Nitrate Chemistry in the Northeast US Part II: Oxygen Isotopes Reveal Differences in Particulate and Gas Phase Formation

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Abstract. The northeastern US represents a mostly urban corridor impacted by high population density, high emissions density and degraded air quality and acid rain that has been a focus of regulatory-driven emissions reductions. Detailing the chemistry of atmospheric nitrate formation is critical for improving model representation of atmospheric chemistry and air quality. The oxygen isotope deltas (δ18O and Δ17O) of atmospheric nitrate are useful indicators in tracking nitrate formation pathways. Here, we measured Δ17O and δ18O for nitric acid (HNO3) and particulate nitrate (pNO3) from three US EPA Clean Air Status and Trends Network (CASTNET) sites in the northeastern US from December 2016 to 2018. The Δ17O, HNO3 and δ18O, HNO3 values ranged from 12.9 ‰ to 30.9 ‰ and from 46.9 ‰ to 82.1 ‰, and the Δ17O, pNO3 and δ18O, pNO3 ranged from 16.6 ‰ to 33.7 ‰ and from 43.6 ‰ to 85.3 ‰, respectively. There was distinct seasonality of δ18O and Δ17O with higher values observed during winter compared to summer, suggesting a shift in O3 to HOx radical chemistry, as expected. Unexpectedly, there was a statistical difference in Δ17O between HNO3 and pNO3, with higher values observed for pNO3.
(27.1±3.8) ‰ relative to HNO$_3$ (22.7±3.6) ‰, and significant differences in the relationship between $\delta^{(18}O)$ and $\Delta^{(17}O)$. This difference suggests atmospheric nitrate phase-dependent oxidation chemistry that is not predicted in models. Based on output from GEOS-Chem, and both the $\delta^{(18}O)$ and $\Delta^{(17}O)$ observations, we quantify the production pathways of atmospheric nitrate. The model significantly overestimated the heterogeneous N$_2$O$_5$ hydrolysis production for both HNO$_3$ and pNO$_3$, a finding consistent with observed seasonal changes in $\delta^{(18}O)$, $\Delta^{(17}O)$ and $\delta^{(15}N)$ of HNO$_3$ and pNO$_3$, though large uncertainties remain in the quantitative transfer of $\delta^{(18}O)$ from major atmospheric oxidants. This comparison provides important insight into the role of oxidation chemistry in reconciling a commonly observed positive bias for model atmospheric nitrate concentrations in the northeastern US.

1. Introduction

Nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) in the atmosphere have an important impact on air quality and human and ecosystem health (Galloway et al., 2004). NO$_x$ plays an important role in influencing the oxidizing efficiency of the atmosphere, including the production of ozone (O$_3$), and leads to the formation of atmospheric nitrate (gas phase nitric acid (HNO$_3$) and nitrate in particulate form (pNO$_3$)) (Crutzen et al., 1979). HNO$_3$ and pNO$_3$ are, in turn, important contributors to dry and wet N deposition. Nitrate is a key component of particulate matter (PM$_{2.5}$), which has direct adverse effects on human respiratory and climate change, and the deposition of N to ecosystems can contribute to soil acidification and eutrophication (Camargo and Alonso, 2006; Schlesinger, 2007; Tai et al., 2010). Thus, changes in the chemistry and chemical feedbacks associated with NO$_x$ have important implications for predicting air quality improvements and climatic responses.

The US Environmental Protection Agency (EPA) reported that NO$_x$ emissions have decreased by 36 % in the United States from 2007 to 2015 due to effective regulations in response to the Clean Air Act and its Amendments (US EPA, 2017; CASTNET, 2019; NEI, 2017; Shah et al., 2018). However, atmospheric pNO$_3$ concentrations have responded sub-linearly to the dramatic NO$_x$ emission reductions with only a 7.8 % pNO$_3$ decrease over the same period in the northeastern US. Uncertainties in our understanding between NO$_x$ reductions and the production of atmospheric nitrate challenge our ability to make effective reductions in reactive nitrogen concentrations. Major factors influencing atmospheric nitrate production include oxidant availability, heterogeneous...
chemistry, gas-to-particle partitioning, and potential aerosol nitrate photolysis (Jaeglé et al., 2018; Shah et al., 2018; Kasibhatla et al., 2018).

Atmospheric nitrate concentrations have been simulated using various chemistry models to detail spatiotemporal variabilities between precursor NOx emissions and nitrate in the US, with somewhat limited success (Walker et al., 2012; Zhang et al., 2012). In particular, the concentrations of nitrate observed in the northeastern US tend to be overestimated in models (e.g., Heald et al., 2012; Zhang et al., 2012), which is an important region to monitor due to its high population density, transport patterns and the tendency for poor air quality (Sickles and Shadwick, 2015). Modeling studies suggest that biases revealed by comparison with observations are likely due to uncertainties in NOx and NH3 emission estimates, dry deposition removal rates, heterogeneous chemical production rates, and changing chemistry due to reductions in NOx and sulfur dioxide emissions (Heald et al., 2012; Holt et al., 2015; Shah et al., 2018).

The nitrate oxygen isotope deltas (\(\Delta^{17}\)O and \(\delta^{18}\)O)) has proven to provide observational constraints on the oxidation pathways that are responsible for the formation of atmospheric nitrate (Hastings et al., 2003; Michalski et al., 2003; Alexander et al., 2009). The isotopic composition is expressed as \(\delta\), which is a standardized notation and quantified as \(\delta = (R_{\text{sample}}/R_{\text{reference}} - 1) \times 1000\)‰. \(R\) is the ratio of the heavy isotope to the light isotope (e.g., \(^{18}\)O/\(^{16}\)O; \(^{17}\)O/\(^{16}\)O) in the sample and internationally recognized isotopic reference material (Oxygen = Vienna Standard Mean Ocean Water), respectively. Several studies have suggested that the distinctive (\(\Delta^{17}\)O) = \(\delta^{17}\)O – 0.52 × \(\delta^{18}\)O) and \(\delta^{16}\)O) signatures of atmospheric oxidants such as O3, O2/RO2/HO2, H2O and OH are incorporated into nitrate, tracking the oxidation chemistry of NOx (Hastings et al., 2003; Michalski et al., 2003; Savarino et al., 2007). Traditionally, the influence of O3 incorporation in nitrate has been quantitively tracked using only \(\Delta^{17}\)O), because of the unique mass independent fractionation that results in O3 carrying excess \(\delta^{17}\)O) yielding a transferrable \(\Delta^{17}\)O) = (39±2)‰ (Thiemens, 2006; Vicars and Savarino, 2014). However, all other atmospheric oxidants contain expected mass dependent signatures such that all have \(\Delta^{17}\)O value of approximately 0‰. The \(\delta^{18}\)O) of atmospheric oxidants could provide further insights into nitrate production mechanisms, especially in cases where oxidants other than O3 are important, since it is distinctive for each oxidant (e.g.,
δ(18O, O3) = (126.3±12) ‰, δ(18O, O2) = 23 ‰, δ(18O, OH) = -43 ‰ (Michalski et al., 2012; Vicars and Savarino, 2014).

