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Daniel Crocker

dcrocker@fas.harvard.edu

Harvard University

Heejeong Kim

Brown University <https://orcid.org/0000-0002-2707-5438>

Emily Doi

Harvard University

Matthew Goss

Harvard University

Meredith Hastings

Brown University <https://orcid.org/0000-0001-6716-6783>

David Johnston

Harvard University <https://orcid.org/0000-0002-2487-1084>

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Triple oxygen isotope constraints on organic aerosol oxidation pathways

*Daniel R. Crocker^{‡,*}, Heejeong Kim[∞], Emily K. Doi[‡], Matthew B. Goss^{§,†}, Meredith G. Hastings[∞],
David T. Johnston^{‡,*}*

AUTHOR ADDRESS

[‡] Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts
02138, USA

[∞] Department of Earth, Environment and Planetary Sciences and Institute at Brown for
Environment and Society, Brown University, Providence, Rhode Island, 02912, USA

[§] John A. Paulson School of Engineering and Applied Sciences, Harvard University,
Cambridge, Massachusetts 02138, United States

[†] Now at CIRES, University of Colorado, Boulder, Colorado 80309, United States; NOAA
Chemical Sciences Laboratory, Boulder, Colorado 80305, United States.

ABSTRACT. Organic aerosols (OA) are a major source of uncertainty in assessing aerosol impacts on atmospheric composition and climate. Atmospheric oxidation governs OA formation and aging, yet the relative contributions of different oxidation pathways are under-constrained by direct observations. Here, we present year-long triple oxygen isotope ($\delta^{18}\text{O}$, $\Delta^{17}\text{O}$) measurements targeting the organic matter in atmospheric OA samples. These isotopic data reveal that the OA contains mass-independent oxygen and detail contributions from multiple oxidants involved in OA oxidation, including O_2 (via radical-initiated chemistry), O_3 , and OH . Using an isotope-based mixing model with Monte Carlo resampling, we combine empirical and observational constraints on oxidant isotopic compositions to deliver quantitative, observation-based estimates of oxidant-specific contributions to atmospheric OA formation. The resulting oxidant contributions support a dominant role for radical-initiated chemistry accompanied by O_2 -derived oxygen incorporation, along with persistent, but minor, contributions from ozonolysis and OH addition reactions. These findings are broadly consistent with independent model predictions of OA formation pathways, demonstrating triple oxygen isotopes as a quantitative tracer for OA oxidation pathways and a new observational framework for independently evaluating and improving representations of OA atmospheric chemistry.

INTRODUCTION

Atmospheric aerosols influence air quality, human health, and Earth's climate.^{1,2} Despite decades of research, aerosols remain the largest source of uncertainty in quantifying anthropogenic perturbations to Earth's radiative balance.³ Organic aerosol (OA), which comprises a significant fraction of global aerosol mass, is particularly challenging to represent in global chemistry and climate models.⁴ Much of this uncertainty stems from an incomplete mechanistic understanding of the underlying oxidation chemistry governing OA formation and aging, which ultimately controls whether OA exerts a net cooling or warming influence on climate.^{5,6}

Photochemical oxidation is a key atmospheric mechanism that transforms volatile organic compounds (VOCs) into lower volatility products, promoting OA formation and growth.^{7,8} Oxidation is initiated by hydrogen abstraction or addition reactions involving highly reactive species such as hydroxyl radical (OH), nitrate radical (NO₃), and ozone (O₃) (Fig. 1),⁹ usually generating organic radicals that then react rapidly with O₂ to form organic peroxy radicals (RO₂). Subsequent RO₂ chemistry is highly complex and involves bimolecular reactions with species like hydroperoxyl radical (HO₂), other RO₂, and NO_x (NO + NO₂),¹⁰ as well as unimolecular autoxidation reactions.^{11,12} These subsequent reactions continue to incorporate oxygen, most commonly from O₂, producing increasingly oxygenated, lower-volatility organics that partition into the particle phase and contribute to new OA formation.¹² However, the relative contributions of different reactive oxygen species to VOC oxygenation (i.e., oxygen incorporation) remain under-constrained by direct atmospheric observations. In this context, oxygen isotope measurements offer a promising novel diagnostic for tracing oxidation pathways and oxidants involved in OA formation and aging.

