Answer to referee comments

We would like to thank the referees for their extensive comments, which helped significantly to improve the manuscript in content and readability.

Anonymous Referee #1 This is a well-written paper with two main parts, (i) computational characterization of HNCO reactions with OH (a refinement which confirms what is known already that that this is very slow) and new data for Cl, NO3 and O3, and (ii) modeling of predicted surface concentrations of HNCO based on the results combined with literature information. My focus will be on the first part. The dominant source of HNCO is biomass burning, and it has a long lifetime in the atmosphere, so this is a relevant topic for Atm. Chem. Phys. Fairly standard and usually reliable computational chemistry techniques are applied to characterize reactants, intermediates, products and barriers for a variety of HNCO reaction pathways. The methodology is described in sufficient detail, along with information such as molecular geometries, to allow others to reproduce the results. I see no errors in the work and the conclusions are sound. The ms. is suitable for publication once some areas are addressed.

1. Page 3, lines 7-13. In this brief discussion of photochemistry, given the various known bond strengths in HNCO, what are the threshold wavelengths at which photodissociation could occur?

The threshold for HNCO dissociation limit starts at wavelengths below 240 nm forming either H+NCO or NH + CO; this is now mentioned and referenced in the text. We also refer to a study at lower energies, but the lifetime would be too long to make it relevant, so we conclude that photolysis is not important. We did not calculate the bond dissociation energies to compare against the experimental thresholds, as these would be calculated for the ground state whereas the photolysis occurs predominantly through the first singlet exited states. Calculating the vertical excitation energies to excited states is well beyond the scope of the present paper, and would require different theoretical methodologies.

2. The uncertainty in barrier heights of 0.5 kcal/mol is quite small. How was this estimated? What are the magnitudes of the room temperature tunneling factors? I would expect large factors to be less reliable.

That should read “at least 0.5 kcal/mol”, we apologize for the confusion. Benchmark studies tend to examine overall uncertainty and thus include many different reaction classes with a wide variety of reactants/molecules, and the uncertainty estimate is thus influenced unduly by reaction classes well beyond the more standard H-abstraction or addition in organic atmospheric chemistry as studied here. Still, CCSD(T)/CBS has been referred to as the “golden standard” because it typically provides chemical accuracy or better. Nowadays, (composite) post-CCSD(T) methods can be used to obtain sub-chemical accuracy with only a few tenths of kcal/mol of uncertainty.
The total factor of 4 on the rate coefficient is estimated from our experience where we typically observe a difference smaller than that when compared against experiment, in many different reaction classes.

3. Page 6. The agreement on Fig. 2, at elevated temperatures of the order of 1000 K, is somewhat fortuitous because the slopes of computed and observed rate constants are different, but the agreement is noted favorably. Therefore factors like hindered internal rotations in the TS do need to be taken into account, even if they are not very important under atmospheric conditions.
5. In the discussion of Cl + HNCO on p. 7 the dominant path is addition. I imagine the calculations are for the high-pressure limit, but is this reached everywhere over 200-450 K? The pressure dependence should be investigated via RRKM theory, especially as data are provided at up to 450 K where falloff is more likely than at room temperature
7. On page 8 there is no mention of the complications of describing the vibronic structure of NO3 accurately with the kinds of computational approaches used here. As studied, for example, by Okumura and Stanton, Jahn-Teller effects break symmetry and change the vibrational energy levels significantly, so that standard evaluation of partition functions may be significantly in error.

While we feel that our calculations are of a high quality, we acknowledge that there are some aspects that could be improved, if one were interested in doing benchmark-level calculations. For the current purposes, i.e. documenting their (lack of) impact on atmospheric chemistry, there is a strongly diminished return in implementing these computationally expensive improvements, for changes that are likely less than a factor of 2, irrelevant compared to the orders of magnitude in rate separating gas phase loss processes from the dominant atmospheric sinks. As such, we choose not to dedicate the necessary resources. We have included an additional paragraph in the methodology section explicitly discussing these refinements of the predictions. We have also included a line in figure 2 (rate coefficient of HNCO+OH) indicating the rate coefficient that would be needed to make the OH reaction significant on a global scale, to further visualize that the conclusions are robust against minor uncertainties in the predictions.

4. Page 6 line 30 and the following line. Here and elsewhere the lifetime is described as "several decades" or 50 years. But 10ˆ10 s is about 300years.

The given lifetime inadvertently lost its pre-exponential significand, increasing the printed lifetime by almost an order of magnitude; the original number is correct and mean lifetime is about 40-50 years. We still changed the wording to "decades to centuries" here and elsewhere when discussing the local gas phase chemical losses. The impact section also has a newly added discussion of the airparcel-specific lifetime of HNCO, where depending on the location in the atmosphere we find lifetimes from 6 years to >500 years.

6. On Line 1 of page 8 redissociation of HNC(Cl)O is stated to be its most likely fate, but given the rate quoted is the addition of molecular oxygen potentially competitive, especially below room temperature?

To our knowledge, there is no data for O2 addition to this type of N-centered, delocalized multifunctionalized radicals. For vinoxy radicals, typical first-order rate coefficients in the atmosphere are of the order of 6E6 s-1 (k(298K) ~ 1E-12 cm3 molecule-1 s-1) but for small species as here redissociation of the RO_2 adduct back to R + O_2 is likely an important path. Hence, even at 200K redissociation of HNC(Cl)O to HNCO + Cl is expected to remain the main route. We have added a sentence to this effect in the paper, with reference. Even if later data indicates that we have severely underestimated the O2 addition rate, the HNCO+Cl reaction will remain a negligible atmospheric sink.

Minor typographical errors:
Page 3 line 3 "...data are available..."
Page 6 line 26."an" should be "a" and there is a double comma
Page 10 line 2 insert a space in"whereasthe"

We corrected the typographical errors accordingly

Anonymous Referee #2: General comments: The authors describe computational chemistry calculations of HNCO with major atmospheric oxidants, including OH, NO3, Cl, and O3, using reliable methods, specifically CCSD(T)/CBS(DTQ)//M06-2X/aug-cc-pVTZ. The authors' conclusion corroborates with previously known conclusions, that the gas phase chemistry is not important for HNCO's lifetime. Then, the authors use the ECHAM/MESSy Atmospheric Chemistry (EMAC) model to evaluate global concentrations of HNCO from update biomass burning inventories. The modelling effort is particularly useful for understanding which populations may be at risk of exposure. I commend the authors on this work, and on updating the model with the latest sources of HNCO and rate constants. This modelling effort is valuable to the community and appropriate to Atmos. Chem. Phys.
The work is done with reliable methods, and the conclusions, although not novel, are robust. I appreciate the authors' systematic approach of considering all possible sites of reactions even if highly improbable (for example, page 7, lines 9-10). A criticism I have is a lack of depth in the interpretation of the results (I've highlighted some specific examples below).

There is also a lack of synergy between the computational data and the model; these 2 studies seem to be separated and the authors can improve their manuscript by clarifying the importance of reporting these two methods together. Was any data used in the model coming from the computational chemistry relative energies?

We apologize for this aspect not being clear. We have modified the initial part of the abstract, the last paragraph of section 1 (introduction) and the beginning of section 4 (global impact), to better clarify the synergy.

My second criticism is the revisiting of the gas phase reactions of an electrophile (HNCO) with other electrophilic oxidants. The tone of the manuscript suggests that the authors were surprised by this finding (for example the text on page 7 lines 1-4), when in reality is makes sense (and was known) that these oxidants would not be important for the fate of HNCO. I'm curious to know which hypothesis the authors were testing with their gas phase mechanism computational chemistry study and why they sought to do these calculations (other than it hadn't been done before).

We ourselves do not sense that tone of surprise in our text. Even before the first calculation was done, we expected to find reaction rates that would confirm negligible contributions. We also do not try to make them appear more important than they are, as is all too often done with negative results, but clearly state where necessary that the reactions can't contribute. Since these reactions were not studied before (at room temperature, for OH), these are new results and we can't easily refer to literature data to fully underline our lack of surprise.

We studied these reactions for a number of reasons. Initially, it was out of mild curiosity how correct the linear extrapolation of the Arrhenius expression from the experimental data for HNCO + OH to room temperature would be, as tunnelling would lead to a curved Arrhenius plot and hence a higher rate coefficient. We indeed found this curvature, but as the TS is broad and low, tunnelling is not all that important, and the curvature is too limited to make a critical difference.

For the other reactions, it is indeed "expected" that the reactions would be slow, but not "known" as no direct data was available. The molecules are fairly small, the computational burden, even at high levels of methodology, is not too high, so we characterized their entrance channels.

With 4 different atomic types in a single molecule, the subsequent chemistry is diverse, an interesting teaching case for early-stage computational scientists, and again the calculations are not overly taxing on resources, so for some of the reactions the extended PES was also investigated (see supporting information). These PESs, other than a brief summary of NCO chemistry, was kept strictly in the supporting information as it is of little to no use for the target audience of this paper.

So, by and large, there was no grand research plan for the theoretical data that led to these negative theoretical results for OH/Cl/NO3/O3, but rather academic interest in filling in some gaps in knowledge that mushroomed a bit beyond the original topic.

In general, I would recommend that the authors justify their choices of methods more clearly, to help make the methods more accessible. Although it's a strength of the work to have combined computational chemistry and atmospheric chemistry modelling, it is also not typical that one has experience with both these methods. To improve the paper, a clearer description of the methods as well as a comparison with previous works would be highly beneficial for the reader. For example, how does the authors' work compare with computational methods with other techniques (basis sets) used in atmospheric chemistry such as (Møller et al., 2016; da Silva, 2013).

We now refer to Vereecken and Francisco, 2012, and Vereecken et al. 2017, for some reviews on the relative merits of theoretical methodologies used in atmospheric chemistry, and the Papajak and Truhlar 2012 paper for basis set choice.

The relative benefits of the myriad of experimental methods, modelling methodologies, quantum chemical methodologies, and theoretical methodologies can't be discussed in each paper, not even concisely, as there are simply too many aspects to discuss. This is even more true when trying to explain this to someone not familiar with the methodologies (as I suspect most readers of this paper won't be), as this would require a very lengthy tutorial first, to then discuss subtleties that can't possibly be covered in a tutorial. The methods used in this work are at the current computational sweet spot, where going beyond the used level would require exponentially higher computational resources, well beyond what is warranted for reactions that are expected to be negligible; at the same time we are using robust methods for all aspects that are known to nearly always provide reliable results.

The Møller et al. 2016 method is a watered-down version of our MC-TST multi-conformer method (Vereecken and Peeters, 2003), using very low levels of theory to investigate the conformational space of molecules. The supporting information of Novelli et al. 2019 contains several pages of discussion on the differences between Møller et al 2016 and Vereecken and Peeters 2003. Neither of these is truly applicable to the current PES as the intermediates here don't have many conformers.

da Silva 2013 is an example of a composite method, of which there are hundreds defined and dozens used on regular basis (CBS-Q, CBS-QB3, G2, G3SX, G4, …). These all aim to combine computationally less expensive methods to estimate the result that would have been obtained at a higher level of theory. The method used in the current study, CCSD(T)/CBS, is often the method aimed for by these composite methods for its general reliability, and the use of composite methods is not expected to provide a better result.

Vereecken, L. and Peeters, J.: The 1,5-H-shift in 1-butoxy: A case study in the rigorous implementation of transition state theory for a multirotamer system, J. Chem. Phys., 119(10), 5159–5170, doi:10.1063/1.1597479, 2003.

Novelli, A., Vereecken, L., Bohn, B., Dorn, H.-P., Gkatzelis, G. I., Hofzumahaus, A., Holland, F., Reimer, D., Rohrer, F., Rosanka, S., Taraborrelli, D., Tillmann, R., Wegener, R., Yu, Z., Kiendler-Scharr, A., Wahner, A. and Fuchs, H.: Importance of isomerization reactions for the OH radical regeneration from the photo-oxidation of isoprene investigated in the atmospheric simulation chamber SAPHIR, Atmos. Chem. Phys., 20, 3333–3355, doi:acp-20-3333-2020, 2020.

Vereecken, L. and Francisco, J. S.: Theoretical studies of atmospheric reaction mechanisms in the troposphere, Chem. Soc. Rev., 41(19), 6259–6293, doi:10.1039/c2cs35070j, 2012.

Vereecken, L., Glowacki, D. R. and Pilling, M. J.: Theoretical Chemical Kinetics in Tropospheric Chemistry: Methodologies and Applications, Chem. Rev., 115(10), 4063–4114, doi:10.1021/cr500488p, 2015.

Papajak, E. and Truhlar, D. G.: What are the most efficient basis set strategies for correlated wave function calculations of reaction energies and barrier heights?, J. Chem. Phys., 137(6), 064110, doi:10.1063/1.4738980, 2012.

Finally, I would also recommend to the authors to add quantitative data throughout discussion of the manuscript by reporting values when possible. It’s always best in scientific communication to be as precise as possible (specific examples are given below).

We have extended the text in several places by adding the specific values obtained from our work or the literature, making the manuscript much easier to follow.

Specific comments:
Title: The title can be better representative of the work. First, the mention of the gas phase loss processes would be very important. It should also be highlighted that the work is theoretical and modelling. A title along the lines of, “Gas phase chemical losses processes of isocyanic acid (HNCO) investigated through computational chemistry and chemical fate transport modeling” would better represent the work. One could also consider highlighting the sources of HNCO investigated, ie. biomass burning.