Using the Clean Air Status and Trends Network (CASTNET) samples, we explore spatiotemporal differences in HNO₃ and pNO₃ concentrations and production mechanisms in the northeastern US. The observations reveal unique oxidant relationships (Δ(¹⁷O) vs. δ(¹⁸O)) for HNO₃ versus pNO₃, which are not predicted in atmospheric chemistry models. Using output from a state-of-the-art atmospheric chemistry model (GEOS-Chem) we find that the model well predicts the seasonality of observed Δ(¹⁷O) values, despite significant overestimation of HNO₃ and pNO₃ concentrations. However, a comparison with the combination of Δ(¹⁷O) and δ(¹⁸O) values of HNO₃ and pNO₃ clearly identify weaknesses in our understanding of the importance of different chemical production mechanisms.

2. Methods

2.1 CASTNET

Atmospheric nitrate samples were collected by the US EPA at several locations of Clean Air Status and Trends Network (CASTNET) sites in the northeastern US (Figure 1). Three CASTNET sites were selected: Abington, CT (ABT147, 41.84° N, -72.01° W), Connecticut Hill, NY (CTH110, 42.40° N, -76.65° W), Woodstock, NH (WST109, 43.94° N, -71.70° W). The samples were collected weekly from December 23, 2016, to December 28, 2018, using a three-stage filter pack system. Based on EPA protocols, pNO₃ was collected using a Teflon filter in the first stage of the filter pack, and gaseous HNO₃ was collected using a Nylon filter in the second stage of the filter pack. We note that due to the semi-volatile characteristic of ammonium nitrate, some pNO₂ might volatilize as HNO₃ and collect downstream of the filter pack leading to negative biases for pNO₃ and positive biases for HNO₃ collection (Hering and Cass, 1999; Ashbaugh and Eldred, 2004).

2.2 Concentration and Isotope Analysis

Filters were extracted and measured for nitrate concentration using Ion Chromatography and then stored in the CASTNET laboratory at room temperature for up to two years. Extracted samples were shipped to Brown University in summer 2020. Nitrate concentrations were measured at Brown University to check for stability of NO₃⁻ using standard colorimetric methods (i.e., US EPA...
Method 353.2) on an automated discrete UV-Vis Analyzer (SmartChem Westco Scientific Instruments, Inc.). The limit of detection was 0.1 and 0.3 μM for NO$_2^-$ and NO$_3^-$, respectively, and the pooled standard deviation of replicate quality control standards was better than 3%. Overall, strong positive correlations were found between measured concentrations at Brown and reported CASTNET data for both HNO$_3$ ($y = 0.99x - 0.08$ ($R^2 = 0.99$); $p < 0.05$) and pNO$_3$ ($y = 1.04x + 0.09$ ($R^2 = 0.99$); $p < 0.05$) (Figure 2); we therefore consider the samples representative of their original concentrations.

The samples were collected once a week, and equal volumes of filter extract were combined for isotope analysis to produce monthly aggregates for HNO$_3$ and pNO$_3$, respectively. Oxygen ($\delta^{18}$O and $\Delta^{17}$O) stable isotopic compositions in HNO$_3$ and pNO$_3$ were analyzed utilizing the bacterial denitrifier method at Brown University (Sigman et al., 2001; Casciotti et al., 2002; Kaiser et al., 2007). Briefly, samples were injected into a buffer solution containing *P. aureofaciens*, which lack the nitrous oxide (N$_2$O) reductase enzyme, and sample NO$_3^-$ is quantitatively reduced to N$_2$O. For $\delta^{18}$O analysis, the generated N$_2$O is injected into a Thermo-Finnegan Delta V Plus isotope ratio mass spectrometry (IRMS) with a modified Gas Bench system after flowing through an automated extraction and purification system. Determination of $\delta^{18}$O in N$_2$O was conducted at an $m/z$ of 44, 45, and 46 and corrected using internationally recognized isotopic reference materials that included IAEA-NO$_3$ (25.6 %o), USGS34 (-27.9 %o), and USGS35 (57.5 %o). The $\Delta^{17}$O was determined in a separate analysis. The bacteria-generated N$_2$O was decomposed to N$_2$ and O$_2$ in a gold furnace heated to 770 ºC and analyzed at $m/z$ 32, 33, and 34 to determine $^{17}$O/$^{16}$O and $^{18}$O/$^{16}$O ratios of the evolved O$_2$. The 33/32 and 34/32 mass ratios were corrected using isotopic reference materials, USGS34 (-0.29 %o) and USGS35 (21.6 %o), and then $\Delta^{17}$O is determined from $\Delta^{17}$O = $\delta^{17}$O – 0.52 × $\delta^{18}$O. Due to sample mass limitations, some samples were only analyzed for $\delta^{18}$O. The number of samples that were not measured for $\Delta^{17}$O was 1 HNO$_3$ sample from CTH110, 2 HNO$_3$ samples from ABT147, 5 pNO$_3$ samples from CTH110, and 16 pNO$_3$ samples from WST109. The overall pooled standard deviations of isotopic reference materials and sample numbers were as followed: USGS34 ($\sigma(\delta^{18}$O)) = 0.5 %o ($n = 21$); $\sigma(\Delta^{17}$O) = 1.1 %o ($n = 26$); USGS35 ($\sigma(\delta^{18}$O)) = 0.4 %o ($n = 27$); $\sigma(\Delta^{17}$O) = 2.4 %o ($n = 26$), and IAEA-N3 ($\sigma(\delta^{18}$O)) = 0.3 %o ($n = 23$).}