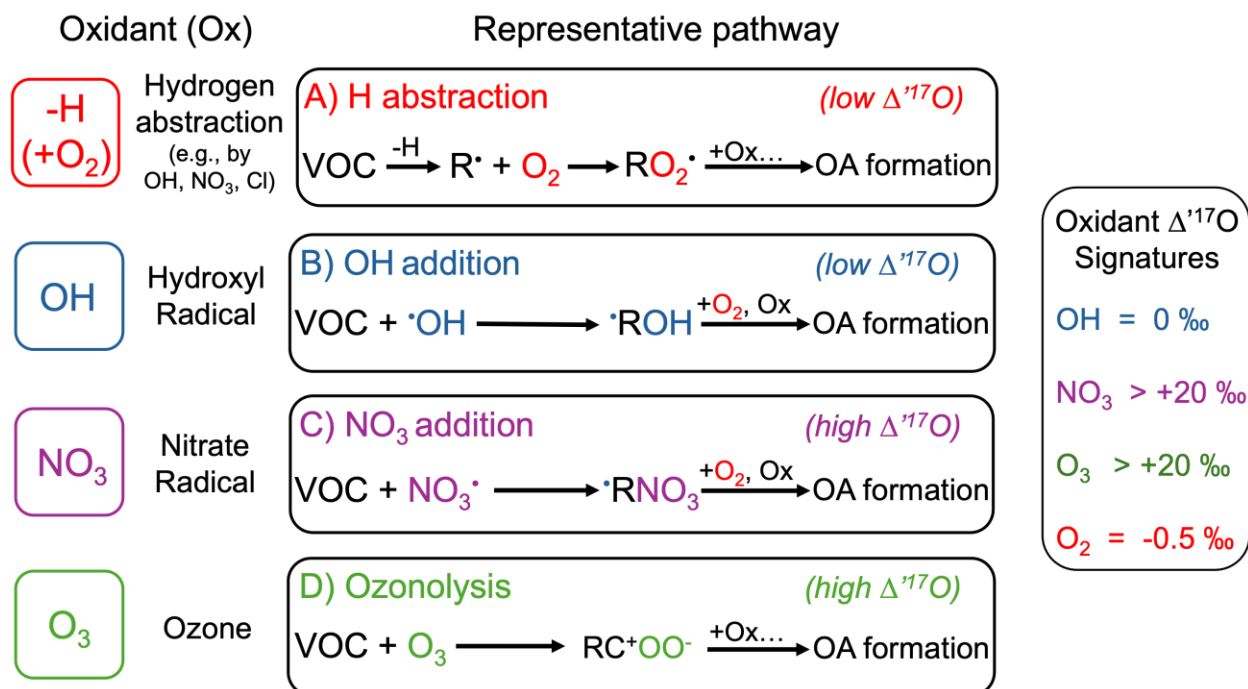


Fig. 1 | Representative VOC oxidation pathways and expected Δ¹⁷O signatures. Pathway A is common to most VOCs, whereas addition pathways (B-D) are specific to unsaturated VOCs (e.g., alkenes).⁷ Downstream VOC oxidation involves numerous intermediates and reaction networks, ultimately culminating in new OA formation (see main text).

The triple oxygen isotope (TOI) system (¹⁶O, ¹⁷O, and ¹⁸O) provides a powerful framework for investigating atmospheric chemistry.¹³ TOI analysis employs the Δ¹⁷O parameter to quantify deviations from the mass-dependent relationship between δ¹⁷O and δ¹⁸O (equation 1), thereby providing a means of tracking atmospheric oxygen reservoirs.¹⁴ In this framework, mass-dependent changes in δ¹⁷O and δ¹⁸O are related by the reference slope, λ_{ref}, for which we use the theoretical high-temperature limit of 0.5305 throughout this study.¹⁵

$$\Delta^{17}\text{O} = \delta^{17}\text{O} - \lambda_{\text{ref}} * \delta^{18}\text{O} \quad (1)$$