We have updated the title to “*Atmospheric chemical loss processes of isocyanic acid (HNCO): a combined theoretical kinetic and global modelling study*”. Since we also cover heterogeneous loss, we chose not to add “gas-phase”. As we do not make significant new contributions to the HNCO sources, but rely mostly on pre-existing emissions, this was also not included in the title.

Abstract: There is a missing introduction in the abstract to the significance of HNCO. The authors should add three to five sentences stating the research problem, then the research gap and finally their methods and findings. I would also encourage the authors to be more specific in their abstract in order to better represent the content of the article. For example, page 1, line 19 should specify which global model is being used. I would also encourage the authors to end their abstract with a summarizing sentence and an outlook.

The abstract was rephrased and extended to include this information.

Introduction: Page 1, line 28: Why is the Wentzell reference used here? There were other references prior to this work identifying HNCO in the atmosphere. See (Roberts et al., 2010; Vereset al., 2010).

The used references (Roberts et al., 2011;Wentzell et al., 2013) are based on measurements in the ambient air. Therefore, these are appropriate for this position. The suggested references (Roberts et al., 2010; Veres et al., 2010) are mostly related to lab measurements. The reference (Wentzell et al., 2013) is only used to give a perspective of the presence of HNCO in the urban ambient air other than the USA.

Page 1, line 31: the monomer is presentative of what? A structure? A conformer? And isomer? Or did the authors mean to write “representation of the chemical structure”?

We rephrased to state that HNCO is near-exclusively present as the monomer in the gas phase at ambient conditions.

Page 1, lines 29-32: In general, these sentences are very vague. Which concentrations, which impurities? Can the authors quantify “fairly stable” with numbers and chemical and physical properties?

These sentences are modified to make the text more readable and avoid vagueries, with mention of the concentration level and the discussion is mainly kept to gaseous-phase.

Page 1, line 33: it would be important here to specify which type of modeling study(model, year, sources) was done by Young et al. The Young et al. study is an important precursor the authors' work and more emphasis should be given to comparing this study throughout the manuscript.

The sentence is modified and more information is included

Page 2, line 1: "highly toxic" is not a claim one can make based on the uncertainty between the current medical literature and a lack of exposure studies. If the authors note that 1ppbv is potentially toxic, they can explain that this number is based on thermodynamic partitioning and is not a number from empirical studies. I would revise this statement in the text.

The text is revised accordingly. The concentration is now referred as "estimated". Details about the calculation are not provided as it would be a lengthy addition and it has been discussed extensively by other studies (Roberts et al., 2011; Leslie et al., 2019).

Page 2, lines 13-15: for an additional reference for the oxidation of nicotine as a source of HNCO, see (Borduas et al., 2016a). The Hems et al. reference should be solely for cigarette smoke. The oxidation of amide references should be (Barnes et al., 2010;Borduas et al., 2015; Bunkan et al., 2015). It would be interesting for the authors to highlight the relevance of their calculations for indoor air vs outdoor air chemistry.

The references are modified accordingly. Here we mainly wish to highlight the presence of HNCO in cigarette smoke (inhaled). Our paper focuses mostly on global models, and a discussion of indoor/outdoor chemistry is outside the scope of the paper.

Page 2, line 16: The Leslie et al. review is referenced here, but best to reference the specific studies looking at these materials. See (Jankowski et al., 2014, 2016, 2017)

The references are modified accordingly.

Page 2, line 22: these references should either be solely the review, or each study should be described. Also consider looking at (Wren et al., 2018).

The references are modified accordingly.

Page 2, line 30: remove the word "very". I would argue that we have a good under-standing of the gas phase fate of HNCO, corroborated by this manuscript.

The word "very" is removed. The statement referred to the total lack of data for NO3/Cl/O3, and the absence of room temperature data for OH; the second part of the sentence already concurs with the referee that sufficient indirect data exists to infer that these reactions are slow.

Page 2, line 34: I think it's worth explaining in one or two sentences why the current data is only from elevated temperatures. Isn't because these reactions are all negligible at room temperature?

It is mostly because the reactions were studied for combustion research, with HNCO being a critical intermediate in chemical NOx reduction strategies (a hot topic at the end of last century but since then mostly obsoleted by catalytic reduction flue gas treatments), and thus using experimental setups appropriate for those conditions. In my younger years I (LV) even published a theoretical study on HNCO + H (not cited as not relevant). The consideration of HNCO at atmospheric conditions is, in comparison, fairly recent, prompted by its emission from AdBlue and similar SCR flue gas treatments (only deployed in quantity in the past decade), and increased interest in the atmospheric impact of biomass burning and wildfires. We added a short note linking the experimental data to the relevant research setting.

Page 3, lines 1-3: the authors state that there currently exists no computational data on the reactivity of NO3, Cl and O3 with HNCO. Although this statement is true, why would one expect these oxidants to react or to be important for the fate of HNCO? Based on our current knowledge of the electrophilic nature of the carbon atom in HNCO, none of these oxidants would favorably react with HNCO. Can the authors state their hypotheses (similarly to comment in the general section)?

See our earlier answer with regard to the reasons for doing this study.

Page 3, line 3: specify which co-reactants

The coreactants O, H, CN, HCO have been added to the text

Page 3, lines 4-5: the authors correctly identify the lack of knowledge and of measurements of the dry deposition of HNCO. An extended discussion on this topic is perhaps warranted. Can the authors address this important piece of missing information with their work?

It is difficult to address this missing information with the current study. However, a separate discussion on this matter and comparisons to Young et al., 2012 is desirable. We thus included a description in the methodology section of the global model of how dry deposition was modelled. A discussion on dry deposition was added to the manuscript and additional information on dry deposition was added to Table 1.

Page 3, lines 7-14: the discussion on photolysis needs to be reconsidered. Isn't the reason why HNCO' absorbance is only reported below 262 nm? Isn't because it doesn't absorb at higher wavelength? By this definition, one would not expect photolysis of HNCO to occur in the troposphere. The way the text is currently written suggests missing information...

We have expanded and rephrased our discussion of the photolysis, with additional references, and now explicitly state that photolysis appears to be of no importance in the lower atmosphere.

Page 3, line 18-19: could be worth adding the values of KH here.

Added

Page 3, lines 21-22: The most up-to-date calculations are arguably from (Borduas etal., 2016c; Roberts and Liu, 2019).

We now refer to the most recent study by Roberts and Liu, 2019

Methods:
Page 3, line 36: can the authors further justify their choice of basis set?

See our earlier comment on the relative merits of the chosen methodologies, and the references listed there.

Page 4, lines 7-8: how was the tunneling correction of 1.5 calculated (perhaps also add a reference)?

Calculation of the tunnelling correction was done using Eckart tunnelling corrections for asymmetric barriers. This is a very widely used, and comparatively simple methodology, that is referenced in the methodology.

Page 4, lines 15-16: I'm curious about the authors' reasoning for doing calculations despite all these reaction channels being negligible at room temperature. This point goes along with my point above which hypothesis were the authors starting with.

See our earlier answer with regard to the reasons for doing this study.

Page 4, paragraph on global modelling: a hierarchal diagram of the model would be useful for visualization and interpretation of the components and subcomponents of the model. This figure could go either in the main text or in the supplementary information.

A model hierarchal diagram of EMAC was already provided in Jöckel et al., 2005 and an updated overview of all model components is given in Jöckel et al., 2010. Describing those technical parts of the model is out of the scope of our study, and we cannot do this justice without adding an overly long discussion in the paper. However, additional references to these papers were added to the manuscript for readers interested in these aspects..

Jöckel, P., Sander, R., Kerkweg, A., Tost, H., and Lelieveld, J.: Technical Note: The Modular Earth Submodel System (MESSy) - a new approach towards Earth System Modeling, Atmos. Chem. Phys., 5, 433–444, https://doi.org/10.5194/acp-5-433-2005, 2005.
Jöckel, P., Kerkweg, A., Pozzer, A., Sander, R., Tost, H., Riede, H., Baumgaertner, A., Gromov, S., and Kern, B.: Development cycle 2 of the Modular Earth Submodel System (MESSy2), Geosci. Model Dev., 3, 717–752, https://doi.org/10.5194/gmd-3-717-2010, 2010.

Page 4, lines 25-26: what is the implication of these grid sizes on the interpretation of the results?

Using this horizontal resolution allows us to assess the impact of HNCO chemical losses while still being computationally affordable. Therefore, we can reliably estimate the global impact, but not the regional ones (e.g. single megacities). By using 90 layers, focusing on the lower and middle atmosphere, we are able to cover the whole troposphere. Additionally, vertical transport processes are represented in a good manner (Jöckel et al., 2010) which allows us to also investigate the impact on the UTLS. An elaborate explanation was added to the text.

Jöckel, P., Kerkweg, A., Pozzer, A., Sander, R., Tost, H., Riede, H., Baumgaertner, A., Gromov, S. and Kern, B.: Development cycle 2 of the Modular Earth Submodel System (MESSy2), Geosci. Model Dev., 3(2), 717–752, doi:10.5194/gmd-3-717-2010, 2010.

Page 4, line 29: why were aromatics and terpenes excluded?

For global model studies the balance of computational demand is of importance. We consider aromatics and terpenes to be of little importance for the processes studied. Thus we excluded them to reduce the computational demand. A statement about this was added to the manuscript.

Page 4, lines 31-32: have the authors considered using SAR factors for amines and amides? (see (Borduas et al., 2016b))

The reaction rates used are average values from all reported experimental data given in Nielsen et al., 2012. The product yields used are the product yields from the same source, including some simplifications. In general, we prefer measured reaction rates over SAR estimates, though the latter are surely useful when modelling the chemical kinetics of larger amines and amides. Using additional SAR factors will likely not improve the product yields accuracy, and thus not improve the reliability of the proposed mechanism. The section covering the global model description was updated to include a more elaborated description on the reaction rates and reaction yields used.

Page 4, lines 37-38: this conclusion would certainly depend on the scale of the modelling correct? As cigarette smoke and cooking on a very local scale could also rival biomass burning, or am I wrong?

Indeed, on local scales other sources could be more significant. However, we consider these sources to be of no importance on a global scale, and due to the grid size used for this global model application such sources would not show in the predictions. Therefore, these sources are not taken into account. Modelling e.g. cigarette smoke is hardly possible within the given resolution. A short explanation was added to the text.

Page 4, line 38: specify the two emission factors.

Done

Page 5, line 2: In light of (Carter et al., 2020)’s conclusions, could the authors comment on the uncertainty of their inventory.

Using different dry matter burned values will definitely impact the primary and secondary biomass burning emissions of HNCO. Estimating the uncertainties introduced by using different dry matter burned sources in EMAC is laborious. The reason is that online calculations of emission strengths are only possible with GFAS in the model version we have used. This will be changed in the next EMAC version (v 2.55). On a global scale, dry matter burned is at the higher end in GFAS but still lower than FINN and QFED and almost twice as high as GFED (Figure 4 in Carter et al., 2020). We expect similar global HNCO burdens simulated when using FINN or QFED. When using GFED, the reduced dry matter burned would result in a lower HNCO burden.

Carter, T. S., Heald, C. L., Jimenez, J. L., Campuzano-Jost, P., Kondo, Y., Moteki, N., Schwarz, J. P., Wiedinmyer, C., Darmenov, A. S., da Silva, A. M., and Kaiser, J. W.: How emissions uncertainty influences the distribution and radiative impacts of smoke from fires in North America, Atmos. Chem. Phys., 20, 2073–2097, https://doi.org/10.5194/acp-20-2073-2020, 2020.

Page 5, line 10: the chosen years are 2010-2011. Can this choice be justified? (Younget al., 2012) used 2008 fire emissions. Can these two years be compared? Why or why not?

The model is initialised using datasets which do not include any information on HNCO (since HNCO was not implemented in EMAC so far). The time period 2010-2011 was chosen, since in 2010 a particular high fire radiative energy was observed (Figure 4 in Kaiser et al., 2012). This results in high biomass burning emissions, leading to high HNCO background concentrations in the spin-up period, which is favourable for the analysis in 2011. Based on Figure 4 in Kaiser et al., 2012, a similar situation is given in 2007. Young et al., 2012 do not provide any information on their spin-up period used. If 2007 was used, the analysis performed in Young et al., 2012 for 2008 would be comparable. A short statement on this matter was added to the manuscript.

Kaiser, J. W., Heil, A., Andreae, M. O., Benedetti, A., Chubarova, N., Jones, L., Morcrette, J.-J., Razinger, M., Schultz, M. G., Suttie, M., and van der Werf, G. R.: Biomass burning emissions estimated with a global fire assimilation system based on observed fire radiative power, Biogeosciences, 9, 527–554, https://doi.org/10.5194/bg-9-527-2012, 2012.

Results

Figure 1: Overall, this figure is particularly well done and clear. I congratulate the authors here! The structures are also done well, using ChemDraw. Actually, could all the structures be drawn with bonds and bond angles similarly to the products with ozone? In addition, where are the energies of the pre-complexes?

The supporting information already has 3D representations with bond lengths and angles for all relevant structures. To avoid overloading the main paper with theoretical data that ultimately yields rate data that is unlikely to be included in the models, we choose not to include it in the main text. For the same reason, the pre-reaction complexes are omitted as they do not affect the kinetics significantly. We now state this explicitly in the caption for figure 1, and refer to the supporting information.

Page 6, line 14: could the authors show graphically on Figure 2 the mentioned experimental uncertainty?

The uncertainty is now indicated as a shaded area. We have also added an indication to this graph which rate coefficient would be needed to make HNCO loss through OH reaction relevant for the atmosphere.

Page 6, line 15: to be more accurate, please give the range instead of an average factor.

