Interactive comment on "Solubility and reactivity of HNCO in water: insights into HNCO's fate in the atmosphere" by N. Borduas et al.
Anonymous Referee #2
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This paper discusses the measurements of the effective Henry's law constant and true Henry's law constant for HNCO by acetate ion CIMS, as well as the hydrolysis rate constants for the three decomposition pathways of HNCO using ion chromatography. Additionally, they determine the pH dependence and temperature dependence of these parameters and use this information to determine the likely lifetime of HNCO over a range of atmospherically-relevant temperatures, pH values, and aerosol/fog/cloud liquid water contents. They find that based on their measurements, the lifetime of HNCO will likely be a longer-lived species than previously thought and exposure might be higher than previously predicted. I found this to be a nicely-written, very thorough paper and recommend that it be published in ACP after addressing the minor comments below.

Comments:
Abstract: The effective Henry's law constant is more atmospherically-relevant than the true Henry's law constant because it encompasses any additional solubility due to the ability of HNCO to possibly hydrate, and to dissociate in the aqueous phase. Therefore, KHeff should be given in the abstract either instead or in addition to KH.

> Agreed. In addition to K_H, K_H^{eff} is now also given at 298 K and pH3. We thank the reviewer for this recommendation.
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> The abstract now reads, "By conducting experiments at different pH values and temperature, a Henry's Law coefficient K_H of 26 ± 2 M atm^{-1} is obtained, with an enthalpy of dissolution of -34 ± 2 kJ mol^{-1}, which translates to a K_H^{eff} of 31 M atm^{-1} at 298 K and at pH 3."

Equation 1: The effective Henry's law constants for small aldehydes such as glyoxal and methylglyoxal incorporate the fact that the carbonyl groups can hydrate to diol groups. HNCO also has such a carbonyl group so the authors may wish to consider that there may be additional processes beyond just pH dependence that determine KHeff .

> HNCO has two π-bond systems and so its reactivity is different than a carbonyl group. In fact, water reacts with HNCO irreversibly rather than form diols like aldehydes (see page 24221, line 4). Once water adds to the C in HNCO, carbamic acid is formed which then decomposes to NH_3 and CO_2.

Section 2.1: A very brief overview paragraph with an overview of the experimental work should be added here prior to section 2.1.1. This will provide some context for the "The CIMS was built in house :" sentence of section 2.1.1.

> Good suggestion! A one sentence description was added, which reads, "To measure the effective Henry's Law coefficient K_H^{eff} of HNCO, we use a bubbler column experimental set

> up and detect HNCO through chemical ionization mass spectrometry." We also did the same for section 2.2.1.

Section 2.1.1: Are the detection limits and sensitivity of HNCO known for acetate CIMS? Why was the acetic anhydride flow passed through a Po-210 radioactive source? You mention that the CIMS monitored 10 m/z values, and then later say that NCO- is detected at m/z 42. Were other m/z values monitored, and if so which ones and why?

> Detection limits and sensitivities for HNCO will depend on the CIMS instrument used. For this work, we did not need to calibrate for HNCO as we report relative kinetics. Background HNCO counts are about 5×10^{-4} ncps, whereas we were operating at HNCO signals ~ 0.1 ncps. (The background counts were added to the text on page 24223, line 16.)
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> Acetic anhydride was passed through a Po-210 radioactive source to generate AcO-, the reagent ion. This reason was added to the sentence in the text.
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> Other ions measured included m/z 59 (CH_3COO^-), m/z 119 ((CH_3COOH)CH_3COO^-)), m/z 51 (black count), m/z 35 (Cl-), m/z 45 (HCOOH), m/z 46 (HONO), m/z 96, m/z 102 and m/z 113. None of these ions was observed to change during the experiments and they were monitored to ensure the CIMS was operating correctly. This list of ions was added to the text after line 12.

Section 2.1.2: What was the disodium phosphate concentration in your buffer? There is recent evidence that the solubility of organic molecules is modulated by salt concentration (e.g. Kampf et al. 2013, Endo et al. 2012, Wang et al. 2014, and Waxman et al. 2015). These effects are more pronounced at the higher salt concentrations typically found in aerosols. Is your phosphate concentration high enough to impact the solubility of HNCO?

> The buffer solutions for the KH experiments were made with solid citric acid, disodium phosphate and deionized water with citric acid concentrations ranging from 0.02 M to 0.0035 M to access a pH range of 2.5-4.0 (page 24223, line 14). The buffer solutions for the hydrolysis experiments were all below 0.002 M. We believe that at these concentrations, the ionic strength of the solution is low enough to have minimal impact on the solubility of HNCO. However, the salting out effect for HNCO remains to be investigated.
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> Clarification was added to the text, which now reads, "All buffer concentrations were < 0.002 M, and we assume that the ionic strength of these solutions had minimal impact on the solubility of HNCO."

Page 24223, lines 8-10: You state that the absolute gas phase concentration of HNCO is not required. This statement makes perfect sense once one has read the Results and Discussion section, but is confusing here as the reader will likely be assuming that you measure aqueous phase concentration and gas phase concentration to calculate M/atm. You could consider adding an additional sentence or two to elaborate on your analysis method to explain why this value is not necessary.

> Good point. The sentence now reads, “the absolute concentration of gas-phase HNCO is not required in this approach since it relies on the decay of the signal, $[HNCO]_t/[HNCO]_0$ and not on the absolute gas phase and aqueous phase concentrations.”

Figures 3 and 4: Why show all measurements rather than average the measurements and propagate the error bars where you have multiple measurements?

> Each point in these figures show a K_H^{eff} determined using 5 different flows at the same pH and same temperature. Each point cannot be averaged as they were determined at different pH and temperatures.

References cited:
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Wang, C.; Lei, Y. D.; Endo, S.; Wania, F.Measuring and Modeling the Salting-out Effect in Ammonium Sulfate Solutions Environ. Sci. Technol. 2014, 48 (22) 13238– 13245, DOI: 10.1021/es5035602

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