

Author response to Reviewer 1:

We thank Reviewer 1 for their thoughtful comments and suggestions.

General Comments:

The paper is too long and could be reduced by about 1/3 without any loss of and significant content.

We have shortened the manuscript by roughly 3 pages total by reducing repetition. Most of the reductions are in the results and conclusions sections, but we have made the introduction and methods section more concise as well. A novel approach is used in this study to assess photochemistry in mid-latitude regions. Since this approach relies heavily on both optical and chemical models and measurements, and is the first of its kind, we feel that it is appropriate to include thorough descriptions of the approach. We leave it to the editor to decide if we should shorten further by reducing content.

The measurements presented here lack context. For example we are not given any summary of what the level of total odd-nitrogen (NO_y) was [Wild et al., 2016], we were not told of the presence of high levels of peroxyntic acid [Veres et al., 2015], nor N₂O₅, nor ClNO₂, all species that might have significant impact on snow pack nitrate.

We have now added a section in the introduction that summarizes the reactive nitrogen and odd-nitrogen measurements in the Uintah Basin by Veres et al. [2015] and Wild et al. [2016].

Interestingly, there is also nitrite in the snow in the Uintah Basin, although at much lower levels than nitrate.

We now present our snow nitrite concentration measurements in Supplemental Material Figure 4A. Snow nitrite concentrations range from 0-14 ng g⁻¹, and are at least 3 to 5 orders of magnitude smaller than snow nitrate concentrations.

The arguments made about how reactive N sources changed with the various events seem weak, but could be made much stronger if the authors took advantage of the extensive measurements of gas phase N species made during this study.

We now use gas-phase N species measurements along with NOAA hysplit back trajectories to shed light on N-source changes during UBWOS2014, which further supports our hypothesis that the depleted $\delta^{15}\text{N}(\text{NO}_3^-)$ measurements at the snow surface on January 31 originated from deposition of nitrate formed outside the polluted Uintah basin. We've also included some additional discussion in the introduction and in section 3.1.1.

There are some gas-phase N species measurements with minimum daily-maximum mixing ratios immediately following the snow event on January 30/January 31. For example, Figure 7 in Veres et al. [2015] suggests that daily-maximum HO₂NO₂ mixing ratios during UBWOS2014 were relatively low after the snow event on January 30 and January 31, also corresponding to a sharp decrease in snow nitrite concentrations. In this manuscript, Figure 1B in Supplementary Material shows that daily-maximum gas and aerosol phase nitrate mixing ratios were also lowest immediately following the snow event.

Two-day NOAA HYSPLIT trajectories show that the air mass in the Uintah Basin on January 31 originated from the Pacific Ocean, which is distinctly different from the other air masses that reached the Uintah Basin during UBWOS2014 (see Supplemental Material, Figures 4B-15B). The large majority of air masses in the Uintah Basin during UBWOS2014 originated in the intermountain west and often centered over eastern Utah for several days.

Related to this, the authors refer several times to light or depleted N in background air. Is this a well-known aspect, or is there a hidden assumption at work here?

There have been a number of field campaigns designed to measure $\delta^{15}\text{N}$ of nitrate in ambient air. Morin et al. [2009] is an especially comprehensive study of background $\delta^{15}\text{N}$ that reports $\delta^{15}\text{N}$ measurements from many unpolluted regions in both the northern and southern hemisphere. The observation in Morin et al. [2009] show lighter $\delta^{15}\text{N}$ values in cleaner air masses, and heavier $\delta^{15}\text{N}$ values in more polluted air masses. This is mentioned in the manuscript near the end of the introduction.

It seems from the introduction, and references therein, that biological activity could also produce the same fractionation as the photolysis effect modeled here. Could the authors please explain how they have discounted this effect?

We have now added the following two sentences to the end of section 3.1.2:

“Emissions of microbial NO from subnival soil could also lead to depleted $\delta^{15}\text{N}(\text{NO}_3^-)$ if this NO is oxidized to nitrate in the snowpack and deposited to the surface of snow grains before escaping to the atmosphere. However, the depleted $\delta^{15}\text{N}(\text{NO}_3^-)$ would also likely correspond with enhanced nitrate concentrations, which is not observed (Figures 3a-c). Additionally, calculations by Zatko et al. [2013] suggest that the lifetime of NO_x against oxidation to HNO₃ in snow interstitial air is long enough so that most NO emitted from soil microbial activity would likely be transported to the atmospheric boundary layer prior to oxidation.”

Several places in the discussion the authors say that re-deposition of “light” nitrate accounts for the top layers seen in some profiles. This seems at odds

with the conclusion that snow-derived light N is a small fraction of the reactive nitrogen source to the basin.