We feel that using a range is actually less informative and more complex, as the uncertainty interval is highly asymmetric. Most uncertainties in theoretical calculations, such as on the barrier height or vibrational characteristics, are incorporated in an exponential factor in the rate calculations, and the symmetric, additive uncertainty on the input data leads to a symmetric multiplicative uncertainty readily reported as a factor. Tunneling uncertainties have likewise non-linear response function. Reporting this as an additive uncertainty requires an asymmetric error with different upper and lower bounds, which is harder to interpret. Reporting it as a range is misleading, as it is then typically assumed that the most likely value is the middle of the interval, contrary to the actual computational result. Symmetrising the additive uncertainty interval either overstates or understates the error. We thus strongly prefer to report our uncertainties as factors.

Page 6, line 18: specify the kinetic model.

This refers to the kinetic model defined in the methodologies. We have changes this to “the theoretical kinetic calculation” and "the predictions” to avoid confusion with the unrelated atmospheric model.

Page 6, lines 26-27: Good conclusion, I would highlight this statement better in the abstract for example.

We now state explicitly both in the abstract and conclusions that the reaction occurs by H-abstraction.

Page 7, line 15-16: define why an acyl chloride is less “stable” than a carboxylic acid? The current statement is rather vague.

Page 8, line 17: explain what is meant by “greater stability” of nitric acid.

The difference reaction energies are due to molecular differences in induction, orbital overlap, electron distribution as influenced by electronegativity, H-bonding... These are also the effects that e.g. make acyl chlorides much more reactive than carboxylic acids, and hence more useful in organic synthesis. As this paper is not the appropriate place to go in detail on the molecular orbital layout of the respective adducts, the statement was removed, and we now refer only to the reduced reaction energy, assuming all readers are familiar with Bell-Evans-Polanyi relationships.

Page 7, lines 17-18: I think this statement is wrong. Isn’t it also true for HNCO + O3 based on Figure 1? It is also inconsistent with conclusions on page 8, lines 1-3

As stated in the ozonolysis reaction section, H-abstraction contributes for 80% in HNCO + O3, despite not having the lowest energy barrier, in agreement with our statement that Cl is only of the studied mechanisms where addition is the main entrance channel. Stating that the Cl addition path is dominant remains consistent with the later conclusion that despite the higher reaction flux through that channel, it does not effectively lead to product formation due to another reaction (in this case adduct redissociation) undoing the product formation. This is true in in atmospheric conditions, but not true in general, and we now emphasise this more, using also the estimated O2 addition pseudo-first order rate coefficient.
We also changed our wording in several places from “the reaction occurs through H-abstraction” (or similar) to “HNCO removal occurs through H-abstraction” (or similar).

Page 8, line 6: the Cl concentration is incorrect. See (Riedel et al., 2012) for example (concentrations of 10s to 100s ppt level). A ratio of OH/Cl of 200 appears to be typical in urban regions based on (Young et al., 2014).

Reidel et al. 2012 reports concentrations of 10s to 100s ppt for chlorinated compounds but did not measure Cl-atom concentrations: these were deduced from a box model based on ClNO2 and Cl2 measurements limited to the coastal region; they make no statements on the global average Cl concentration that I could find. However, even using the momentary peak concentrations in that region of about ~10^5 Cl / cm^{-3} reported in the supporting information of Reidel et al. 2012 would not make this reaction important.
Our global model simulations neglect the heterogeneous production of $ClNO_2$ and compute tropospheric chlorine radical concentrations of about 2×10^3 molecules cm^{-3}, comparable to the number stated in the text.
We have now included a paragraph looking at minimum and maximum co-reactant concentrations, and estimated lifetimes in the reaction conditions where these maxima are found, further strengthening the link between the theoretical predictions and the model.

Riedel, T. P., Bertram, T. H., Crisp, T. A., Williams, E. J., Lerner, B. M., Vlasenko, A., Li, S.-M., Gilman, J., de Gouw, J., Bon, D. M., Wagner, N. L., Brown, S. S. and Thornton, J. A.: Nitryl Chloride and Molecular Chlorine in the Coastal Marine Boundary Layer, Environ. Sci. Technol., 46(19), 10463–10470, doi:10.1021/es204632r, 2012.

Page 8, lines 26-27: doesn’t the sentence on lines 27-28 contradict the preceding statement?

There is no contradiction: removal by NO3 at night is comparable to removal by OH by day, and both are ineffective compared to other loss processes. We now state “likewise considered” instead of “still considered” to make this more clear.

Page 8, line 37: specify which atoms have the reported bond energies. O-O or H-O?

It is stated explicitly that it falls apart to OH + O2.

Page 9, line 16: specify which mechanisms are “the described mechanisms”. There are many mechanisms reported in this work.

This sentence refers explicitly to the mechanism in table 1 and 2 in the supplementary material. Changed the wording to “kinetic model”.

Page 9, line 18: be consistent with writing out the name of isocyanic acid and using the molecular formula HNCO.

We have harmonized mostly on notation as HNCO, other than to mention the chemical name in the abstract, introduction and conclusions, for the benefit of readers that only skim these sections.

Page 9, line 21-22: would be interesting to show this result/data. How was this number obtained?

The number was obtained by taking the total HNCO mass above the planetary boundary layer and below the tropopause into account and compare it to the total modelled HNCO mass. A figure was added showing the vertical profile of HNCO and HCN for different areas and time periods. This figure is referred to in the text to improve this discussion.

Page 9, lines 33-34: it would be very important to expand this sentence into a whole paragraph for comparison. And if the argument on lines 34-35 are true, then which contribution (percentage for example) is formamide a source of HNCO? This value could be very important for the gas phase atmospheric community.

Formamide as a source of HNCO heavily depends on the emission factors used. Information on this matter was added to the text, and can be found in Table 1 for the simulation using the emission factors of Koss et al., 2018 and Kumar et al., 2018. Table 1 also provides a detailed comparison between our results and the results from Young et al., 2012. The table headers were changed to make it more clear that the results given in this table tabulates results from our own study, using the aforementioned emission factors.

Page 9, lines 36-37: specify which heterogeneous loss terms.

It is based on dry and wet deposition. This information was added to the text.

Page 10, lines 1-2: this lifetime is calculated based on which values?

The atmospheric lifetime is calculated based on all HNCO loss terms (chemical and heterogeneous). The chemical lifetime is based solely on the chemical losses. The chemical lifetime is significantly higher, since chemical losses are significantly lower than heterogeneous loss terms. The information on how these values are calculated is added to the text.

Page 10, lines 5-7: interesting calculation. How do the authors interpret that number with the observed diurnal profiles in (Roberts et al., 2014)?

As mentioned in the manuscript, we only obtained daily mean values in this study. Comparing these to diurnal profiles would unfortunately require to repeat expensive model simulations. Additionally, we expect the model to reproduce the diurnal profiles of surface HNCO discussed by Roberts et al., 2014 since we take the strong secondary source from formamide into account. Such a comparison may be subject of a subsequent study that could make use of in-house HNCO measurements in urban environments and possibly in the stratosphere, as part of ongoing research.

Page 10, line 7: did the authors consider photolysis as a sink in the stratosphere? Refer to the discussion on photolysis on page 3.

Within the global modelling photolysis as a stratospheric sink was not taken into account. This information was added to the discussion.

Page 10, lines 12-14: show this result graphically. It is particularly interesting.Page 10, lines 25-27: What is the role of the model’s resolution in this analysis?

An additional figure was added to show this graphically over South East Asia before and after the Indian monsoon.
In our modelling approach, 90 vertical layers were used extending to the lower mesosphere. As discussed earlier, many studies showed that EMAC represent the vertical transport well and is used for many studies focusing on stratospheric processes.

Page 11: useful graphic and table. Could the authors also add a column to their table relating to their own results? What is the implications of modelling different years of fire inventories when comparing the results in Table 1? I would also be consistent with significant figures throughout the table.

Table 1 already included results from this study, but the presentation was confusing. The table was updated such that it is clearer that the column 2 and 3 give results from this study, but using the emission factors of Koss et al., 2018 and Kumar et al., 2018, respectively. A discussion on the different years simulated was added, as related to an earlier comment.

Page 11, line 8: is the wrong reference used here? Should it be Kumar et al 2018?

Correct. The reference was updated accordingly.

Page 12, starting at line 5: I would move this section before the global modelling data to help with the flow of the manuscript.

The NCO section is now moved to a more logical place directly after the other theoretical kinetic calculations.

Page 12, line 11: describe RAPRNOx

We now describe that the RAPRENOx process involves introducing HNCO in a combustion system through injection of cyanuric acid.

Page 12, lines 21-22: unclear statement. What is being referred to as "total rate coefficients"?

We now indicate that we did not do all possible reaction channels, but that the expected dominance of H-abstraction thus implies that it is a good estimate for the total rate of reaction through all reaction channels.

Page 12, lines 28-29: why not be consistent with p6, line 5 with 298K?

These numbers are for combustion applications (300-3000K), where "room temperature" is not a very important temperature and multiples of 100K seem more common. We also used this for the Arrhenius expression for HNCO + OH at combustion temperatures.

Conclusions:
Page 13, lines 18-19: 5 Gg/y out of (insert number of total losses).

This information was added to the manuscript.

Page 13, line 19: first time ammonia is mentioned in the conclusion – the authors can refer to (Leslie et al., 2019) for a back of the envelop calculation on ammonia budget from HNCO. How was ammonia implemented into the model? This discussion is rather important for the fate of HNCO and I would encourage the authors to discuss these numbers in the text as well.

The information on the implemented ammonia aqueous-phase mechanism is updated in the model description. Ammonia gas-phase sinks are already in the standard model version used. Aqueous-phase chemistry of ammonia is limited to the acid-base equilibrium in cloud droplets. With the current model setup we neglected ammonia (ammonium nitrate) in aerosols. We estimate HNCO hydrolysis produces ~120 Tg/yr of ammonia, which, on a global basis, contributes little to the ammonia budget. Our estimate is a factor 5-6 lower than the upper limit estimated by Leslie et al. (2019). We changed the text accordingly in section 4.

Page 13, lines 28-30: this sentence appears to be out of place, and outside the scope of this work. Unless a connection with the authors' HNCO modeling can be made?

We have added several pieces of information throughout the manuscript regarding transport of HNCO to the UTLS and the stratosphere, also related to the Indian Monsoon. As this part of the atmosphere is not the focus of the work at this time, we choose not to extend this aspect by more than the current additions, as this would require additional computational studies. The current work is related to ongoing work at our institute on HNCO emissions both at surface level and its role in the stratosphere.

Technical comments:
Reference of SUVA should have the acronym written out.

The English translation of the acronyms is now spelled out.

Page 1, line 28: what is meant by “first recognized”? First studied? First synthesis? I would encourage the authors to be more precise.

We now state explicitly that it’s the molecular structure and synthesis that was discovered.

Page 2, line 21: instead of “slippage” did the authors means “seepage” (especially for gas seeping out)?

The text was rephrased.

Page 2, line 36: remove the word “very”

The text was rephrased.

Page 3, line 5: best to remove the word “recent”.

Removed

Strangely enough, the numbers reported in the text do not match the numbers in the figure. Could the authors double check the numbers on: Page 5, line 24; page 5, line 26 (2 numbers); page 7, line 12.

The numbers match, but are rounded to the nearest kcal/mol in the text, as the extra digits serve no need and only makes the reading harder. To avoid confusion we added the additional digits to the text, matching the figure.

Page 9, line 23: should be written HNCO (not HCNO).

Corrected

Page 13, line 15: remove the word “fairly”.

Removed

~~Chemical~~Atmospheric chemical loss processes of isocyanic acid~~, ~~ (HNCO~~, in the atmosphere~~): a combined theoretical kinetic and global modelling study

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Abstract

~~The impact of chemical loss processes of isocyanic acid was studied by a combined theoretical and modeling study.~~Isocyanic acid (HNCO) is a chemical constituent known to be harmful to humans if ambient concentrations exceed ~1 ppbv. HNCO is mainly emitted by combustion processes, but is also inadvertently released by NO_x mitigation measures in flue gas treatments. With increasing biomass burning and more widespread usage of catalytic converters in car engines, good prediction of HNCO atmospheric levels with global models is desirable. Little is known directly on the chemical loss processes of HNCO, which limits the implementation in global Earth system models. This study aims to close this knowledge gap by combining a theoretical kinetic study on the major oxidants reacting with HNCO with a global modelling study. The potential energy surfaces of the reactions of HNCO with OH and NO_3 radicals, Cl atoms, and ozone, were studied using high-level CCSD(T)/CBS(DTQ)//M06-2X/aug-cc-pVTZ quantum chemical methodologies, followed by TST theoretical kinetic predictions of the rate coefficients at temperatures of 200-3000K. It was found that the reactions are all slow in atmospheric conditions, with $k(300K) \leq 7\times10^{-16}$ cm^3 molecule^{-1} s^{-1}, and that product formation occurs predominantly by H-abstraction; the predictions are in good agreement with earlier experimental work, where available. The reverse reactions of NCO radicals with H_2O, HNO_3, and HCl, of importance mostly in combustion, were also examined briefly.