### 2.3 GEOS-Chem
The GEOS-Chem global model of atmospheric chemistry (www.geos-chem.org) was utilized to track the production of NO\(_2\) and HNO\(_3\) at the CASTNET sites to model \(\delta^{(18)}\text{O}\) and \(\Delta^{(17)}\text{O}\) isotope following previous framework (Alexander et al., 2020). We use version 13.2.1 (doi:10.5281/zenodo.5500717) of the model driven by GEOS5-FP assimilated meteorology from the NASA Global Modeling and Assimilation Office (GMAO). A nested grid (0.25° latitude × 0.3125° longitude horizontal resolution; ~25 km) simulation was conducted over the northeastern United States (97°-60° W; 35°-60º N) in 2017 and 2018. Boundary conditions were from global simulations performed at 4° latitude × 5° longitude horizontal resolution for the same years after a one-year initialization. Gas- and aerosol-phase chemistry was simulated using the default “fullchem” mechanism (Bates and Jacob, 2019; Wang et al., 2021). Inorganic gas and aerosol partitioning were conducted using version 2.2 of the ISORROPIA II thermodynamic equilibrium model (Fountoukis and Nenes, 2007). All default anthropogenic emissions were applied, which is primarily version 2.0 of the Community Emissions Data System (Hoesly et al., 2018) as implemented by McDuffie et al. (2020). Natural emissions respond to local meteorology and include biogenic VOCs from terrestrial plants and the ocean (Millet et al., 2010; Guenther et al., 2012; Hu et al., 2015; Breider et al., 2017), NO\(_3\) from lightning and soil microbial activity (Murray et al., 2012; Hudman et al., 2012), mineral dust (Ridley et al., 2012), and sea salt (Jaeglé et al., 2011; Huang and Jaeglé, 2017). Biomass burning emissions were monthly means from version 4.1s of the Global Fire Emissions Database (GFED4.1s; van der Werf et al., 2017). Wet deposition for water-soluble aerosols is described by Liu et al. (2001) and by Amos et al. (2012) for gases. Dry deposition is based on the resistance-in-series scheme of Wesely (1989). Diagnostics were implemented to archive the total production and loss pathways of NO\(_2\), NO\(_3\), NO\(_2\), RONO\(_2\), HNO\(_3\) and pNO\(_3\), including the net flux of mass between HNO\(_3\) and pNO\(_3\) in ISORROPIA II. Model skill was assessed with the Normalized Mean Bias (B) metric, defined as \(B = (\sum (\bar{Q}_m - \bar{Q}_o) / \sum \bar{Q}_o)\) where \(\bar{Q}_m\) = modeled quantities and \(\bar{Q}_o\) = observed quantities.

### 2.4 \(\delta^{(18)}\text{O}\) and \(\Delta^{(17)}\text{O}\) calculations

The oxygen isotope compositions (\(\delta^{(18)}\text{O}\) and \(\Delta^{(17)}\text{O}\)) of nitrate were calculated based on oxygen isotope mass-balance using production rate outputs from the GEOS-Chem global 3-D model and compared with our observations. Expected \(\delta^{(18)}\text{O}\) and \(\Delta^{(17)}\text{O}\) ranges resulting from nitrate production pathways have been previously described and calculated using oxygen mass-balance.
Briefly, the \( \delta^{(18} \text{O}) \) and \( \Delta^{(17} \text{O}) \) of nitrate are determined by both NO\(_x\) photochemical cycling and nitrate formation reactions (Alexander et al., 2009; Walters et al., 2018). During NO\(_x\) photochemical cycling, the oxygen isotopic compositions of NO\(_x\) is determined by the relative production rates of NO\(_2\) via reaction of NO with O\(_3\), peroxy and hydroperoxyl radicals, and halogen oxides (XO; BrO, ClO). The proportional contribution of O\(_3\) during NO oxidation is denoted as A and is calculated using

\[
A = \frac{k(O_3+NO)[O_3] + k(XO+NO)[XO]}{[O_3][O_3] + k(XO+NO)[XO] + k(PO_2+NO)[PO_2] + k(RO_2+NO)[RO_2]}
\]

(Eq. 1)

where \( k \) is the respective rate constant for NO oxidation via O\(_3\), XO, HO\(_x\), and RO\(_2\). The \( \Delta^{(17} \text{O}) \) value of the terminal oxygen atom in O\(_3\)(O\(_3^+\)) is assumed to be (39±2)‰ based on observations, while all other oxidants are assumed to be 0‰ (Vicars et al., 2012; Vicars and Savarino, 2014; Alexander et al., 2020). \( \delta^{(18} \text{O}) \) and \( \Delta^{(17} \text{O}) \) values of nitrate from each production pathway were then determined using O mass-balance based on the O transfer from varying oxidants involved in its formation (Table 1).

The GEOS-Chem global model has been previously used to quantify nitrate production pathways based on \( \Delta^{(17} \text{O}) \) (Alexander et al., 2009, 2020), but this has not been done for \( \delta^{(18} \text{O}) \). Using a similar framework as for \( \Delta^{(17} \text{O}) \), we expect that \( \delta^{(18} \text{O}) \) of NO\(_2\) reflects isotopic signatures of both O\(_3\) and O\(_2\), as it has been assumed that the O isotopic composition of RO\(_2\) and HO\(_x\) is equal to O\(_2\) (Michalski et al., 2012; Walters et al., 2018). Accordingly, the values of \( \delta^{(18} \text{O}, \text{NO}_2\) can be predicted by the proportional contribution of O\(_3\) and both HO\(_x\) and RO\(_2\) during NO\(_x\) cycling with their distinct \( \delta^{(18} \text{O}) \) values of O\(_3\) and O\(_2\) (Eq. 2; Table 1).

\[
\delta^{(18} \text{O}, \text{NO}_2\) = A(\delta^{(18} \text{O}, \text{O}_3^+) + (1-A)(\delta^{(18} \text{O}, \text{O}_2)\)
\]

(Eq. 2)