The re-deposition of isotopically-light nitrate is mentioned in the last paragraph of section 3.2.2. These lines describe a sensitivity study in which we have varied the quantum yield for nitrate photolysis (ϕ) in TRANSITS until there is a significant deviation between measured and modeled $\delta^{15}\text{N}(\text{NO}_3^-)$ profiles in snow. When $\phi = 0.2$, the model suggests that there is re-deposition of isotopically-light nitrate to the snow surface and enrichment in $\delta^{15}\text{N}(\text{NO}_3^-)$ with depth. When $\phi = 0.2$, the emissions of N_r from snow are still at least 7 times smaller compared to the N_r emissions from other sources within the Uintah Basin.

When the upper limit of ϕ is replaced with a more realistic ϕ in TRANSITS, there is considerably less re-deposition of isotopically-light nitrate to the snow surface in the Uintah Basin. Additionally, our measurements suggest that the $\delta^{15}\text{N}(\text{NO}_3^-)$ signature in the surface-snow layers is dominated by the deposition of nitrate from primary sources in the basin, and from sources beyond the basin during snow events.

Specific Comments

Line 61: “source of snow-sourced N_r ” seems a bit awkward, how about just “source of N_r ”, you’ve already said it’s from the snow.

We have removed “snow-sourced” from this sentence.

Line 99: O_3 precursor emissions aren’t necessarily higher in the summer. It is usually the stagnant summer high pressure events that contribute by limiting advection.

This sentence now reads:

“Maximum boundary layer O_3 concentrations are typically observed during the summer in major cities, where O_3 precursors are abundant and when conditions favor efficient O_3 production (high ultraviolet (UV) radiation) and air stagnation.”

Lines 118-123 or so: The authors have not explained that these stable “build-up” events usually end when a storm front comes through, often dropping snow.

We have now added this sentence in the introduction:

“ O_3 exceedance events end when stable boundary layers are disrupted by the passage of storm fronts, which often deposit snow”.

Line 167: The pKa of HONO is about 2.9. Would the snow surface ever approach that and if it did would direct volatilization of HONO be a Nr loss mechanism? Does this equilibrium have an isotope effect?

Figure 3A presents estimates of snow pH based upon ion measurements made during UBWOS2014. The estimated pH of surface snow is typically between 2 and 4.

We have added a note about acidity in the introduction which reads:

“Under acidic conditions ($pK_a < 2.8$), aqueous-phase HONO can also be transferred to the gas phase ($\text{HONO (aq)} \leftrightarrow \text{HONO (g)}$) [Anastasio and Chu, 2009] and released into the boundary layer, where it can photolyze to produce gas-phase NO and OH [Zhou et al., 2001].”

We have also added the following sentence in section 4.2:

“The surface snow pH ranged from 2-4 during the campaign (see Figure 3A in Supplemental Material), which is low enough to enable direct volatilization of HONO from the snow.”

We are unaware of any studies that reveal information about the isotopic effect associated with HONO volatilization. Frey et al. [2009] show that nitrate volatilization has an order of magnitude smaller N-isotope fractionation compared to photolysis, and it is likely that HONO volatilization has a similarly small isotope effect.

Lines 202-204: The authors mention all these processes that can influence ^{15}N abundance but give no information about what direction or the magnitude.

Since $\delta^{15}\text{N}$ is a ratio of the abundance of $\delta^{15}\text{N}$ in a sample compared to reference material (N_2 in air), the $\delta^{15}\text{N}$ values associated with these processes do provide information about both the direction and magnitude of the enrichment/depletion of “heavy” nitrogen in a sample compared to the standard. For example, soil microbial activity tends to deplete (direction) samples of heavy nitrogen by 20 to 50 parts per thousand (magnitude), which is described as -50‰ to -20‰.

Line 449: How does a cascade impactor provide a measurement of HNO_3 , which I presume is gas phase nitric acid?

Thank you for catching this error. The cascade impactor only provides measurements of aerosol phase nitrate. This has been fixed in the manuscript.

Lines 721-723: Here is where the inconsistency really rears its head. How can “light snow- sources nitrate” have such an impact if it is a small fraction of N emitted to the basin?

Please see our response above to the comment about re-deposition of light nitrate to the snow surface layer being at odds with the conclusion that snow-derived light N is a small fraction of the reactive nitrogen source to the basin.

Line 739: The smoke stack does not extend above the boundary layer, the buoyancy of the warmer plume causes the emissions to settle in a layer just above the cold boundary layer.

This sentence now reads:

“The power plant is excluded because its emissions occur above the boundary layer due to the plume’s positive buoyancy.”

References:

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