Most terrestrial oxygen reservoirs are mass-dependent (i.e., $\Delta^{17}\text{O} = 0 \text{ ‰}$).¹⁶ However, atmospheric photochemical reactions generate O_2 and O_3 with mass-independent $\Delta^{17}\text{O}$ signatures ($\Delta^{17}\text{O} \neq 0$), that are in turn distributed across many O-bearing atmospheric oxidants.^{17–19} These anomalous $\Delta^{17}\text{O}$ signatures can also be transferred to other species (e.g., organics) through atmospheric reaction networks, providing a record of chemical interactions and oxidation pathways (Fig. 1).²⁰ Consequently, TOI measurements have proven valuable in reconstructing the formation pathways of many atmospheric constituents – including CO_2 , CO , sulfate, and nitrate.²¹ However, despite similar diagnostic potential, the TOI framework has not yet been applied to organic matter (OM) in atmospheric aerosols, largely because of challenges associated with isolating organic-bound oxygen for isotopic analysis. In this study, we apply a recently developed TOI method²² to OM extracted from atmospheric aerosols sampled in an urban northeastern U.S. city (Providence, RI), providing a year-long time series of OA $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ measurements to evaluate the potential of the TOI system as a tracer of OA oxidation chemistry.

RESULTS

We analyzed 25 PM_{10} aerosol samples collected over 24-hour intervals in Providence, Rhode Island throughout 2007. Water-soluble OM was isolated by solid-phase extraction and analyzed for its elemental (C, N, O) and isotopic ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, $\Delta^{17}\text{O}$) compositions (see Methods). Back-trajectory analyses indicated predominantly continental air-masses, with occasional subtropical North Atlantic influence during May-September (Extended Data Fig. 1). Accordingly, OA $\delta^{13}\text{C}$ (-26.5 to -27.9 ‰) and $\delta^{15}\text{N}$ (5.0-12.3 ‰) values are consistent with contributions from mixed continental sources (Extended Data Table 1).²³ The OA concentrations ranged from

0.40-1.66 $\mu\text{g}/\text{m}^3$ with accompanying O/C ratios of 0.26-0.57 that are comparable to those reported for secondary OA formed through VOC oxidation (Extended Data Table 1).^{24,25}