The \( \delta^{(18} \text{O}) \) values of O\(_3\) and O\(_2\) are adopted from previous studies that determined \( \delta^{(18} \text{O}, \text{O}_3^+) \) and \( \delta^{(18} \text{O}, \text{O}_2\) as 126.3‰ and 23‰ (Vicars and Savarino, 2014; Kroopnick and Craig, 1972, respectively). For the calculation of \( \delta^{(18} \text{O}) \) of nitrate, the value of \( \delta^{(18} \text{O}) \) of H\(_2\)O(l) is assumed to
be -6 ‰, which is a typical mid-latitude value and represents water in the liquid phase incorporated into nitrate formation associated with heterogeneous reactions by N₂O₅ or NO₂ hydrolysis (Michalski et al. 2012). The δ₁⁸O value of OH can be dependent on both O₃ and H₂O(g), as well as environmental conditions since oxygen in OH can exchange with H₂O(g) (Dubey et al. 1997). Fractionation factors associated with the O transfer into NOₓ products are unknown and therefore were not considered. The Δδ₁⁸O of H₂O(g) was estimated based on the equilibrium between H₂O(l) and H₂O(g) with a temperature-dependent fractionation factor (1.0094 at 298K); it is assumed that OH and H₂O(g) exist in isotopic equilibrium, which has a theoretically determined fractionation factor (1.0371 at 298K) and leads to an estimate of Δδ₁⁸O (OH) of -43 ‰ (Michalski et al. 2012; Walters and Michalski, 2016). We note that the typical annual temperature for the northeast US is approximately 287 K, yielding a Δδ₁⁸O (OH) of -45 ‰; for comparison purposes with prior publications, we utilize -43 ‰, which makes little difference in the quantitative results below. In the final step, Δδ₁⁸O or ΔΔ₁⁷O of total atmospheric nitrate were calculated based on the monthly-averaged production rates from GEOS-Chem and the seven major reactions that produce nitrate in the model (Table 1) to compare with observations.

3. Results and discussions
3.1 Spatiotemporal variations of atmospheric nitrate concentration

Figure 3 shows the monthly averaged spatiotemporal variations of HNO₃ and pNO₃ mass concentration (denoted as γ). The observed HNO₃ concentrations (γ(HNO₃)) ranged from 0.11 µg m⁻³ to 0.88 µg m⁻³, with a mean value of 0.46 µg m⁻³ across the three CASTNET sites. The observed pNO₃ concentrations (γ(pNO₃)) ranged from 0.04 µg m⁻³ to 2.01 µg m⁻³, with a mean value of 0.50 µg m⁻³, and showed clear seasonality at all three sites with averaged higher values (0.75±0.52) µg m⁻³ in the cold season (October to March) and lower values (0.25±0.17) µg m⁻³ in the warm season (April to September), which were significantly different (p < 0.01). On the other hand, γ(HNO₃) was seasonally invariable with (0.42±0.17) µg m⁻³ for cold season and (0.50±0.24) µg m⁻³ for warm season that was not statistically different (p > 0.05). Averaged γ(HNO₃) was generally lower than pNO₃ across the sites, but the difference was statistically insignificant (p > 0.05). Both γ(HNO₃) and γ(pNO₃) indicated spatial variability with higher values at ABT147 and
CTH110 than the WST109 site. The mean annual $\gamma_o(HNO_3)$ and $\gamma_o(pNO_3)$ were $(0.61\pm0.15)$ $\mu$g m$^{-3}$ and $(0.66\pm0.34)$ $\mu$g m$^{-3}$ at ABT147, $(0.55\pm0.13)$ $\mu$g m$^{-3}$ and $(0.68\pm0.58)$ $\mu$g m$^{-3}$ at CTH110, and $(0.22\pm0.06)$ $\mu$g m$^{-3}$ and $(0.17\pm0.13)$ $\mu$g m$^{-3}$ at WST109, respectively.

The modeled HNO$_3$ concentrations ($\gamma_m(HNO_3)$) ranged from 0.20 $\mu$g m$^{-3}$ to 2.36 $\mu$g m$^{-3}$, with a mean value of 0.82 $\mu$g m$^{-3}$ and modeled pNO$_3$ concentrations ($\gamma_m(pNO_3)$) ranged from 0.20 $\mu$g m$^{-3}$ to 5.27 $\mu$g m$^{-3}$, with a mean value of 1.89 $\mu$g m$^{-3}$. Contrary to our observed data, no consistent spatial variability was observed for $\gamma_m(HNO_3)$ and $\gamma_m(pNO_3)$. The mean $\gamma_m(HNO_3)$ and $\gamma_m(pNO_3)$ were $(1.09\pm0.62)$ $\mu$g m$^{-3}$ and $(1.73\pm1.13)$ $\mu$g m$^{-3}$ at ABT147, $(0.74\pm0.46)$ $\mu$g m$^{-3}$ and $(2.42\pm1.71)$ $\mu$g m$^{-3}$ at CTH110, and $(0.64\pm0.22)$ $\mu$g m$^{-3}$ and $(1.52\pm1.24)$ $\mu$g m$^{-3}$ at WST109, respectively. Overall, simulated atmospheric nitrate in the GEOS-Chem model is significantly overestimated across the three CASTNET sites: $\gamma_m(HNO_3)$ are 2-3 times higher than the $\gamma_o(HNO_3)$ and $\gamma_m(pNO_3)$ are 3-9 times higher than $\gamma_o(pNO_3)$.

As stated above, there can be negative biases for pNO$_3$ and positive biases for HNO$_3$ collection, but these should be reduced by comparing the model to total atmospheric nitrate (tNO$_3$ = HNO$_3$ + pNO$_3$). Still, the simulated tNO$_3$ concentration ($\gamma_m(tNO_3)$) with GEOS-Chem is significantly overestimated relative to observations ($\gamma_o(tNO_3)$; $B = 182 \%$; Figure 3). While the simulated pNO$_3$ well reproduces the observed seasonality (high concentrations in the cold season and vice versa), it highly overestimated the concentrations for most of the year ($B = 276 \%$; Figure 3). The simulated HNO$_3$ did not capture the observed relative lack of seasonality, instead showing clear seasonality with generally high concentrations in the warm season and low in the cold season. The lack of agreement between GEOS-Chem and nitrate observations is consistent with previously reported results in other studies (Heald et al., 2012; Zhang et al., 2012; Walker et al., 2012). Uncertainties in N$_2$O$_5$ hydrolysis rate, emission estimates, or dry and wet deposition removal rates have been suggested as possible causes for predicted nitrate biases. For instance, Luo et al., 2019; 2020 reported dramatic improvement of nitric acid and nitrate biases by updating wet scavenging parameterization in the GEOS-Chem model; however, this update leads to biases in oxidized nitrogen wet deposition between model predictions and observations.
3.2 Oxygen isotopic compositions (δ(18O) and Δ(17O)) – Oxidation Chemistry and Phase Difference