The findings are implemented into the atmospheric model EMAC to estimate the importance of each chemical loss processes, on a global ~~model confirms that~~scale. The EMAC predictions confirm that the gas phase chemical loss of HNCO is a negligible process, contributing less than 1~~%. Removal~~%, leaving heterogeneous losses as the major sinks. The removal of HNCO by clouds and precipitation ~~is a larger sink, contributing~~contributes for about 10% of the total loss, while globally dry deposition is the main sink, accounting for ~90%. The global simulation also shows that due to its long chemical lifetime in the free troposphere, HNCO can be efficiently transported into the UTLS by deep convection events. ~~Average daily concentrations~~Daily average mixing ratios of ground level HNCO are found to regularly exceed 1 ppbv, in regions dominated by biomass burning events, but rarely exceed levels ~~considered potentially toxic~~above 10 ppt, though locally instantaneous toxic levels are expected.

1 Introduction

The existence of isocyanic acid (HNCO) in the atmosphere has been established only recently (Roberts et al., 2011; Wentzell et al., 2013) despite its molecular structure and chemical synthesis being first ~~recognized~~discovered in the 19th century (Liebig and Wöhler, 1830). HNCO can form H-bonded clusters (Zabardasti et al., 2009, 2010; Zabardasti and Solimannejad, 2007), and in ~~concentrated/~~pure form appreciably polymerizes to other species~~, but becomes fairly stable in the presence of impurities~~ (Belson and Strachan, 1982), ~~such that the~~ but becomes relatively stable in the gaseous phase (ppm level) under ambient temperature conditions (Roberts et al., 2010). It is thus near-exclusively present as a monomer ~~is the near-exclusive representative especially~~ in the gaseous phase under ambient temperature conditions (Fischer et al., 2002; Roberts et al., 2010). The background ambient mixing ratios of HNCO as determined by Young et al. (2012) using a global chemistry transport model vary in the range of a few pptv over the ocean and remote Southern Hemisphere, to tens of pptv ~~(Young et al., 2012), while in~~over landmass. In urban regions, HNCO mixing ratio increases from tens of pptv to hundreds of pptv (Roberts et al., 2014; Wentzell et al., 2013). Peak levels can reach up to a few ppbv under the conditions impacted by direct emissions (Chandra and Sinha, 2016).

HNCO ~~is considered a highly toxic species and~~ has been linked to adverse health effects ~~[(~~such as cataracts, cardiovascular disease, and rheumatoid arthritis via a process called protein carbamylation [see (Leslie et al., 2019; Roberts et al., 2011; Suarez-Bertoa and Astorga, 2016; SUVA, 2016; Wang et al., 2007) and references therein~~],~~]. To our knowledge, no past studies have been performed to provide a direct link between inhalation exposure and related adverse health effects. However, human exposure to HNCO concentrations ~~larger than~~of 1 ppbv is ~~considered as~~estimated to be potentially ~~toxic~~sufficient to start the process of protein carbamylation (Roberts et al., 2011). Unfortunately, an air quality standard for HNCO does not exist in most of the countries, whereas an occupational exposure limit has been established by law in only a few countries, including ~~Sweden~~the Swedish Work Environment Authority (SWEA, 2011) and ~~Switzerland~~the Swiss National Accident Insurance Fund (SUVA, 2016). For example, the Swedish work environment authority sets the level limit value (LLV) for HNCO at about 0.018 mg m^{-3}, i.e. 10 ppbv (SWEA, 2011). The potential negative impact on health makes it important to assess the atmospheric sources and sinks of HNCO to determine its fate and lifetime.

HNCO emission into the atmosphere is driven primarily by combustion processes based on both natural and anthropogenic activities ~~[(~~[see (Leslie et al., 2019) and references therein], where the pyrolysis of nitrogen-containing biomass materials during the events of wildfires and agricultural fires leads to the emission of HNCO into the atmosphere. The presence of HNCO in ~~the~~ cigarette smoke has been established via the pyrolysis of urea ~~(~~used as a cigarette additive (Baker and Bishop, 2004), oxidation of nicotine~~,~~ (Borduas et al., 2016a), and oxidation of formamide (~~Hems et al., 2019; Roberts~~Barnes et al., ~~2011).~~2010; Borduas et al., 2015; Bunkan et al., 2015). Even the combustion of almost all sorts of common household materials ~~(e.g.,~~including fiber glass, rubber, wood, PVC-based carpet and cables (Blomqvist et al., 2003), and polyurethane-based foam~~, etc.)~~ (Blomqvist et al., 2003; Jankowski et al., 2014), leads to HNCO emissions along other isocyanates ~~[(~~(Leslie et al., 2019~~) and references therein].~~). HNCO emissions from traffic are originating mainly from usage of recent catalytic converters in the exhaust systems of gasoline (Brady et al., 2014) and diesel (Heeb et al., 2011) based vehicles. These converters are implemented to control the emission of primary pollutants such as

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hydrocarbons, carbon monoxide, particulate matter, and nitrogen oxides. However, these implementations have promoted (Suarez-Bertoa and Astorga, 2016) the formation and emissions of HNCO via surface-bound chain reactions at different stages of the flue gas exhaust, and additionally due to ~~a~~emission of unreacted HNCO ~~slippage~~ in the most commonly used urea-based SCR (Selective Catalytic Reduction) ~~convertion~~ system ~~[e.g., (Brady et al., 2014;~~ (Heeb et al., 2011~~; Leslie et al., 2019; Suarez-Bertoa and Astorga, 2016)].~~). The usages of catalytic converters in modern vehicles potentially give rise to the emission of HNCO especially in urban regions with a growing density of vehicles. A few studies also reported a direct formation of HNCO in the diesel engines during fuel combustion without any after-treatments (Heeb et al., 2011; Jathar et al., 2017). A tabular overview of past studies for gasoline or diesel exhaust related HNCO emissions can be found in Wren et al. (2018) and Leslie et al. (2019). HNCO emissions via fossil fuel usage are not limited to on-road activity. Off-road fossil fuel activities (e.g., tar sands) also contribute to significant HNCO emissions on regional scales (Liggio et al., 2017). Finally, secondary HNCO formation in the atmosphere is also known through the oxidation of amines and amides [e.g., (Borduas et al., 2016a; Parandaman et al., 2017)].

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The number of studies examining HNCO gas-phase chemistry ~~is very~~are limited, and mostly focused on its role in the chemistry in NO_x mitigation strategies in combustion systems. The scarce data suggests that HNCO destruction in the atmosphere by typical pathways such as reactions with oxidizing agents or by photolysis is ineffective. We give a short overview here, to supplement a recent review (Leslie et al., 2019). The reaction of HNCO with the hydroxyl radical (OH), the most important day-time oxidizing agent, has only been studied experimentally at temperatures between 620 and 2500K (Baulch et al., 2005; Mertens et al., 1992; Tsang, 1992; Tully et al., 1989; Wooldridge et al., 1996), where the extrapolated rate expressions lead to ~~a very low~~an estimated rate coefficient of 5-12 × 10^{-16}~~-~~ cm^{3}~~-~~ molecule^{-1} s^{-1} at 298 K, i.e. a HNCO-lifetime towards OH of over ~~20~~25 years when assuming a typical OH concentration of 1 × 10^{6}~~-~~ molecule~~-~~ cm^{-3}. Early theoretical work by Sengupta and Nguyen (1997) at temperatures ≥ 500 K showed that the mechanism proceeds predominantly by H-abstraction, forming NCO + H_2O, with an energy barrier of ~6 kcal mol^{-1}. Wooldridge et al. ~~, in agreement with the~~(1996) determined an upper limit ≤ 0.1 for the fraction of CO_2 + NH_2 formation~~ as determined by~~ .~~Wooldridge et al. (1996).~~ To our knowledge, no experimental or theoretical data are available on HNCO reactions with other dominant atmospheric oxidants, including the nitrate radical (NO_3), chlorine atoms (Cl), or ozone (O_3). Some data is available for H- and O-atom co-reactants of importance in combustion, as well as estimates for HCO and CN (Baulch et al., 2005; Tsang, 1992), but these are not reviewed here. There is no direct measurement for the dry deposition of HNCO. In a~~ recent~~ global chemical transport model-based study, the deposition velocity was considered to be similar to formic acid, yielding an HNCO-lifetime of 1 – 3 day (over the ocean) to 1 – 2~~-~~ weeks (over vegetation) (Young et al., 2012). The UV absorption for HNCO is only reported at wavelengths < 262 nm and photolysis is mostly reported for energies at wavelengths below 240 nm by excitation to the first singlet excited states, forming H + NCO or NH + CO (Keller-Rudek et al., 2013; Okabe, 1970; Spiglanin et al., 1987; Spiglanin and Chandler, 1987; Uno et al., 1990; Vatsa and Volpp, 2001~~), whereas in~~). In the troposphere photolysis occurs only at UV absorption wavelength band > 290 nm due to filtering of shorter-wavelength radiation (Hofzumahaus et al., 2002). ~~The contribution~~DrozGeorget et al. (1997) have reported the photolysis of ~~photolytic destruction is thus uncertain, and can only be determined by measuring~~ HNCO forming NH($a^1\Delta$) + CO($X^1\Sigma^+$) at 332.4 nm, but the HNCO absorption cross-~~sections directly for the~~

~~relevant tropospheric wavelengths as suggested by Young et al. (2012).~~section at this wavelength would lead to a lifetime of months (Roberts et al., 2011). Therefore, HNCO loss due to photo-dissociation appears to be negligible in the lower atmosphere. HNCO has absorption bands in the infra-red (Sharpe et al., 2004) but at these wavelengths ~~generally~~ the photon energy is generally too limited for photo-dissociation (Hofzumahaus et al., 2002). The main atmospheric loss processes are considered to be the ~~transition~~transfer to the liquid-phase ~~via~~followed by hydrolysis, and deposition. This process depends on the varying atmospheric liquid water contents, relevant temperatures, and pH of cloud droplets. Therefore, the gas-to-liquid partitioning, in the varying atmospheric properties, i.e. water content, temperature, and pH of cloud droplets become important parameters to determine the atmospheric fate of HNCO (Leslie et al., 2019). The gas-to-liquid partitioning has been described by the Henry's Law coefficient K_H (ranging from 20 to 26 ± 2 M atm^{-1}) and related parameters by a handful of studies (Borduas et al., 2016b; Roberts et al., 2011; Roberts and Liu, 2019). Based on a recent ~~studies(Barth et al., 2013;~~ study (Roberts and Liu, 2019), the lifetime of HNCO due to heterogeneous processes is known to be of the order of a few hours (in-cloud reactions) to weeks (aerosol deposition).

The emissions and sources of HNCO have been focused on by many past studies, but there remain large uncertainties in our understanding of HNCO removal process, especially in gas-phase chemistry. ~~The limited number of available studies suggests that the (photo)chemical~~This missing information on HNCO ~~loss~~removal processes ~~in the atmosphere appear~~limits global models to ~~be slow,~~predict HNCO with ~~liquid-phase processes acting as the dominant sink.~~confidence. To alleviate the dearth of direct data and therefore improve the representation of HNCO in global models, we first provide ~~in this work~~ a theoretical analysis of the chemical reactions of HNCO with the dominant atmospheric oxidants: OH and NO_3 radicals, Cl atoms, and O_3 molecules, ~~predicting~~including the prediction of each rate ~~coefficients of these reactions~~coefficient at atmospheric conditions. ~~The~~In a second step, these results are included in a global numerical chemistry and climate model to assess the impact of chemical loss of HNCO in competition against hydrolysis within cloud droplets and against deposition to the Earth's surface. ~~The~~Additionally, the model is ~~also~~ used to provide an estimate of the relative importance of primary and secondary HNCO sources.

2 Methodologies

2.1 Theoretical methodologies

The potential energy surfaces of the initiation reactions of all four reaction systems were characterized at the M06-2X/aug-cc-pVTZ level of theory (Dunning, 1989; Zhao and Truhlar, 2008), optimizing the geometries and rovibrational characteristics of all minima and transition states. The relative energy of the critical points was further refined at the CCSD(T) level of theory in a set of single point energy calculations using a systematic series of basis sets, aug-cc-pVxZ (x = D, T, Q) (Dunning, 1989; Purvis and Bartlett, 1982). These energies were extrapolated to the complete basis set limit (CBS) using the aug-Schwartz6(DTQ) scheme as proposed by Martin (1996). The rate coefficients were then obtained by transition state theory (Truhlar et al., 1996) in a rigid rotor, harmonic oscillator approximation, applying a scaling factor of 0.971 to the vibrational wavenumbers (Alecu et al., 2010; Bao et al., 2017). The spin-orbit splitting of the OH radicals of 27.95 cm^{-1} was taken into account (Huber and Herzberg, 1979). Tunneling was incorporated using an asymmetric Eckart correction

(Johnston and Heicklen, 1962). ~~The expected uncertainty of the predictions at room temperature is a factor of 4, based on an estimated uncertainty on the barrier height of 0.5 kcal mol^{-1}, and on the tunneling correction of a factor of 1.5.~~

To further complete our knowledge on some of the reactions beyond their initiation steps, the full potential energy surfaces of the HNCO + Cl and HNCO + O_3, were characterized at the M06-2X/aug-cc-pVTZ or B3LYP/aug-cc-pVTZ level of theory (Becke, 1993; Dunning, 1989; Lee et al., 1988), combined with CCSD(T)/aug-cc-pVTZ single point energy calculations. To our knowledge, these are the first characterizations of these surfaces. At atmospheric temperatures, most of the reaction channels are negligible, and a detailed kinetic analysis is not performed at this time.