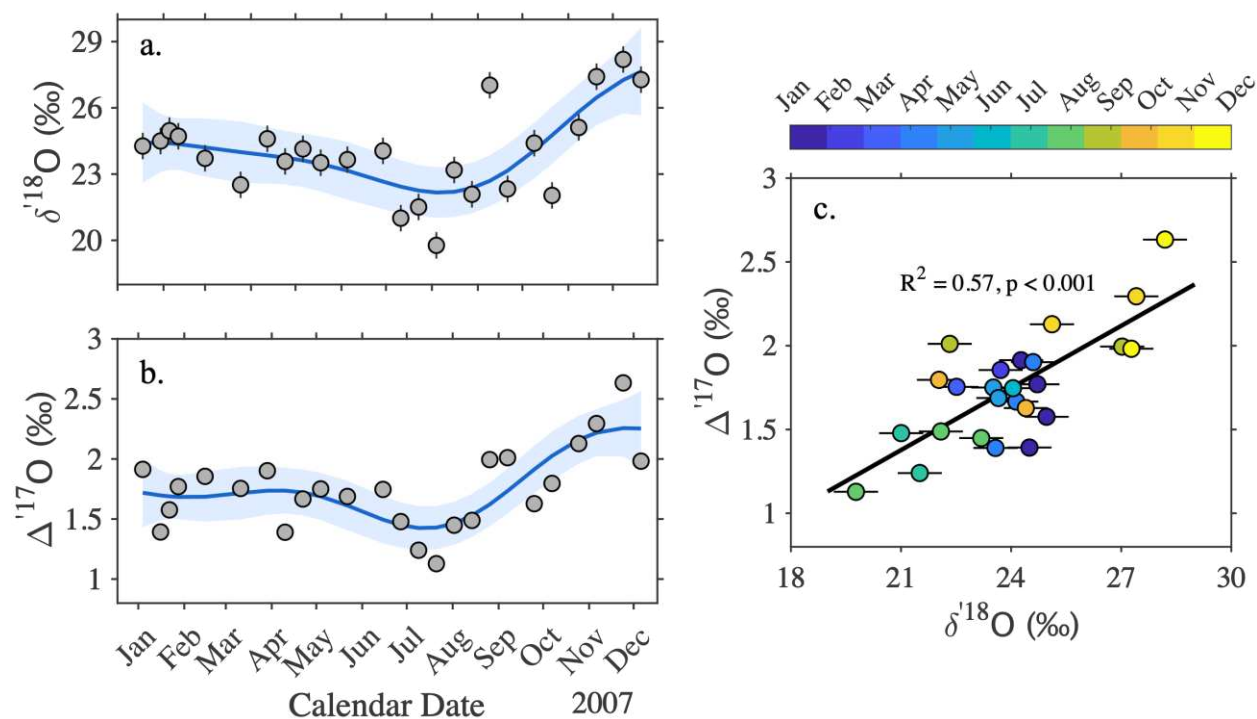


Fig. 2 | Temporal variability and covariation of OA TOI compositions. Annual timeseries of **a)** $\delta^{18}\text{O}$ and **b)** $\Delta^{17}\text{O}$ measured throughout 2007. Temporal structure was assessed using multiple linear regression incorporating annual harmonic terms and a linear time trend;²⁶ the regression mean and 95% confidence interval are shown as the blue line and shading. Both $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ exhibit statistically significant temporal variability (multiple linear regression trend, $p < 0.01$). **c)** Relationship between OA $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$, showing their positive correlation ($R^2 = 0.57$, $p < 0.001$) with a mass-independent $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ slope of 0.65 ± 0.02 . The data points are shaded according to collection date. Error bars represent 1σ uncertainties; the 1σ uncertainty in $\Delta^{17}\text{O}$ is smaller than the plotting symbols.

The year-long TOI dataset reveals several distinctive isotopic characteristics of atmospheric OA. Most notably, the $\delta^{18}\text{O}$ ranged from 19.8 to 28.2 ‰ and all samples carried positive, mass-independent $\Delta^{17}\text{O}$ compositions between 1.1 and 2.6 ‰ (Fig. 2a,b). Both $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ exhibit statistically significant seasonal structure, characterized by a modest summertime minimum followed by more pronounced enrichments later in the year that exceed those observed at the beginning of 2007. Thus, while seasonal processes may contribute to the intra-annual isotopic variability, the absolute $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values likely vary from year-to-year. The $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values are also positively correlated throughout the annual record ($R^2 = 0.57$; Fig. 2c), with a $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ slope of 0.65 ± 0.02 that lies well outside the 0.50-0.53 range for mass-dependent fractionation,²⁷ consistent with the observed contribution of mass-independent oxygen to the OA. Neither $\delta^{18}\text{O}$ nor $\Delta^{17}\text{O}$, however, were significantly correlated with the OA concentration or O/C ratio (Extended Data Fig. 2), suggesting that the processes controlling the TOI compositions are largely decoupled from OA abundance and bulk oxidation state.

DISCUSSION

Identifying atmospheric oxidants participating in OA oxygenation. The OA TOI compositions reflect the isotopic signatures of the oxidants contributing oxygen atoms during OA formation and aging – hereafter termed oxygenation – providing a unique perspective on the pathways governing these processes. Despite exhibiting statistically significant seasonal variability, the OA $\delta^{18}\text{O}$ values only span an 8 ‰ range (20-28 ‰) that is much smaller than that of atmospheric oxidants (~150 ‰).²⁸ Moreover, these values differ markedly from the $\delta^{18}\text{O}$ compositions of the primary VOC oxidation initiators (OH, NO₃ radical, and O₃),²⁸ but closely resemble that of atmospheric O₂ (23.6 ± 0.4 ‰).²⁹ At first glance, this correspondence suggests that O₂ may exert a stronger

influence on the OA $\delta^{18}\text{O}$ signatures than these primary oxidants, consistent with the established role of O_2 as an important oxygen source in radical-mediated OA oxygenation chemistry (Fig. 1A).^{11,12}

The inclusion of $\Delta^{17}\text{O}$ provides an additional constraint on OA oxidation chemistry because all samples carried positive, mass-independent $\Delta^{17}\text{O}$ values (Fig. 2b). The OA $\Delta^{17}\text{O}$ compositions were positively correlated with $\delta^{18}\text{O}$, indicating that the processes or reservoirs responsible for imparting the mass-independent isotopic signal also influence the $\delta^{18}\text{O}$ composition. The observed $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ covariation could reflect isotopic variability in a single dominant oxygen source, of which O_2 seems the most plausible given its similarity to OA $\delta^{18}\text{O}$ and established role in OA oxygenation^{11,12} However, the well mixed nature of atmospheric O_2 (i.e., no seasonality)³⁰ and its firmly established negative $\Delta^{17}\text{O}$ composition (-0.5‰),²⁹ preclude it from exclusively explaining the OA TOI variability and uniformly positive $\Delta^{17}\text{O}$ values (Fig. 2). The next obvious consideration is that the observed TOI compositions and isotopic covariance reflect mixing between two or more oxygen sources. Here, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ variability could arise from changes in the source oxidant isotopic composition(s) and/or their relative contributions to OA oxygenation, the latter potentially reflecting seasonal changes in oxidant abundances and VOC composition. Such a scenario requires oxygen sources both more enriched and more depleted in $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ than the OA itself.