The oxygen isotopic compositions in atmospheric nitrate are used to evaluate NO3 oxidation chemistry and to assess seasonal changes in nitrate formation mechanisms. For the CASTNET sites, the Δ(17O, HNO3) and Δ(17O, pNO3) values ranged from 12.9 ‰ to 30.9 ‰ and from 16.6 ‰ to 33.7 ‰, with a mean value of (22.7 ± 3.6) ‰ and (27.1± 3.8) ‰, respectively (Figure 4a and b). The δ(18O, HNO3) and δ(18O, pNO3) values ranged from 46.9 ‰ to 82.1 ‰ and from 43.6 ‰ to 85.3 ‰, with a mean value of (68.1 ± 7.1) ‰ and (68.2 ± 8.3) ‰, respectively (Figure 4c and d). These observations are in the range of previously reported values in polluted mid-latitudes: δ(18O, HNO3) and δ(18O, pNO3) in CASTNET sites in Ohio, Pennsylvania, and New York from April 2004 to March 2005 ranged from 51.6 ‰ to 94.0 ‰ and from 45.2 ‰ to 92.7 ‰ (Elliott et al., 2009), respectively. They are also consistent with observations of polluted air masses in Canada from September 2010 to January 2014 were from 62.4 to 81.7 ‰ for δ(18O, HNO3), from 19.3 to 29.0 ‰ for Δ(17O, HNO3), from 48.4 to 83.2 ‰ for δ(18O, pNO3), and from 13.8 to 30.5 ‰ for Δ(17O, pNO3) (Savard et al., 2018).

Previous studies and modeling results have indicated that the seasonality of oxygen isotopic compositions in HNO3 and pNO3 is driven by a shift in oxidation chemistry (Hastings et al., 2003; Michalski et al., 2012; Alexander et al., 2009; 2020). Globally, the seasonality reflects a shift in O3 to HOx radical chemistry during winter to summer, respectively. Wintertime has higher NO + O3 branching ratios than summer, which has increased NO + RO2/HO2. The high values of δ(18O) and Δ(17O) in HNO3 and pNO3 during the cold season are caused by the increased incorporation of O3 into the nitrate product through N2O5 heterogeneous hydrolysis on aerosols. In contrast, the dominance of gas-phase production by the NO2 + OH reaction dilutes the isotopic influence of O3 during warm seasons leading to the low values of δ(18O) and Δ(17O) in HNO3 and pNO3 (Figure 4). Spatial variability is observed in δ(18O) and Δ(17O) of HNO3, with highest values at CTH110 (δ(18O): (71.5±5.6) ‰ (n = 24) and Δ(17O): (25.0±3.1) ‰ (n = 23)) followed by ABT147 (δ(18O): (70.1±4.8) ‰ (n = 24) and Δ(17O): (23.1±2.2) ‰ (n = 24)) and WST109 (δ(18O): (62.8±7.7) ‰ (n = 24) and Δ(17O): (20.2±3.7) ‰ (n = 24)). However, δ(18O) and Δ(17O) of pNO3 were not significantly different across the stations: for ABT147 (δ(18O): (68.6±7.1) ‰ (n = 24) and Δ(17O):
Our observations indicate a significant phase-dependent difference in oxidation chemistry between HNO₃ and pNO₃ that is unexpected. Many modeled mechanisms of gas- and aqueous-phase chemistry produce HNO₃, then HNO₃ is partitioned into the aerosol phase based on thermodynamic equilibrium (i.e., NH₄NO₃(s) ⇌ HNO₃(g) + NH₃(g)) or coarse uptake. Conventional understanding would expect Δ(¹⁷O) of HNO₃ and pNO₃ to be the same (e.g., Alexander, 2020). However, observed Δ(¹⁷O, pNO₃) tends to be significantly higher than Δ(¹⁷O, HNO₃) (p < 0.01 at ABT and CTH, p = 0.088 at WST). This phase difference in Δ(¹⁷O) cannot be explained by potential sample biases caused by volatilization, which leads to mass-dependent fractionation. This difference might be related to the differences in particulate nitrate size-dependent production pathways. Previous studies of size-segregated Δ(¹⁷O, pNO₃) indicated higher values for coarse pNO₃ (aerodynamic diameter (Dₐ) > 0.95 μm) relative to fine pNO₃ (Dₐ < 0.95 μm) that was concluded to reflect the increased importance of heterogeneous N₂O₅ hydrolysis on coarse particles relative to fine particles (Vicars et al., 2013). The CASTNET pNO₃ samples reflect total suspended particles (TSP) such that increased importance of N₂O₅ heterogeneous chemistry for coarse particulate nitrate formation could explain the higher Δ(¹⁷O, pNO₃) values we observe relative to Δ(¹⁷O, HNO₃).

We also observed different δ(¹⁸O) and Δ(¹⁷O) relationships for HNO₃ and pNO₃, which further suggests phase-dependent nitrate oxidant chemistry. Positive linear relationships between δ(¹⁸O) and Δ(¹⁷O) were observed for HNO₃ and pNO₃ across the CASTNET sites, with similar slopes but different oxygen isotopic signatures indicated by different intercepts (Figure 5). For the relationship of δ(¹⁸O) and Δ(¹⁷O), the high end-member should result from O₃ and the lower end-member depends on the isotopic signature of the atmospheric oxidants involved. The transferable δ(¹⁸O) signatures of atmospheric oxidants are not fully understood yet, reflecting a complex combination of atmospheric oxidant source signatures and isotope fractionation during reaction and incorporation into the nitrate end-product. While ozone has a notable high Δ(¹⁷O) value (39±2‰; Vicars and Savarino, 2014), Δ(¹⁷O) values of other atmospheric oxidants such as O₂/RO₂/HO₂, H₂O and OH are equal to or close to 0‰ (Michalski et al., 2012; Walters et al., 2019). Overall,
our results suggest more O₃ is incorporated during the formation of pNO₃ than HNO₃. We further analyze the oxidation chemistry involved in atmospheric nitrate formation based on output from the GEOS-Chem chemical transport model.