The expected uncertainty of the rate predictions at room temperature is a factor of 4, based on an estimated uncertainty on the barrier height of at least 0.5 kcal mol^{-1}, and on the tunneling correction of a factor of 1.5. Though the level of theory used is robust, there are some aspects that are not treated with the highest possible precision. For example, post-CCSD(T)/CBS calculations could refine the predicted energies, but is not expected to change our values by more than a few tenths of kcal mol^{-1}. The calculation of the state densities could be improved for internal rotation (especially at temperatures outside the atmospheric range), for the notoriously complex rovibronic structure of the NO_3 radical (Stanton, 2007, 2009; Stanton and Okumura, 2009), or by treating the transition states (micro)variationally to better characterize the energy-specific kinetic bottleneck. Another aspect is the effect of redissociation of chemically activated adducts, which decreases the effective rate of HNCO loss. Finally, tunnelling corrections for the H-abstraction reactions could benefit from higher-dimensional (curvature and corner-cutting) corrections. The tunnelling corrections are currently predicted to be smaller than a factor 15 at room temperature due to the low and broad energy barriers, except for a factor ~40 for the HNCO + NO_3 H-abstraction with a somewhat higher barrier. Incorporating any of the aforementioned improvements in the theoretical predictions, however, has a high to very high computational burden with strongly diminished return, as none are expected to change the rate coefficient by a factor large enough to affect the conclusions of our calculations, i.e. that the reactions are negligibly slow by many orders of magnitude compared to other HNCO loss processes (see further). This is also illustrated in Figure 2. We refer to Vereecken and Francisco (2012), Vereecken et al. (2015), and Papajakand and Truhlar (2012) for further information on theoretical methodologies in atmospheric chemistry.

2.2 Global modeling

The ECHAM/MESSy Atmospheric Chemistry (EMAC) model is a numerical chemistry and climate simulation system that includes sub-models describing tropospheric and middle atmosphere processes and their interaction with oceans, land and human influences (Jöckel et al., 2010). It uses the second version of the Modular Earth Submodel System (MESSy2) to link multi-institutional computer codes. The core atmospheric model is the 5th generation European Centre Hamburg general circulation model (ECHAM5) (Roeckner et al., 2006). A hierarchal diagram of EMAC is given in Jöckel et al. (2005). Additionally, Jöckel et al. (2010) provides an update on all modelling components used. For the present study we applied EMAC (ECHAM5 version 5.3.02, MESSy version 2.54.0) in the T63L90MA-resolution, i.e. with a spherical truncation of T63 (corresponding to a quadratic Gaussian grid of approximately 1.875 by 1.875 degrees in latitude and longitude) with 90 vertical hybrid pressure levels up to 0.01 hPa. By using this horizontal resolution, assessing the global impact is still feasible while at the same time being of a computationally reasonable cost. The 90 vertical layers used (focusing on the lower and middle atmosphere) represent tropospheric and stratospheric transport processes reasonable well (Jöckel et al., 2010), such that the tropospheric impact and the impact on the UTLS (upper troposphere/lower stratosphere) can be addressed. The applied model setup comprised the submodel MECCA (Module Efficiently Calculating the Chemistry of the Atmosphere) to calculate atmospheric chemistry using parts of the Mainz Organic Mechanism (MOM) (Sander et al., 2011~~), excluding~~). Within MOM, aromatics and terpenes were excluded to reduce the computational demand of all simulations performed; this chemistry has no relevant impact on HNCO. The mechanism was extended to include the proposed changes of this study, formamide as an additional chemical source of ~~isocyanic acid~~HNCO (Bunkan et al., 2016), and chemical mechanisms for nitromethane (Calvert, 2008; Taylor et al., 1980), methylamine, dimethylamine and trimethylamine (Nielsen et al., 2012). The reaction rates used for the latter three are average values of the measured values reported in Nielsen et al. (2012). The product yields reported in the same source are simplified to suit a global model application. The submodel SCAV (SCAVenging submodel) was used to simulate the physical and chemical removal of trace gases and aerosol particles by clouds and precipitation (Tost et al., 2006). The aqueous phase mechanism was extended to include the ~~isocyanic acid~~HNCO and formamide mechanism proposed by Borduas et al. (2016b), Barnes et al. (2010), and Behar (1974). These lead to the formation to ammonia in the aqueous-phase, which was before limited to the acid-base equilibrium in cloud droplets. The representation of cyanide was improved based on Buechler et al. (1976). Table 1 and 2 in the supplementary material summaries all additional changes to the chemical mechanism in gas and aqueous phase, respectively. The submodel DDEP (Dry DEPosition) is used to simulate the dry deposition of HNCO, using the default scheme with non-stomatal uptake effectively not being considered by mean of a large and constant resistance (Kerkweg et al., 2006a). The effective Henry's law coefficient (H*) is used, as proposed by Borduas et al. (2016b), modified to a pH of 7. Differently from Young et al. (2012), the same H* over the ocean is used. This approximation is reasonable since the levels of HNCO in the marine boundary layer are expected to be minor. In a global context, the major sources of ~~isocyanic acid~~HNCO and formamide are biomass burning emissions. From literature two emission factors are available, which differ substantially: 0.53 g kg^{-1} (Koss et al., 2018~~;~~) versus 0.2 g kg^{-1} (Kumar et al., 2018~~) which differ substantially.~~). Thus two simulations are performed, to quantify the uncertainty in those emission factors. The MESSy submodel BIOBURN is used to calculate biomass burning fluxes based on the selected emission factor and Global Fire Assimilation System (GFAS) data. GFAS data are calculated based on fire radiative power observations from Moderate Resolution Imaging Spectroradiometer (MODIS) satellite instruments, which are used to calculate the dry matter combustion rates (Kaiser et al., 2012). The biomass burning emission fluxes are then obtained by combining these dry matter combustion rates with the defined biomass burning emission factors per unit of dry matter burned. The MESSy submodel OFFEMIS (~~OFFLine Emissions~~OFFline EMISsions) then calculates the resulting concentration changes for each tracer due to the biomass burning emissions (Kerkweg et al., ~~2006~~2006b). Anthropogenic ~~isocyanic acid~~HNCO emission from diesel cars are scaled to ammonia EDGAR (Crippa et al., 2016) road emission by 15% (Heeb et al., ~~2011).~~2011). Other known sources of HNCO (e.g. cigarette smoke) were not taken into account due to the resolution of the spatial grid used. The model was run for two years (2010-2011) in which the first year was used as spin up and 2011 for analysis. In 2010, the biomass burning emissions were particular high (Kaiser et al., 2012), providing higher background HNCO concentrations during spin up, improving the representation of HNCO which allows for a more representative comparison in 2011.

3 Loss processes by chemical oxidants

3.1 HNCO + OH

The reaction of ~~isocyanic acid~~HNCO with OH can proceed by 4 distinct pathways: H-abstraction, or OH addition on the carbon, nitrogen, or oxygen atom of HNCO; a potential energy surface is shown in Figure 1. Formation of the $HN{=}C^{\bullet}OOH$ and $HN(OH)C^{\bullet}{=}O$ adducts through OH-addition on the oxygen or nitrogen atom is highly endothermic by 20 kcal mol^{-1} or more, and is not competitive at any temperature. The two remaining pathways are exothermic, with $HN^{\bullet}C({=}O)OH$ being the most stable nascent product, ~~20~~19.8 kcal mol^{-1} below the reactants, followed by H_2O + $^{\bullet}N{=}C{=}O$, at 7.5 kcal mol^{-1} exoergicity. Despite the higher energy of the products, we predict this latter reaction to have a lower barrier, 6.0 kcal mol^{-1}, compared to the addition process, ~~9~~8.7 kcal mol^{-1}, in agreement with the theoretical predictions of Sengupta and Nguyen (1997). Furthermore, the H-abstraction process allows for faster tunneling, making this process the fastest reaction channel, while addition contributes less than 0.5% of product formation at temperatures below 400K. From this data, we derive the following rate coefficient expressions (see also Figure 2):

$$k_{OH}(298K) = 7.03\times10^{-16}\ cm^3\ molecule^{-1}\ s^{-1}$$

$$k_{OH}(200\text{-}450K) = 3.27\times10^{-34}\ T^{7.01}\ \exp(685K/T)\ cm^3\ molecule^{-1}\ s^{-1}$$

$$k_{OH}(300\text{-}3000K) = 1.79\times10^{-23}\ T^{3.48}\ \exp(-733K/T)\ cm^3\ molecule^{-1}\ s^{-1}$$

Our predictions are in very good agreement between 624-875K, when compared with experimental data from Tully et al. (1989), which served as the basis for the recommendation of Tsang (1992); our predictions reproduce the rate coefficients within a factor 1.7, comparable to the experimental uncertainty of a factor 1.5 (see Figure 2). Likewise, our predictions agree within a factor 1.7 with the experimental determination of Wooldridge et al. (1996), over the entire 620-1860 K temperature range. Our predictions overshoot the upper limit estimated by Mertens et al. (1992) by a factor of up to 4 at the upper end of the temperature range (2120 to 2500 K). At these elevated temperatures, it is expected that our theoretical kinetic ~~model is~~calculations are less accurate since anharmonicity, internal rotation, and possibly pressure effects are not fully accounted for. At this time, we choose not to invest the computational cost to improve the ~~model~~predictions at these temperatures. The predicted rate at room temperature is within a factor of 2 of the extrapolation of the recommended expression derived by Tsang (1992), k(298 K) $\approx 1.24\times10^{-15}$ cm^3 molecule^{-1} s^{-1}, and very close to the extrapolation of the expression by Wooldridge et al. (1996), 7.2×10^{-16} cm^3 molecule^{-1} s^{-1}. The good agreement of our rate coefficient with the experimental data extrapolated to room temperature is mainly due to the curvature predicted in the temperature-dependence (see Figure 2), as our calculations have a slightly steeper temperature dependence than the experiments in the high-temperature range. Though negligible at low temperature~~,~~, we find that OH addition on the C-atom of HNCO accounts for 7 to 8 % of the reaction rate between 2000 and 3000 K, with other non-H-abstraction channels remaining negligible (<0.1%). The addition channel is the likely origin of CO_2 + NH_2

products (Sengupta and Nguyen, 1997), for which Wooldridge et al. (1996) experimentally determined an upper limit ≤ 0.1 over the temperature range 1250-1860 K, corroborating our predictions to its low contribution.

Typical concentrations of the OH radical during daytime are measured at ~10^6 molecule cm^{-3} (Stone et al., 2012), leading to ~~an~~a pseudo-first order rate coefficient for HNCO loss by OH radicals of k(298K) = 7×10^{-10} s^{-1}, i.e. ~~a~~suggesting an atmospheric chemical lifetime of decades to several ~~decades~~centuries, depending on local temperature and OH concentration, negligible compared to other loss processes like scavenging. Even in extremely dry conditions, where aqueous uptake is slow, heterogeneous loss processes will dominate, or alternatively atmospheric mixing processes will transport HNCO to more humid environments where it will hydrolyze.

3.2 HNCO + Cl

From the potential energy surface (PES) shown in Figure 1, we see that the reaction between HNCO and Cl atom can occur by abstraction of the H atom from HNCO, or by addition of the Cl atom on the C-, N- or O-atoms. Contrary to the OH-reaction, all entrance reactions are endothermic, with formation of the HN$^{\bullet}$C(Cl)=O alkoxy radical nearly energy-neutral (see Figure 1). Formation of this latter product, proceeding by the addition of a Cl atom to the carbon atom of HNCO, also has the lowest energy barrier, 7.3 kcal mol^{-1} above the reactants. The hydrogen abstraction, forming HCl and $^{\bullet}$NCO, requires passing a higher barrier of 11.2 kcal mol^{-1}, whereas addition on the N- and O-atoms have very high barriers exceeding 34 kcal mol^{-1}. The product energy difference between addition and H-abstraction is much smaller compared to the HNCO + OH reaction~~, because of the absence of the stabilizing effect of the –COOH functionality in the Cl adduct. Despite this~~. Despite this reduced reaction energy, the addition barrier remains 4 kcal mol^{-1} below the H-abstraction barrier, making the HNCO + Cl reaction the only reaction studied here where H-abstraction is not dominant. For the HNCO + Cl reaction, we then obtain the following rate coefficients (see also Figure 3):

$$k_{Cl}(298K) = 3.19\times10^{-17}\ cm^3\ molecule^{-1}\ s^{-1}$$

$$k_{Cl}(200\text{-}450K) = 1.11\times10^{-17}\ T^{1.97}\ \exp(-3031K/T)\ cm^3\ molecule^{-1}\ s^{-1}$$

We find that the overall rate coefficient of the HNCO + Cl reaction is almost one order of magnitude below that for the OH radical. The HN$^{\bullet}$C(Cl)=O radical formed, however, has a weak C–Cl bond requiring only 5.4 kcal mol^{-1} to redissociate. The rate coefficient of 8×10^8 s^{-1} for dissociation at room temperature (k(T) = 8.3×10^{12} exp(-2760/T) s^{-1}), is over an order of magnitude faster than O_2 addition under atmospheric conditions, assuming the latter is equally fast as for $H_2C^{\bullet}CH{=}O$ vinoxy radicals, *i.e.* k(298K, 0.2 atm O_2) ≤ 10^7 s^{-1} (IUPAC Subcommittee on Atmospheric Chemical Kinetic Data Evaluation, 2017). This makes redissociation to the reactants the most likely fate of the HN$^{\bullet}$C(Cl)=O adduct. Addition is thus an ineffective channel for HNCO removal, and the effective reaction with Cl atoms is dominated by the H-abstraction reaction, forming HCl + $^{\bullet}$NCO, with the following rate coefficient (see also Figure 3):

$$k_{Cl,eff}(298K) = 2.23\times10^{-19}\ cm^3\ molecule^{-1}\ s^{-1}$$

$$k_{Cl,eff}(200\text{-}450K) = 1.01\times10^{-24}\ T^{4.40}\ \exp(-3799\ K/T)\ cm^3\ molecule^{-1}\ s^{-1}$$

Globally, Cl atoms have a lower concentration, about 5 × 10^3 atom cm^{-3}, compared to OH radicals (Finlayson-Pitts and Pitts, 1999). Under such conditions, lifetimes estimated for HNCO towards Cl atoms are about 3×10^7 years, which is much longer than toward the OH radial. Therefore, HNCO loss by Cl radicals is negligible.