We first consider the potential enriched endmembers capable of generating the positive OA $\Delta^{17}\text{O}$ values. One obvious candidate is O_3 , given its highly enriched isotopic composition ($\delta^{18}\text{O} = 110 \pm 15\text{‰}$ and $\Delta^{17}\text{O} = 26 \pm 5\text{‰}$)^{31,32} and established role in VOC and particle-phase OA oxidation (Fig. 1D).^{33,34} Laboratory experiments using ^{18}O -labelled O_3 have confirmed that alkene ozonolysis directly incorporates oxygen atoms from O_3 ,³⁵ while separate experiments

demonstrated that these reactions transfer the $\Delta^{17}\text{O}$ signature of O_3 to the oxidation products.³⁶ This transfer of O_3 -derived, mass-independent oxygen is also well established for atmospheric sulfate and nitrate, where O_3 oxidation exerts a major control on variations in their TOI compositions.^{37,38} Analogously, variability in the contribution of O_3 to OA oxygenation could also credibly generate the observed $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ relationship.

A second potential oxygen source is the NO_3 radical, whose enriched isotopic composition is inherited largely from O_3 through the $\text{NO}_2 + \text{O}_3$ reaction pathway.³⁹ Consequently, although the NO_3 radical itself cannot be measured directly, it is inferred to possess elevated $\delta^{18}\text{O}$ (~100 ‰) and $\Delta^{17}\text{O}$ (up to 40 ‰) values.^{39,40} The NO_3 radical is also a potent oxidant that reacts with organics through both hydrogen abstraction and direct addition pathways, the latter incorporating NO_3 radical-derived oxygen into the reaction products (Fig. 1C).⁴¹ This chemistry is strongly seasonal with large modeled increases in NO_3 radical and organonitrate (RONO_2) concentrations occurring during the warmer months in this region (Extended Data Figs. 3 and 4). Because these reactions simultaneously incorporate nitrogen and oxygen into the oxidation products, a substantial contribution from NO_3 radical-derived oxygen is expected to produce a positive relationship between OA nitrogen content and $\Delta^{17}\text{O}$. However, OA nitrogen content remained low (1.6-3.1 wt.%), seasonally invariant, and exhibited no correlation with OA $\Delta^{17}\text{O}$ throughout the study (Extended Data Fig. 4). Likewise, OA $\Delta^{17}\text{O}$ was not correlated with the seasonally varying $\Delta^{17}\text{O}$ of particulate nitrate (Extended Data Fig. 4),⁴² the stable oxidation product from the same NO_x - O_3 chemistry responsible for NO_3 radical formation.⁴³ These observations provide little evidence that NO_3 -derived oxygen (and its strong seasonality) contributed substantially to the observed OA TOI compositions. Of note, rapid particle-phase hydrolysis of RONO_2 can remove NO_3 -derived oxygen from the organic fraction,⁴⁴ such that NO_3 may play a larger role in initiating OA oxidation than

is preserved in the OA isotopic composition. Consequently, among the isotopically enriched atmospheric oxidants considered here, direct incorporation of O₃-derived oxygen appears the most likely source of the positive OA $\Delta^{17}\text{O}$ values.