### 3.3 Quantifying oxidation chemistry in atmospheric nitrate production mechanisms

Observations of the oxygen isotopic composition were utilized to quantify the relative importance of different nitrate formation pathways and to assess model representation of the chemistry of nitrate formation. Using atmospheric nitrate production rates from the GEOS-Chem model, \( \Delta^{17}\mathrm{O} \) was calculated within a grid cell corresponding to our CASTNET sites and compared with observed \( \Delta^{17}\mathrm{O}, \) HNO₃, pNO₃ at each site. The dominant annual pathway for nitrate formation in the GEOS-Chem model (“base case”) was N₂O₅ hydrolysis, which accounts for 50% (Figure 6), followed by NO₂ + OH (31%) and RONO₂ hydrolysis (13%) across all CASTNET sites. Nitrate production via reaction of XNO₃ hydrolysis and NO₃ + HC was small (< 1%) at all sites. Strong seasonality in nitrate production was observed as expected with high portions of N₂O₅ hydrolysis in winter and NO₂ + OH in summer (Figure 6). Overall, the calculated \( \Delta^{17}\mathrm{O} \) showed a better agreement with observed \( \Delta^{17}\mathrm{O} \) of pNO₃ (\( y = 0.55x + 12.62 \) \( R^2 = 0.48 \)) than \( \Delta^{17}\mathrm{O} \) of HNO₃ (\( y = 0.46x + 10.68 \) \( R^2 = 0.44 \)) at all CASTNET sites (\( B = -2 \% \) and \( 15 \% \), respectively) (Figure 7). The averaged residuals over the collection period for each site were 3.9 \%, 2.8 \%, and 5.6 \% for \( \Delta^{17}\mathrm{O}, \) HNO₃, and 1.5 \%, 1.7 \%, and 6.1 \% for \( \Delta^{17}\mathrm{O}, \) pNO₃ at ABT147, CTH110, and WST109, respectively (Figure 4). Calculated \( \Delta^{17}\mathrm{O} \) based on GEOS-Chem output reproduced the observed temporal variations very well (Figure 4 a and c). The GEOS-Chem model, however, does not capture observed spatial \( \Delta^{17}\mathrm{O} \) variabilities. For instance, higher \( \Delta^{17}\mathrm{O} \) values (especially for HNO₃) were observed at CTH110 compared to WST109; while no significant spatial \( \Delta^{17}\mathrm{O} \) difference was predicted from GEOS-Chem.

The GEOS-Chem model \( \delta^{18}\mathrm{O} \) was also calculated in the same manner as \( \Delta^{17}\mathrm{O} \) (Figure 4 b and d). Unlike calculated \( \Delta^{17}\mathrm{O} \), calculated \( \delta^{18}\mathrm{O} \) showed remarkably positive biases compared with measured \( \delta^{18}\mathrm{O} \) of HNO₃ (\( B = 22 \% \)) and pNO₃ (\( B = 21 \% \)). The averaged residuals for \( \delta^{18}\mathrm{O}, \) HNO₃ at each site were 13.9 \%, 12.9 \%, and 19.6 \%, and for \( \delta^{18}\mathrm{O}, \) pNO₃ were 15.4 \%, 14.2 \%, and 18.2 \% at ABT147, CTH110, and WST109, respectively. Modeling the \( \delta^{18}\mathrm{O} \) values of nitrate is more challenging than \( \Delta^{17}\mathrm{O} \) because not all oxidant \( \delta^{18}\mathrm{O} \) values have been directly
observed and fractionation factors associated with the O transfer into NO3 products is unknown. Uncertainty in $\delta^{18}O$ values could be a major factor causing disagreement between observed and calculated $\delta^{18}O$. Additionally, biases in the chemical mechanisms in GEOS-Chem could account for the discrepancy.

Many studies have used $\Delta^{17}O$ to quantify and/or constrain modeled chemical mechanisms. Here, GEOS-Chem production rates were optimized based on our observed $\Delta^{17}O$ to find the best linear fit between observed and calculated $\Delta^{17}O$, and therefore constrain the predicted chemical formation pathways. In other words, what relative production rates are predicted based on the observations compared to the simulated values. GEOS-Chem was optimized based on $\Delta^{17}O$ of HNO3 and pNO3 separately. Calculated $\Delta^{17}O$ from the base GEOS-Chem model was generally 1.15 times higher than observed $\Delta^{17}O$, HNO3 and 0.98 times lower than $\Delta^{17}O$, pNO3 across all CASTNET sites. After optimization, the residuals between observed and calculated $\Delta^{17}O$ dramatically decreased (Figure 4a and c) and the linear relationships had slopes much closer to the 1:1 line (i.e., from 0.46 to 1.03 for HNO3 and from 0.55 to 0.78 for pNO3; Figure 7a and b) than the base GEOS-Chem model across the three CASTNET site (the relationships for each site before and after optimization are shown in Figure 7). On a subannual basis, the $\Delta^{17}O$ comparison for the cold season showed better improvement than the warm season, especially for $\Delta^{17}O$, HNO3).

Newly optimized nitrate production in GEOS-Chem was also applied to $\delta^{18}O$ calculation and compared with previous results. As with $\Delta^{17}O$, a slope of the regression line between (optimized) calculated and observed $\delta^{18}O$ became closer to 1 (i.e., from 0.30 to 0.74 for HNO3 and from 0.39 to 0.49 for pNO3; Figure 7c and d) and residuals improved at each site after the optimization (Figure 4b and d). Overall, optimized GEOS-Chem $\delta^{18}O$ calculation shows better agreement than the base GEOS-Chem model ($B = -6 \%$ for $\delta^{18}O$, HNO3 and $B = 13 \%$ for $\delta^{18}O$, pNO3), but still has discrepancies, especially in the cold season (Figure 4b and d).