The supporting information provides information on the extended potential energy surface of the HNCO + Cl reaction, with information on 9 intermediates, 19 transition states, and 16 products.

3.3 HNCO + NO_3

The reaction of NO_3 with HNCO shows the same four radical mechanisms found for OH and Cl, i.e. H-abstraction and addition on the 3 heavy atoms. As for Cl-atoms, none of the reactions are exothermic, and the energy difference between the two most stable products~~,~~ is reduced to 3 kcal mol^{-1}, indicating that NO_3 addition is even less favorable than Cl addition. Formation of HNO_3 + $^{\bullet}NCO$ is more favorable than HCl + NCO formation, by about 2 kcal mol^{-1}~~, owing to the greater stability of nitric acid.~~. The barrier for H-abstraction, however, is larger compared to abstraction by both OH and Cl, and exceeds 12 kcal mol^{-1}. The most favorable addition process, forming $HN^{\bullet}C(=O)NO_3$ has a barrier of 15.1 kcal mol^{-1}, but contributes less than 0.01% to the reaction rate at room temperature. The overall reaction thus proceeds near-exclusively by H-abstraction forming HNO_3 + $^{\bullet}NCO$, for which we derived the following rate coefficients (see also Figure 3):

$$k_{NO3}(298K) = 1.11\times10^{-21}\ cm^3\ molecule^{-1}\ s^{-1}$$

$$k_{NO3}(200\text{-}450K) = 8.87\times10^{-42}\ T^{9.06}\ \exp(-1585K/T)\ cm^3\ molecule^{-1}\ s^{-1}$$

While this rate coefficient is almost 5 orders of magnitude below that of the OH radical, the nitrate radical is known to be present in higher concentrations during night time, reaching concentrations as high as 10^9 molecule cm^{-3} (Finlayson-Pitts and Pitts, 1999). The effective rate of the NO_3 reaction at night time is similar to the reaction with OH at day time. The NO_3 radical is thus ~~still~~likewise considered to be ineffective for atmospheric removal of HNCO, compared to heterogeneous loss processes.

3.4 HNCO + O_3

The chemistry of ozone with organic compounds is drastically different from radicals, where O_3 typically reacts by cycloaddition on double bonds in unsaturated compounds. For ~~isocyanic acid~~HNCO, cycloaddition pathways have been characterized for both double bonds (HN=C=O). Only cycloaddition on the N=C bond leads to an exothermic reaction, with the oxo-ozonide product being 12 kcal mol^{-1} more stable than the reactants (see Figure 1). In addition to the traditional cycloaddition channels, three further channels were found, corresponding to H-abstraction, forming HO_3 + NCO, oxygen transfer to the N-atom, forming ON(H)CO + $^1O_2$, and addition on the C- and N-atom, forming HN(OO)C(O)O. The HO_3 product radical is known to be only weakly bonded by 2.94 kcal mol^{-1}, falling apart to OH + O_2 (Bartlett et al., 2019; Le Picard et al., 2010; Varandas, 2014).

The cyclo-addition channels on the hetero-double bonds have high energy barriers, exceeding 30 kcal mol^{-1}, significantly larger than typical barriers for C=C bonds with aliphatic substitutions. Surprisingly, this allows H-abstraction to become competitive to cycloaddition, with a comparable barrier of 32 kcal mol^{-1}. For the overall reaction, we obtain the following rate coefficients (see also Figure 3):

$$k_{O3}(298K) = 2.95\times10^{-37}\ cm^3\ molecule^{-1}\ s^{-1}$$

$$k_{O3}(200\text{-}450K) = 3.72\times10^{-23}\ T^{2.96}\ \exp(-14707K/T)\ cm^3\ molecule^{-1}\ s^{-1}$$

At room temperature, H-abstraction contributes 80% to the total reaction, and cycloaddition on the N=C bond the remaining 20%. All other channels are negligible. The rate coefficient is exceedingly low, ~10^{-37} cm^3 $molecule^{-1}$ s^{-1}, such that even in areas with very high ozone concentrations of 100 ppbv the loss by ozonolysis is expected to be negligible.

The supporting information provides information on the extended potential energy surface of the HNCO + O_3 reaction, with information on 10 intermediates, 30 transition states, and 15 products. The lowest-energy unimolecular product channel leads to formation of CO_2 + HNOO by breaking of the cyclic primary ozonide (see Figure 1) following the traditional Criegee mechanism (Criegee, 1975).

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4 H-abstraction reactions by NCO radicals

The radical reactions characterized above proceed by H-abstraction, forming the NCO radical with an H_2O, HNO_3, or HCl co-product. Likewise, the ozonolysis reaction proceeds for a large part by H-abstraction, forming NCO with a HO_2 coproduct that readily dissociates to OH + O_2. Though NCO radical formation through these reactions is found to be negligibly slow in atmospheric conditions, this radical remains of interest in other environments. Examples include combustion chemistry, where it can be formed directly from nitrogen-containing fuels, and where it is a critical radical intermediate in e.g. the RAPRENOx nitrogen-oxide mitigation strategy which employs HNCO introduced in the combustion mixture through $(HOCN)_3$ (cyanuric acid) injection (Fenimore, 1971; Gardiner, 2000). The NCO radical has also been observed in space (Marcelino et al., 2018). There is extensive experimental and theoretical information of the reactions of NCO radicals, tabulated e.g. in Tsang (1992), Baulch et al. (2005) and other works. To our knowledge, the rate coefficients of the reactions of NCO radicals with H_2O, HNO_3, and HCl have not been determined before, though Tsang (1992) has estimated a rate coefficient k(NCO + H_2O) = 3.9×10^{-19} $T^{2.1}$ exp(-3046K/T) cm^3 $molecule^{-1}$ s^{-1} based on the equilibrium constant and rate coefficient of the HNCO + OH reaction. Since the H–N bond in HNCO is quite strong, with a bond energy of ~110 kcal/mol (Ruscic, 2014; Ruscic and Bross, 2019), it is expected that NCO can readily abstract a hydrogen atom from most hydrogen-bearing species to produce HNCO, and that H-abstraction is the main reaction channel. Hence, despite that our potential energy surfaces do not include an exhaustive search of all possible reaction channels in the NCO radical chemistry, we expect that the single-channel H-abstraction rate predictions for NCO from H_2O, HNO_3 and HCl is sufficiently dominant that these rates are fair estimates of the total rate coefficients including all possible channels for each of these reactions.

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The energy barriers for the NCO radical reactions with H_2O, HNO_3 and HCl, being 14, 7, and 4 kcal mol^{-1} respectively (see Figure 1), follow the bond strength trend in these reactants, with D_0(H–OH) = 118 kcal mol^{-1}, D_0(H–NO_3) = 104 kcal mol^{-1}, and D_0(H–Cl) = 103 kcal mol^{-1} (Luo, 2007; Ruscic et al., 2002). Figure 1 also shows that the NCO + H_2O reaction is endothermic by 8 kcal mol^{-1}, while the HNO_3 and HCl paths are exothermic by -5 and -7 kcal mol^{-1}, respectively. The predicted rate coefficients are then:

$k_{NCO+H2O}(300K) = 1.36\times10^{-21}\ cm^3\ molecule^{-1}\ s^{-1}$

$k_{NCO+HNO3}(300K) = 3.37\times10^{-17}\ cm^3\ molecule^{-1}\ s^{-1}$

$k_{NCO+HCl}(300K) = 1.39\times10^{-14}\ cm^3\ molecule^{-1}\ s^{-1}$

$k_{NCO+H2O}(300\text{-}3000K) = 4.59\times10^{-24}\ T^{3.63}\ \exp(-4530K/T)\ cm^3\ molecule^{-1}\ s^{-1}$

$k_{NCO+HNO3}(300\text{-}3000K) = 7.18\times10^{-26}\ T^{4.21}\ \exp(-1273K/T)\ cm^3\ molecule^{-1}\ s^{-1}$

$$k_{NCO+HCl}(300\text{-}3000K) = 3.73\times10^{-20}\,T^{2.63}\,\exp(-662K/T)\ cm^3\ molecule^{-1}\ s^{-1}$$

The indirect estimate of Tsang (1992) compares well to our prediction for NCO + H_2O, reproducing our values within a factor 15 at 1000K and factor 3 at 2000K, i.e. within the stated uncertainties. An analysis of the impact of the NCO reactions in combustion or non-terrestrial environments is well outside the scope of this paper, and reactions with other co-reactants not discussed in this paper are likely to be of higher importance, e.g. H-abstraction from organic compounds, or recombination with other radicals. In atmospheric conditions, the fate of the NCO radical is likely recombination with an O_2 molecule, leaving H_2O, HNO_3, and HCl as negligible co-reactants. Hence, the NCO radical will not affect the atmospheric fate of any of these compounds to any extent. Subsequent chemistry of the $^{\bullet}$OONCO radical is assumed to be conversion to an $^{\bullet}$ONCO alkoxy radical through reactions with NO, HO_2 or RO_2, followed by dissociation to NO + CO.

5 Global impact

~~From our global~~Global atmospheric simulations~~, we~~ allow us to gain ~~many~~ insights on the ~~impact of the described mechanism (~~significance of the chemical loss processes of HNCO and its distribution. Table 1 shows the corresponding HNCO budget for both performed simulations. The full kinetic model including our theoretically predicted gas-phase chemical reactions of HNCO is detailed in Table 1 and 2 ~~in~~of the supplementary material~~) under atmospheric conditions.~~. Figure 4 shows the mean seasonal surface mixing ratio of ~~isocyanic acid~~HNCO using the biomass burning emission factors by Koss et al. (2018). It can be observed that high levels persist in each season. In general, high HNCO levels occur in regions associated with frequent biomass burning activities. Regions with no biomass burning activities have low HNCO concentrations, mainly caused by free tropospheric entrainment from regions with higher concentrations. ~~This becomes evident when taking into account~~The global vertical profile of HNCO is well illustrated by that for January as given in Figure 5, showing that the free troposphere contains about 81% of the total HNCO mass.

~~Table 1 shows the corresponding HCNO budget for both performed simulations.~~ The gas-phase production via formamide differs greatly ~~in relation to~~depending on the biomass burning emissions used. In the case of Kumar et al. (2018), significantly more formamide is emitted, leading to a higher production of ~~isocyanic acid in the gas phase. Gas phase chemical losses of HNCO are small, with only the reaction of HNCO with OH leading to some destruction of HNCO, while the other chemical sinks (O_3, NO_3 and Cl) are negligible. When compared to the major loss processes, however, all these loss processes are on a global scale negligible. The major sinks are dry deposition and scavenging (heterogeneous losses), where the latter contributes 274.60 and 377.19 Gg/year when using the emission factors by Koss et al.~~ HNCO in the gas phase. The hydrolysis of HNCO produces ~120 Tg/yr of ammonia, thus contributing little to the global ammonia budget. Our estimate is a factor 5-6 lower than the upper limit estimated by Leslie et al. (2019).~~(2018) and Kumar et al. (2018), respectively. Therefore, it can be concluded that the gas-phase chemical sinks analysed in this study (OH, Cl, NO_3, O_3) can be considered to be insignificant when compared to heterogeneous loss processes. This is independent of the high uncertainty in the available biomass burning emission factors or missing road emission datasets. The results in this study are in a similar order as the modelling study by Young et al. (2012). These authors have lower total HNCO emissions and do not include formamide as a secondary source of HNCO. They still have a higher chemical loss via OH,~~

~~which is due to a higher rate constant used. The lifetime is still higher due to generally lower heterogeneous loss terms.~~

The model predictions for OH radical concentrations range from 1.15×10^{0} to 1.56×10^{7} molecule cm^{-3}, with a weighted atmospheric global average of 1.14×10^{6} molecule cm^{-3}; in the air parcel where the highest OH concentration is found this leads to an HNCO lifetime towards OH of more than 500 years when accounting for the temperature-dependent rate coefficient (~276K). In the planetary boundary layer, the highest OH concentration predicted is 7.6×10^{6} molecule cm^{-3} at a temperature of 297.8K, leading to an HNCO lifetime to OH of ~6 years in that air parcel. The calculated average OH concentration of 1.20×10^{6} molecule cm^{-3} in the boundary layer leads to lifetimes towards OH of about 40 years near the surface. For O_3, Cl, and NO_3, with maximum oxidant concentrations of 1.0×10^{13}, 7.8×10^{5}, 1.5×10^{9} molecule cm^{-3}, and atmospheric average concentrations of 1.0×10^{12}, 2.0×10^{3}, 1.1×10^{7} molecule cm^{-3}, respectively, even longer temperature-dependent lifetimes are found, exceeding 5000 years even in the airparcels with the most favourable co-reactant concentration and temperature. The relative contributions of the different co-reactants varies locally and temporally, and shorter lifetimes might occur locally when co-reactant concentration and temperature are at their most favourable, but it is clear that gas phase chemical losses of HNCO are small. Only the reaction of HNCO with OH leads to some destruction of HNCO, while the other chemical sinks (O_3, NO_3 and Cl) are negligible. When compared to the major loss processes, however, all these loss processes are on a global scale negligible (see Table 1). Young et al. (2012) have a somewhat higher chemical loss via OH compared to our result, which is due to the higher rate constant used. Figure 2 shows the rate coefficient that would be required to allow the gas phase loss of HNCO by reaction with OH radicals to contribute 10% of the total atmospheric sink, which is well outside the expected uncertainty of the theoretical kinetic rate predictions. It can therefore be robustly concluded that the gas-phase chemical sinks predicted and assessed in this study (OH, Cl, NO_3, O_3) are insignificant when compared to heterogeneous loss processes, confirming earlier assumptions. This is independent of the high uncertainty in the available biomass burning emission factors or missing road emission datasets.

