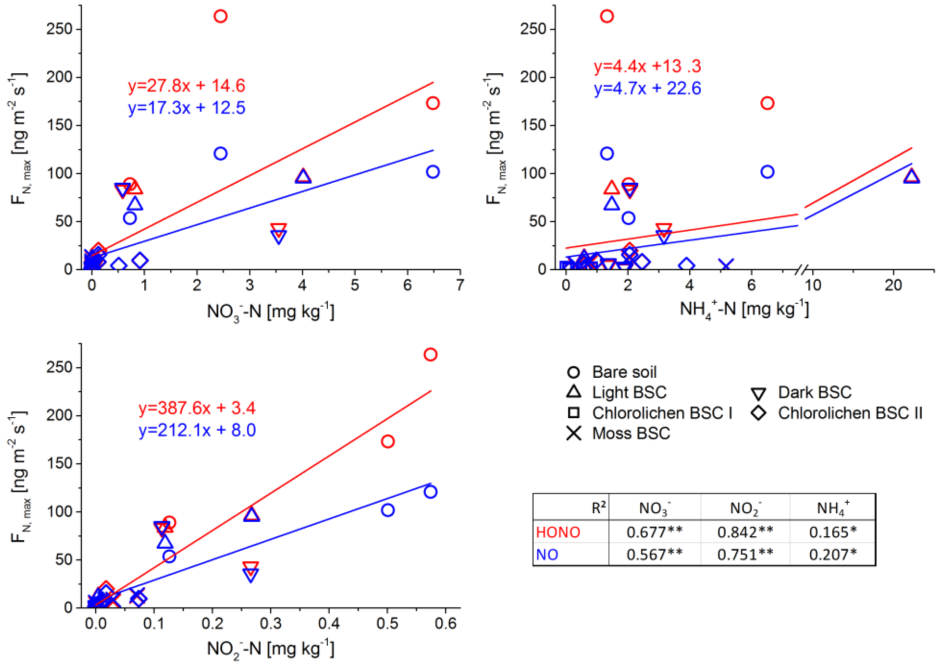
Table 1: Results of regressions performed by excel (Cantrell, 2008):

| **Nitrite – HONO**<br>(< LOD = LOD) | **Nitrite-NO**<br>(< LOD = LOD) |
|---|---|
| a) Errors (x , y) 10% of measured value<br>Regression: y = 410.9*x+7.4 ($R^2$ = 0.867)<br>standard error m = 0.078, b = 6.52<br>b) Without errors<br>Regression: y=394.14*x+0.804 ($R^2$=0.885)<br>standard error m =30.4, b=5.5<br><br> | a) Errors (x , y) 10% of measured value<br>Regression: y = 216.1*x+11.5 ($R^2$ = 0.76)<br>standard error m = 0.017, b = 5.04<br>b) Without errors<br>Regression: y=213.88.14*x+6.94 ($R^2$=0.776)<br>standard error m =24.5, b=4.4<br><br> |

| **Nitrate – HONO**<br>(< LOD = LOD) | **Nitrate-NO**<br>(< LOD = LOD) |
|---|---|
| a) Errors (x , y) 10% of measured value<br>Regression: y = 25.97*x+27.46($R^2$ = 0.484)<br>standard error m = 0.060, b = 11.3<br>b) Without errors<br>Regression: y=22.68*x+10.74 ($R^2$=0.674)<br>standard error m =3.46, b=6.19 | a) Errors (x , y) 10% of measured value<br>Regression: y = 23.33*x+5.96 ($R^2$ = 0.475)<br>standard error m = 0.074, b = 9.16<br>b) Without errors<br>Regression: y=17.19*x+12.55 ($R^2$=0.547)<br>standard error m =3.31, b=6.02 |



As the modified regressions are very similar to the original ones, we decided to keep the simple regressions, but added the regression details (lines and formula) into the plots of the revised manuscript.



| R² | NO$_3^-$ | NO$_2^-$ | NH$_4^+$ |
|---|---|---|---|
| HONO | 0.677** | 0.842** | 0.165* |
| NO | 0.567** | 0.751** | 0.207* |

(new Fig. 7, in the revised manuscript fig. 6)

**Comment:**
*Figure 2 needs to be streamlined to present the relevant information for the contents of the manuscript. The level of detail here is not necessary.*

**Response:**
Figure 2 was moved to the supplement and a diel pattern of soil or surface climate is shown now in Fig 8.

**Minor Comments:**
*Fix tense and plurality issues throughout the manuscript.*
*Many sentences have issues with comma splicing, making them long and the purpose of the sentence difficult to follow.*

**Response:**

We read through the manuscript again and carefully checked the tense and rewrote several sentences.

## Reference

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