After optimization, the dominant pathway for nitrate formation in GEOS-Chem changed compared to the base case. For $\Delta^{17}O$, pNO3), NO2 + OH (60 \%) was the dominant pathway for nitrate formation in the optimized GEOS-Chem calculation followed by N2Os hydrolysis (31 \%) and NO3
hydrolysis (4%) (Figure 6). At the same time, Δ(17O, HNO3) was almost entirely driven by NO2 + OH reaction (98%) in the optimized GEOS-Chem case. The optimized GEOS-Chem calculations suggest that the fraction of nitrate produced by N2O5 hydrolysis was significantly overestimated in GEOS-Chem base case since N2O5 hydrolysis contributes to high Δ(17O) and δ(18O) values due to O3 transfer. In the base case, N2O5 hydrolysis dominated nitrate production, especially in the cold season with a fraction of over 68% at all CASTNET sites (Figure 6). This may also partly explain major nitrate concentration overestimates, particularly in the cold season.

3.4 δ(18O) optimization of atmospheric oxidants

After optimization of relative nitrate production rates in GEOS-Chem based on Δ(17O), we applied the optimized chemical production to calculate δ(18O), but still observed discrepancy between observed and predicted δ(18O). The discrepancy could be related to variable and somewhat unconstrained δ(18O) values of atmospheric oxidants important for nitrate formation. To test this, the assumed (literature) δ(18O) values of oxidants were optimized by selecting the best linear fit between the observations and calculated δ(18O, HNO3 and pNO3) (Figure 8). After optimization for δ(18O) of oxidants, the discrepancy between observation and calculation was significantly alleviated (Figure 9) with a decrease in B from 21 to 1%. The optimization predicts δ(18O) of H2O values similar to what was expected (-6.5‰ vs. -6.0‰), however significantly different values were predicted for δ(18O) of O2, OH, and O3 (Table 2). It is possible that this reflects isotope effects associated with the incorporation of these oxidants during nitrate production, rather than further issues with model chemistry since the relative production rates here are constrained based on Δ(17O). The δ(18O, O2) was a best fit with calculated δ(18O) of nitrate values when assuming a value of 11.1‰ (vs. the initial 23‰). Since atmospheric O2 is incorporated into nitrate via NO oxidation by HO2 and RO2 radicals, it was assumed that the δ(18O) value of RO2 and HO2 is equal to O2 such that it does not consider any potential isotope effects associated with HO2 and RO2 formation and reaction with NO.

The observed δ(18O) of O3 and OH for the CASTNET samples were a best fit with calculated δ(18O) when assuming values of 89.9‰ for δ(18O, O3) and 42.2‰ for δ(18O, OH), respectively. In the previous section, we noted that NO2 + OH and N2O5 hydrolysis reactions were the dominant pathways for nitrate formation, indicating that OH and O3 play an important role in determining
the $\delta^{(18}O)$ value in nitrate. Indeed, optimizing $\delta^{(18}O)$ values to find the best agreement between observation and calculation are largely dependent on $\delta^{(18}O)$ values of $O_3$ and OH (see also Table 2). The optimized $\delta^{(18}O, O_3^+)$ value (89.9 ‰) was lower than the average reported $\delta^{(18}O, O_3^+)$ ((126.3±12) ‰; Vicars and Savarino, 2014), though the $\delta^{(18}O)$ is known to vary with temperature and pressure, and could also potentially be fractionated during reactions (Brenninkmeijer et al., 2004). For example, Walters and Michalski, 2016 calculated an isotopic enrichment factor near -20 ‰ associated with $O_3$ transfer in its reaction with NO, which would lower the transferable $\delta^{(18}O)$ of $O_3$, consistent with our predictions. For $\delta^{(18}O, OH)$, the optimized value dramatically increased compared to the initial assumed value (-43.0 ‰). The initial $\delta^{(18}O, OH)$ value is based on several assumptions that may not be correct regarding isotope exchange with $H_2O(g)$. Additionally, Fang et al., 2021 suggested that $\delta^{(15}N)$ of nitrate is largely controlled by an isotope effect in the NO$_2$ + OH pathway, and it could be conceivable that $\delta^{(18}O)$ may be affected by a similar isotope effect as well. Overall, the optimization of $\delta^{(18}O, OH)$ is highly dependent on the $\delta^{(18}O, O_3^+)$ (see Table 2), which makes sense given the proportional control of the NO$_2$ + OH and N$_2$O$_5$ hydrolysis reaction. Despite the uncertainty in the transferrable $\delta^{(18}O)$ from major oxidants, the comparison between predicted and observed $\delta^{(18}O)$ and $\Delta^{(17}O)$ both suggest a larger relative importance of NO$_2$ +OH chemistry than reflected in the model simulations. We note here that this finding is also consistent with our study of $\delta^{(15}N, HNO_3)$ and $\delta^{(15}N, pNO_3)$, as well from our companion study (acp-2022-621).

4. Conclusions

Using a combination of concentration and isotopic analyses, we evaluated atmospheric nitrate formation pathways in the northeastern US in 2017–2018. The GEOS-Chem model showed large positive biases for HNO$_3$ and pNO$_3$ concentrations, an important issue that is common in atmospheric chemistry models. The observed oxygen isotopic compositions ($\Delta^{(17}O)$ and $\delta^{(18}O)$) revealed that the model chemistry overpredicted heterogeneous hydrolysis of N$_2$O$_5$ for atmospheric nitrate in the northeastern US A more important relative role of NO$_2$+OH chemistry is also consistent with predicted seasonality in $\delta^{(15}N)$ of atmospheric nitrate in a companion study (acp-2022-621). We also observed nitrate-phase differences in $\Delta^{(17}O)$ and $\delta^{(18}O)$, which are not
captured in current models. Further investigation of size-segregated nitrate chemistry is recommended to improve model prediction of nitrate formation.

Traditionally, Δ(^17O) has been used to quantitatively assess nitrate production pathways. The use of δ(^18O) as well can enhance our understanding of the oxidants contributing to nitrate formation, particularly for distinguishing oxidants that have similar Δ(^17O) values (i.e., all are near 0 ‰ except ozone). However, our study also observed a discrepancy between observed and calculated δ(^18O) values, even after accounting for an optimized chemical production based on Δ(^17O). The best match of the observations suggests that the transferrable δ(^18O) values of oxidants may vary more than is currently suggested in the literature. Better constraints, particularly on the isotopic composition of OH and variability in δ(^18O, O3) would add significant value to modeling and interpretation of major oxidation chemistry in the atmosphere.

**Data Availability.** Data presented in this article are available on the Harvard Dataverse at https://doi.org/10.7910/DVN/X6BB1I, US EPA CASTNET database.