As seen in Table 1 the major sinks are dry deposition and scavenging (heterogeneous losses), where the former contributes between 2519.61 and 2891.85 Gg/year, and the latter from 274.60 to 377.19 Gg/year, when using the emission factors by Koss et al. (2018) and Kumar et al. (2018), respectively. The results in this study are in a similar range as the modelling study by Young et al. (2012). These authors had lower total HNCO emissions and did not include formamide as a secondary source of HNCO. The lower total HNCO emissions could be explained by a different year simulated in that study and different biomass burning emission model approaches used. Young et al. (2012) also scaled their HNCO emissions to the HCN emissions by a factor of 0.3, whereas in this study actual measured emission factors are used. In our study, formamide contributes between 17.16% and 70.46% of the total HNCO emissions when using the biomass burning emission factors by Koss et al. (2018) and Kumar et al. (2018) respectively. Young et al. (2012) find a higher HNCO lifetime due to generally lower total heterogeneous loss terms (dry and wet deposition). The total dry deposition varies slightly depending on the biomass burning emission factor used (see Table 1). In both scenarios, most HNCO is deposited over the ocean. For biomass burning emission factors from Koss et al. (2018) this contribution, 53.3%, is significantly lower when compared to the simulation using emission factors from Kumar et al. (2018), where about 62.5% of the total HNCO deposition is deposited over the ocean. The larger fraction of computed HNCO deposition over the ocean is a consequence of the much larger secondary HNCO production from formamide far from its source regions (continents). Young et al. (2012) found that the importance of both heterogeneous loss processes depends on the clouds pH. In the SCAV submodel, as used in this work, cloud droplet pH is calculated online and includes an explicit hydrolysis scheme for HNCO, whereas Young et al. (2012) used a simplified approach. The relative importance of dry deposition is higher in the simulation in which Young et al. (2012) calculated pH online, when compared to the findings in this study.

The atmospheric lifetime of HNCO is dominated by its heterogeneous loss processes, leading to an atmospheric lifetime of multiple weeks~~, whereasthe~~ when accounting for all HNCO losses (chemical and heterogeneous), as opposed to a gas-phase lifetime in the free troposphere ~~is~~of about 50 years when calculated solely based on the chemical losses towards the four chemical oxidants described in this study. This long gas-phase lifetime and the fact that mainly surface sources are relevant indicate that atmospheric HNCO distribution is ~~highly impacted~~significantly affected by transport processes. Our simulations even show that HNCO is transported from the surface into the UTLS ~~(upper troposphere/lower stratosphere)~~ and that about 10% of the total atmospheric HNCO mass is located in the stratosphere~~,~~ (see Figure 5), with modelled concentrations of HNCO in the lower stratosphere of typically tens of pptv but reaching up to hundred pptv in tropical regions. ~~Since~~In the chemical model, photolysis in the stratosphere was not taken into account. Thus, OH is the only significant stratospheric sink~~, the~~ included, resulting in a stratospheric lifetime ~~increases to~~of more than 330 years. During the monsoon period, the total stratospheric HNCO mass increases from 15.04 Gg before, to 19.75 Gg at the end of monsoon season. Pumphrey et al. (2018) demonstrated that in 2015 and 2016, elevated levels of stratospheric hydrogen cyanide (HCN) can be linked to biomass burning emissions from Indonesian fires. ~~Similar to HNCO in our simulations,~~Figure 5 shows the vertical profiles of HCN and HNCO over South East Asia well before (January) and after (November) the Indian monsoon. It becomes evident that, similar to HNCO in our simulations, tropospheric and stratospheric concentrations of HCN increase during the Indian monsoon period. In the performed simulations, the ratio between stratospheric HCN and HNCO is very similar throughout the year, indicating that HCN and HNCO are similarly affected by transport processes within this period. The combination of strong biomass burning events and strong vertical transport during the monsoon period leads to high HNCO concentrations in the UTLS, indicating that pollutants from biomass burning events could potentially influence stratospheric chemistry.

Figure 6 shows the number of days exceeding a daily mean HNCO concentration of 1 ppbv. Mainly regions impacted by biomass burning events have frequent concentration above this threshold. When using 10~~-~~ ppbv as limit for toxic concentrations of HNCO, as proposed by the Swedish work environment authority (SWEA, 2011), only a few days can be observed in which this limit is exceeded. The maximum number of days exceeding 10 ppbv is 10 days over Africa, compared to 120 days above 1 ppbv. It is important to take into account that this analysis is limited by the computational output available in this study, which has only daily averages. Therefore, it is expected that areas which frequently exceed daily averages of 1 ppbv are potentially areas in which peak HNCO can be observed above 10 ppbv throughout the day.

No correlation exists between the number of days exceeding 1 or 10 ppbv and road traffic emissions. This becomes evident since typical areas of high road traffic activities (i.e. USA and Europe) do not exceed daily averages of 1 ppbv (see~~ Figure 5).~~Figure 6). Road traffic activities occur on a smaller spatial scale than biomass burning events. The EMAC model used is not capable to represent, for example, inner city road traffic activities, due to the spatial resolution of the model used (1.875 by 1.875 degrees in latitude and longitude). Therefore, we are not capable to draw any conclusion if 10 ppbv is exceeded regionally in densely populated areas, impacted by high traffic emissions.

~~. Biomass burning emission factors are based on Koss et al. (2018)~~

~~5 H-abstraction reactions by NCO radicals~~

~~The radical reactions characterized above proceed by H-abstraction, forming the NCO radical with an H_2O, HNO_3, or HCl co-product. Likewise, the ozonolysis reaction proceeds for a large part by H-abstraction, forming NCO with a HO_3 coproduct that readily dissociates to OH + O_2. Though NCO radical formation through these reactions is found to be negligibly slow in atmospheric conditions, this radical remains of interest in other environments. Examples include combustion chemistry, where it can be formed directly from nitrogen-containing fuels, and where it is a critical radical intermediate in e.g. the RAPRENOx nitrogen-oxide mitigation strategy (Fenimore, 1971; Gardiner, 2000). The NCO radical has also been observed in space (Marcelino et al., 2018). There is extensive experimental and theoretical information of the reactions of NCO radicals, tabulated e.g. in Tsang (1992), Baulch et al. (2005) and other works. To our knowledge, the rate coefficients of the reactions of NCO radicals with H_2O, HNO_3, and HCl have not been determined before, though Tsang (1992) has estimated a rate coefficient k(NCO + H_2O) = 3.9×10^{-19} $T^{2.1}$ exp(-3046K/T) cm^3 $molecule^{-1}$ s^{-1} based on the equilibrium constant and rate coefficient of the HNCO + OH reaction. Since the H–N bond in HNCO is quite strong, with a bond energy of ~110 kcal/mol (Ruscic, 2014; Ruscic and Bross, 2019), it is expected that NCO can readily abstract a hydrogen atom from most hydrogen-bearing species to produce HNCO, and that H-abstraction is the main reaction channel. Hence, despite that our potential energy surfaces do not include an exhaustive search of the NCO radical chemistry, we expect that predictions of the H-abstraction rate for NCO from H_2O, HNO_3 and HCl are fair estimates of the total rate coefficients of these reactions.~~

~~The energy barriers for the NCO radical reactions with H_2O, HNO_3 and HCl, being 14, 7, and 4 kcal mol^{-1} respectively (see Figure 1), follow the bond strength trend in these reactants, with D_0(H–OH) = 118 kcal mol^{-1}, D_0(H–NO_3) = 104 kcal mol^{-1}, and D_0(H–Cl) = 103 kcal mol^{-1} (Luo, 2007; Ruscic et al., 2002). Figure 1 also shows that the NCO + H_2O reaction is endothermic by 8 kcal mol^{-1}, while the HNO_3 and HCl paths are exothermic by -5 and -7 kcal mol^{-1}, respectively. The predicted rate coefficients are then:~~

~~$k_{NCO+H2O}(300K) = 1.36\times10^{-21}\ cm^3\ molecule^{-1}\ s^{-1}$~~

~~$k_{NCO+HNO3}(300K) = 3.37\times10^{-17}\ cm^3\ molecule^{-1}\ s^{-1}$~~

~~$k_{NCO+HCl}(300K) = 1.39\times10^{-14}\ cm^3\ molecule^{-1}\ s^{-1}$~~

~~$k_{NCO+H2O}(300\text{-}3000K) = 4.59\times10^{-24}\ T^{3.63}\ \exp(-4530K/T)\ cm^3\ molecule^{-1}\ s^{-1}$~~

~~$k_{NCO+HNO3}(300\text{-}3000K) = 7.18\times10^{-26}\ T^{4.21}\ \exp(-1273K/T)\ cm^3\ molecule^{-1}\ s^{-1}$~~

~~$k_{NCO+HCl}(300\text{-}3000K) = 3.73\times10^{-20}\ T^{2.63}\ \exp(-662K/T)\ cm^3\ molecule^{-1}\ s^{-1}$~~

~~The indirect estimate of Tsang (1992) compares well to our prediction for NCO + H_2O, reproducing our values within a factor 15 at 1000K and factor 3 at 2000K, i.e. within the stated uncertainties. An analysis of the impact of the NCO reactions in combustion or non-terrestrial environments is well outside the scope of this paper, and reactions with other co-reactants not discussed in this paper are likely to be of higher importance, e.g. H-~~

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~~abstraction from organic compounds, or recombination with other radicals. In atmospheric conditions, the fate of the NCO radical is likely recombination with an O_2 molecule, leaving H_2O, HNO_3, and HCl as negligible co-reactants. Hence, the NCO radical will not affect the atmospheric fate of any of these compounds to any extent. Subsequent chemistry of the •OONCO radical is assumed to be conversion to an •ONCO alkoxy radical through reactions with NO, HO_2 or RO_2, followed by dissociation to NO + CO.~~

6 Conclusions

The isocyanic acid molecule, HNCO, is found to be chemically ~~fairly~~ unreactive towards the dominant atmospheric gas phase oxidants, i.e. OH and NO_3 radicals, Cl atoms, and O_3 molecules. The reactions all ~~occur~~remove HNCO predominantly by H-abstraction, and have ~~comparatively~~ low rates of reactions with $k(298) \leq 7\times10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}, leading to chemical gas phase lifetimes of decades~~.~~ to centuries. Yearly loss of HNCO towards these reactants is only ~5 Gg/y~~.~~ out of ~3000 Gg/y total losses. Removal of HNCO by clouds and precipitation ("scavenging"), ~~leading to~~with hydrolysis to ammonia, is also implemented in the global model, and was found to contribute significantly more, ~300 Gg/y, than the gas phase loss processes. Still, these combined processes are overwhelmed by the loss of HNCO by dry deposition, removing ~2700 Gg/y. These conclusions are robust against modifications of the emission scenarios, where two distinct sets of emission factors were used, incorporating HNCO formation from biomass burning, as well as anthropogenic sources such as formamide oxidation and road traffic. The inefficiency of gas-phase chemical loss processes confirms earlier assumptions; inclusion of the gas-phase chemical loss processes in kinetic models appears superfluous except in specific experimental conditions with very high co-reactant concentrations. The long gas-phase chemical lifetime (multiple decades to centuries) allows HNCO to be transported efficiently into the UTLS demonstrating that surface emissions may impact the upper troposphere. Further research is necessary to identify the importance of strong biomass burning events coupled to strong vertical transport processes (i.e. monsoon systems) on the chemical composition of the UTLS.

On a global scale, the daily average concentrations of HNCO rarely exceed 10 ppbv, the threshold assumed here for toxicity; the exceedances are mainly located in regions with strong biomass burning emissions. Average daily concentrations of the order of 1 ppbv are encountered more frequently, with about 1/3th of the year exceeding this limit. This suggests that local concentrations might peak to much higher values, e.g. in urban environments where road traffic emissions are highest, or in the downwind plume of biomass burning events, and could impact regional air quality. Such regional effects were not studied in the current work, as the resolution of the global model used here is not sufficiently fine-grained.

Though not important for the atmosphere, we briefly examined the reactions of the NCO radical formed in the chemical reactions studied. The rate coefficients of the H-abstraction reactions with H_2O, HNO_3 and HCl suggest that these reactions might contribute in high-temperature environments, such as combustion processes.

Supplement

The supplement related to this article is available online, and contains extended information on the chemical model, and the quantum chemical characterizations (geometric, energetic and entropic data)

Author contributions

The quantum chemical calculations where performed by H.M.T. Nguyen, G.H.T. Vu, and T.V. Pham, while L. Vereecken performed the theoretical kinetic calculations. U. Javed, S. Rosanka and D. Taraborrelli collected the literature data on HNCO sources and sinks, and implemented these in the kinetic model; the model runs were performed by S. Rosanka and D. Taraborrelli. All authors contributed significantly to the writing of the manuscript.

Competing interests

The authors declare that they have no conflict of interest.