**Author Contributions.** HK, WWW, MGH designed the varying aspects of the study. CB and WWW carried out the laboratory measurements. HK interpreted data, conducted statistical analysis, and analyzed model results. LTM contributed GEOS-Chem simulations. HK and WWW prepared the article with contributions from all co-authors.

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**Competing Interests.** The authors declare no competing financial interest.

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Reference


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Figure 1. Map of the United States (left) and selected CASTNET sites (right) for this study in the northeastern US. The image was created using © Google Earth (©2022 Google).
Figure 2. Relationship of HNO₃ and pNO₃ filter extract concentrations reported by CASTNET and re-measured at Brown University.
Figure 3. Time series of monthly mean total nitrate, HNO$_3$, and pNO$_3$ concentrations (γ) observed and simulated at ABT147, CTH110, and WST109 CASTNET sites. B refers to the normalized mean bias for comparison of the model to observations (see section 2.3 in Methods).
Figure 4. Time series of the monthly mean for observed and calculated $\Delta^{17}$O and $\delta^{18}$O for HNO$_3$ (a and b) and pNO$_3$ (c and d) over ABT147, CTH110, and WST109 CASTNET sites. Calculated $\delta^{18}$O and $\Delta^{17}$O using base (black) and optimized (grey) GEOS-Chem are shown in the plot together. Bars indicate the residuals between calculation and observation.
Figure 5. Relationship between the monthly mean (δ(18O) and Δ(17O)) for observed HNO₃ (green) and pNO₃ (blue) across all CASTNET sites with correlation coefficient (R²) and slope:

- HNO₃: $Y = 0.44 (\pm 0.03) x - 7.22 (\pm 2.1)$, $R^2 = 0.75$
- pNO₃: $Y = 0.44 (\pm 0.04) x - 2.57 (\pm 2.65)$, $R^2 = 0.72$
Figure 6. Relative proportions for major nitrate production pathways by season from (a) base GEOS-Chem output, (b) optimized GEOS-Chem for HNO₃ production, and (c) optimized GEOS-Chem for pNO₃ production based on comparison with observations across the three CASTNET sites.
Figure 7. Correlation between observed and calculated $\Delta^{(17}\text{O}, \text{HNO}_3$ and pNO$_3$) and $\delta^{(18}\text{O}, \text{HNO}_3$ and pNO$_3$), respectively, using base GEOS-Chem (black) and optimized GEOS-Chem (grey) by each site.
Figure 8. Time series of observed and calculated $\delta^{18}O$ for (a) HN0₃ and (b) pNO₃ for ABT147, CTH110, and WST109 sites. Calculated $\delta^{18}O$ using base GEOS-Chem (black) and using optimized $\delta^{18}O$ values (grey) are shown in the plot together.
Figure 9. Correlation between observed and calculated δ(18O, HNO3 and pNO3) by each site. Calculated δ(18O) values using base GEOS-Chem, optimized GEOS-Chem, and optimized δ(18O) values indicated as black, grey, and green (for HNO3) or blue (for pNO3), respectively.
Table 1. Equations for δ(18O) and Δ(17O) calculations by different nitrate formation pathways.

<table>
<thead>
<tr>
<th>Gas-phase reactions</th>
<th>Δ(17O, tNO3)</th>
<th>δ(18O, tNO3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO2 + OH</td>
<td>(\frac{2}{3} A \Delta (17O, O_3^*))</td>
<td>(\frac{2}{3} \delta^{(18O, NO_2)} + \frac{1}{3} \delta^{(18O, OH)})</td>
</tr>
<tr>
<td>NO3 + Hydrocarbons</td>
<td>(\frac{2}{3} A \Delta (17O, O_3^*))</td>
<td>(\frac{2}{3} \delta^{(18O, NO_2)} + \frac{1}{3} \delta^{(18O, O_3^*)})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Heterogeneous reactions</th>
<th>Δ(17O, tNO3)</th>
<th>δ(18O, tNO3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2O3 hydrolysis (water + Cl-)</td>
<td>(\frac{2}{3} A \Delta (17O, O_3^*))</td>
<td>(\frac{4}{6} \delta^{(18O, NO_2)} + \frac{1}{6} \delta^{(18O, O_3^*)} + \frac{1}{6} \delta^{(18O, H_2O)})</td>
</tr>
<tr>
<td>NO3 hydrolysis</td>
<td>(\frac{2}{3} A \Delta (17O, O_3^*))</td>
<td>(\frac{2}{3} \delta^{(18O, NO_2)} + \frac{1}{3} \delta^{(18O, O_3^*)})</td>
</tr>
<tr>
<td>NO2 hydrolysis</td>
<td>(\frac{2}{3} A \Delta (17O, O_3^*))</td>
<td>(\frac{2}{3} \delta^{(18O, NO_2)} + \frac{1}{3} \delta^{(18O, H_2O)})</td>
</tr>
<tr>
<td>RONO2 hydrolysis</td>
<td>(\frac{1}{3} A \Delta (17O, O_3^*))</td>
<td>(\frac{2}{3} \delta^{(18O, NO_2)} + \frac{1}{3} \delta^{(18O, NO_2)})</td>
</tr>
<tr>
<td>XNO3 hydrolysis (X = Br + Cl + I)</td>
<td>(\frac{2}{3} A \Delta (17O, O_3^*))</td>
<td>(\frac{2}{3} \delta^{(18O, NO_2)} + \frac{1}{3} \delta^{(18O, O_3^*)})</td>
</tr>
</tbody>
</table>
Table 2. $\delta^{(18}O)$ values for each oxidant before and after optimization based on different scenarios

<table>
<thead>
<tr>
<th>Atmospheric Oxidants</th>
<th>Assumed $\delta^{(18}O)$ (‰)</th>
<th>Optimized $\delta^{(18}O)$ (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Non-fixed</td>
<td>Fixed O$_3^*$</td>
</tr>
<tr>
<td>O$_3^*$</td>
<td>126.3</td>
<td>89.9</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-6.0</td>
<td>-6.5</td>
</tr>
<tr>
<td>O$_2$/RO$_2$/HO$_2$</td>
<td>23.0</td>
<td>11.1</td>
</tr>
<tr>
<td>OH</td>
<td>-43.0</td>
<td>42.2</td>
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