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Table 1: Yearly global HNCO budget in 2011 for both biomass burning emission datasets by Kumar et al. (2018) and Koss et al. (2018). Additionally, the HNCO budget from Young et al. (2012) is given for comparison.

	Simulations in this study based on emission factors from:		Comparable literature:
	Koss et al., 2018	**Kumar et al., 2018**	**Young et al., 2012**
Emissions [Gg/year]			
Biomass burning (HNCO)	2158.94	814.69	661.00
Anthropogenic (HNCO)	177.14	177.14	828.00
Gas phase production [Gg/year]			
$NH_2CHO + OH$	482.52^a	2365.53^b	-
Gas phase loss [Gg/year]			
HNCO + OH	3.98	5.41	~ 5.96
$HNCO + O_3$	1.88×10^{-16}	2.37×10^{-16}	-
$HNCO + NO_3$	1.15×10^{-4}	1.43×10^{-4}	-
HNCO + Cl	9.99×10^{-8}	1.37×10^{-7}	-
Heterogeneous losses [Gg/year]			
Dry deposition	2519.61	2891.85	~ 1421.99
Over land	1174.92	1086.13	-
Over ocean	1344.69	1805.72	-
Scavenging	274.60	377.19	-
Wet deposition	0.13	0.16	~ 67.01
Yearly mean burden [Gg]	201.15	271.94	~ 150.00
Atmospheric lifetime [days]	26.24	30.31	36.62

[a] Of which 50.59 Gg/year NH_2CHO biomass burning emissions (Koss et al., 2018)

[b] Of which 2335.01 Gg/year NH_2CHO biomass burning emissions (Kumar et al., 2018)

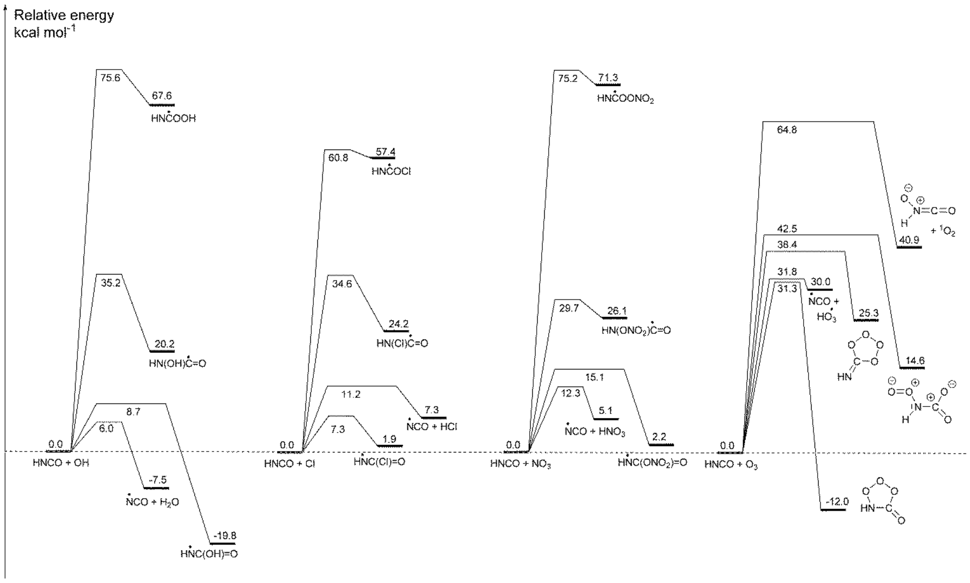

Figure 1: Potential energy surfaces for the initiation reactions of HNCO with OH radicals, Cl atoms, NO_3 radicals, and ozone, showing CCSD(T)/CBS(DTQ) energies (kcal mol^{-1}) based on M06-2X/aug-cc-pVTZ geometries. The pre-reactive complexes are omitted as they do not influence the kinetics,; similarly, the subsequent reactions of the products are not shown. The supporting information has additional energetic and rovibrational data, more complete potential energy surfaces for some of the reactions, as well as three-dimensional representations of the molecular structure with bond lengths and angles.

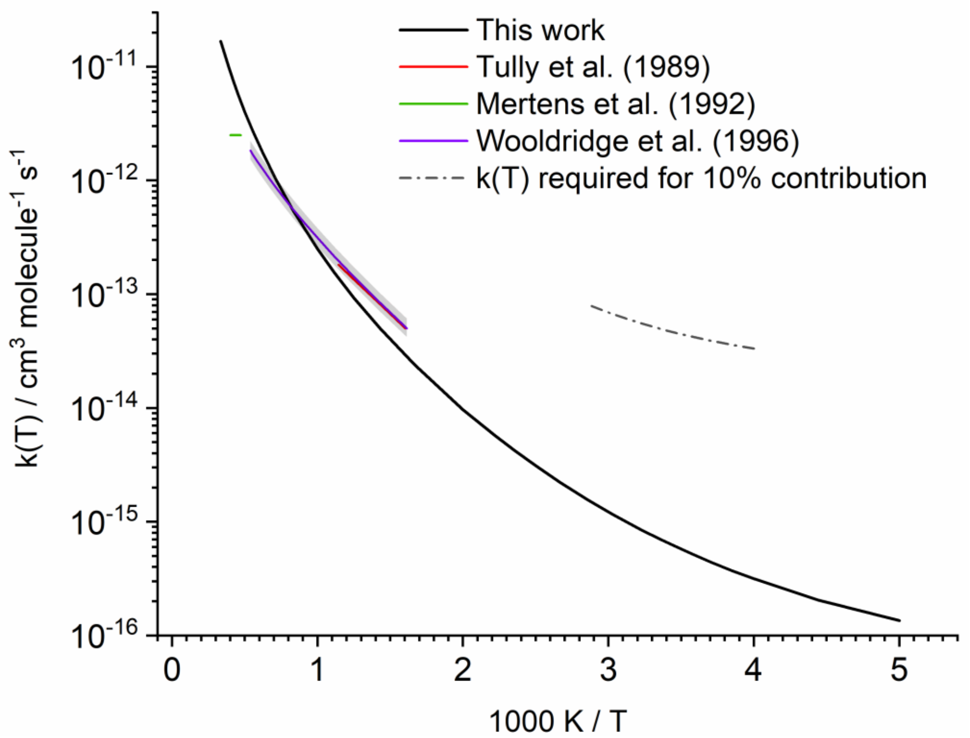

Figure 2: Predicted rate coefficient k(T) for the reaction of HNCO + OH, compared against experimental data. The shaded area indicates the experimental uncertainty reported by Wooldridge et al. (1996). The dashed line estimates the 298 K rate coefficient that would be needed to remove 10% of the atmospheric HNCO by reaction with OH (see text).

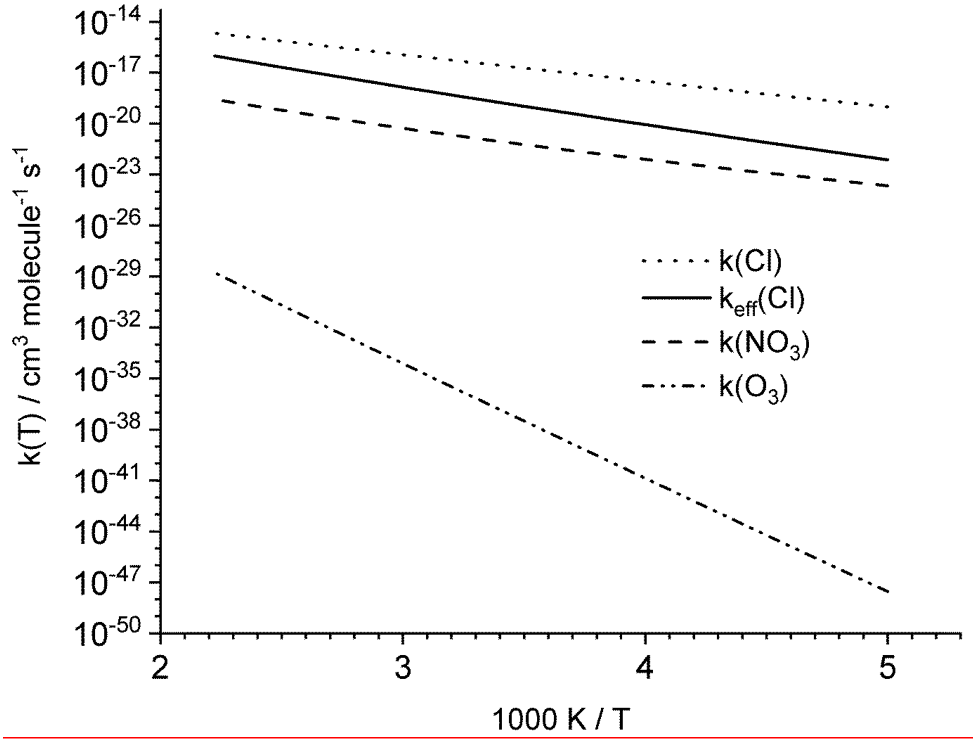

Figure 3: Total rate coefficient predictions for the reaction of HNCO with NO_3, Cl and O_3. The addition of Cl atoms on HNCO leads to the formation of a very short-lived adduct, which rapidly redissociates to the reactants; the effective rate coefficient for HNCO loss by Cl atoms, k_{eff}(Cl), is thus equal to the H-abstraction rate forming HCl + NCO (see text).

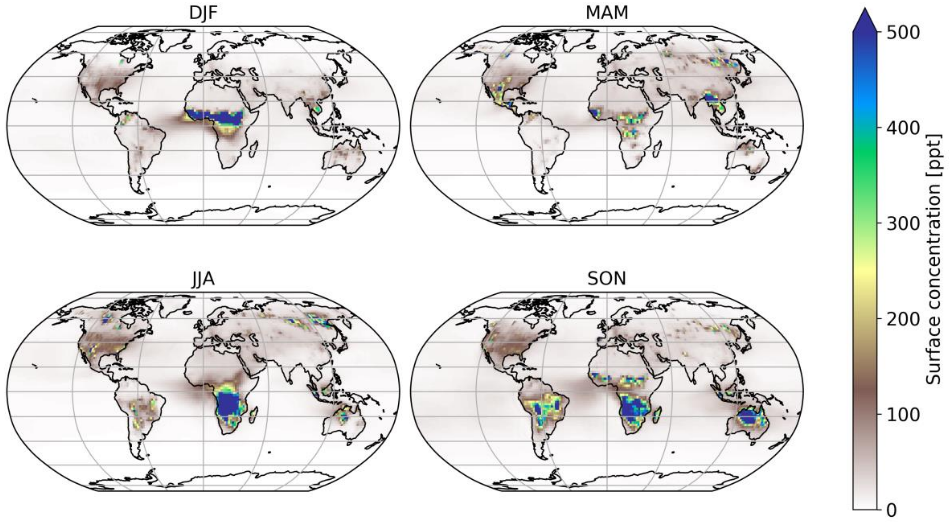

Figure 4: Mean seasonal surface concentration of HNCO using Koss et al. (2018) biomass burning emission factors.

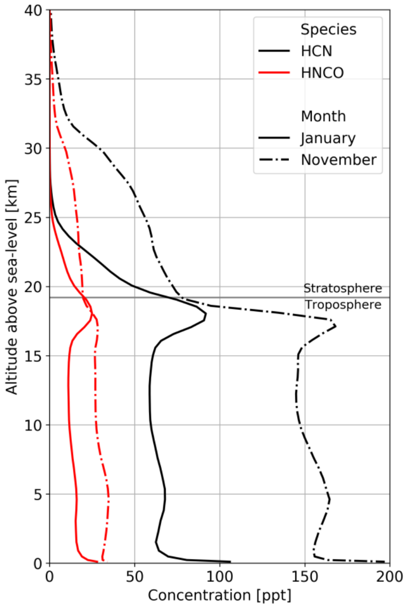

Figure 5: Mean vertical profiles of HCN (black) and HNCO (red) for January (solid lines) and November (dash-dotted lines) over South East Asia. Biomass burning emission factors are based on Koss et al. (2018)

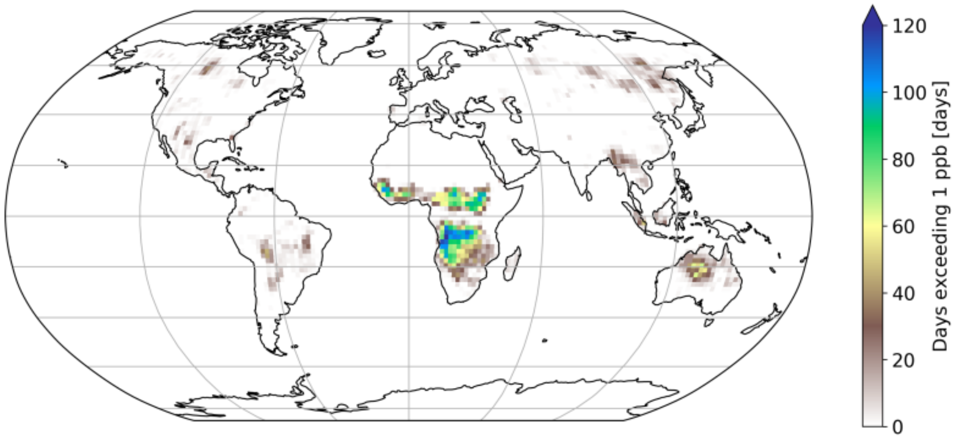

Figure 6: Number of days exceeding 1 ppb of HNCO at the surface. Biomass burning emission factors are based on Koss et al. (2018)