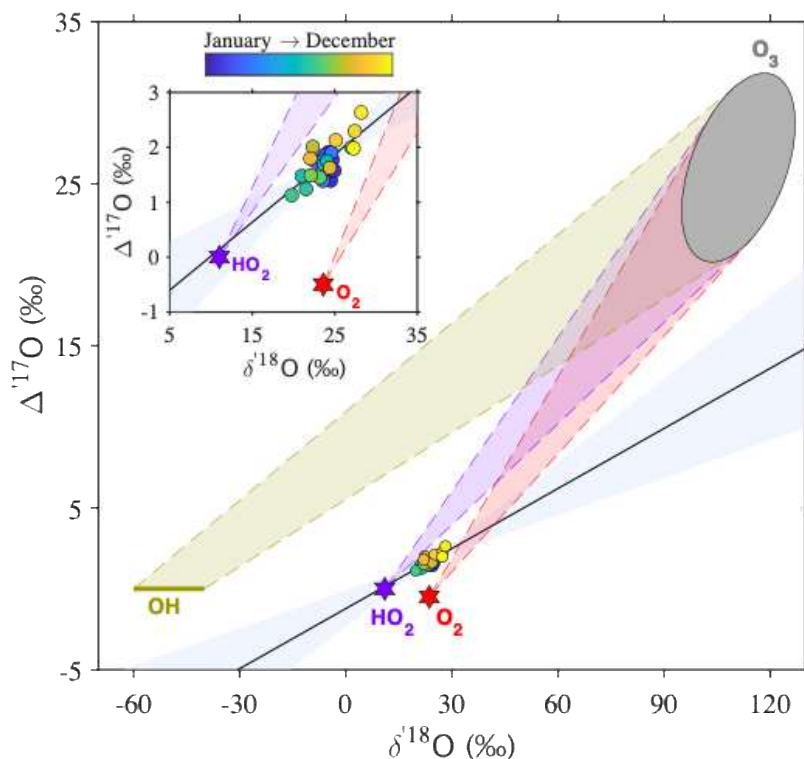


Fig. 3 | Isotopic constraints on two-endmember mixing during OA oxygenation. Observed OA TOI compositions compared with all possible two-endmember mixing relationships between atmospheric O₃ and O₂, HO₂, or OH. The OA TOI compositions throughout the annual sampling period are shown as shaded circles. The solid black line and light blue shaded region denote the OA regression and its 95 % confidence interval. Dashed lines show the bounds of all possible two-endmember mixtures defined by the reported range of atmospheric O₃ TOI compositions (gray ellipse)^{31,32} and the isotopic endmember for either atmospheric O₂ (red star),²⁹ HO₂ (purple star),^{39,45} or OH (bronze line).⁴⁰ Insets show the same isotopic data on constricted axes. In all cases, the OA compositions lie outside the corresponding mixing envelopes, indicating that binary mixing involving the oxidants considered here cannot explain their observed TOI compositions.

Two-component mixing as a potential explanation for the OA TOI compositions. While O₃ is a plausible source of isotopically enriched oxygen in OA, the measured OA TOI compositions still require one or more additional oxygen sources with lower $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values than the OA itself. Among the atmospheric oxidants commonly implicated in OA chemistry, O₂, OH, and HO₂ span this depleted isotopic space (Fig. 3). Given its $\delta^{18}\text{O}$ similarity to the OA, O₂ defines the upper isotopic limit of plausible depleted endmembers. Lying at the opposite extreme, the theoretically derived isotopic composition of OH ($\delta^{18}\text{O} = -40$ to -60 ‰, $\Delta^{17}\text{O} = 0$ ‰)^{40,46} defines the lower isotopic limit. Finally, HO₂ occupies an intermediate position. Although atmospheric isotope work has generally treated HO₂ as mass-dependent (i.e., $\Delta^{17}\text{O} = 0$ ‰) with a $\delta^{18}\text{O}$ similar to O₂,^{47,48} recent studies have empirically inferred a lower $\delta^{18}\text{O}$ value of ~ 11 ‰ for oxygen transfer from HO₂ during NO_x oxidation.^{39,45} We therefore consider this inferred HO₂ composition as a potential intermediate $\delta^{18}\text{O}$ depleted endmember between that of O₂ and OH (see Fig. 3).

As a first order test, we evaluated whether two-component mixing between O₃ and each candidate depleted oxidant could satisfy the population of OA isotopic compositions (Fig. 3). Under this scenario, the OA TOI compositions should fall within the isotopic bounds defined by mixing between these two endmembers. In every case, however, the observed OA TOI compositions lie outside the corresponding mixing fields, indicating that binary mixing involving the oxidants most commonly implicated in OA chemistry cannot adequately reproduce the observed isotope systematics. These observations suggest contributions from at least three isotopically distinct oxygen sources within the oxidant framework considered here. We therefore next evaluated whether a three-endmember mixing approach could account for the isotopic observations and provide quantitative constraints on the relative contributions of these candidate oxidants to OA oxygenation.

A multi-component isotopic mixing model to quantify OA oxidation pathways. The TOI data point to multiple oxygen sources potentially contributing to OA oxygenation, including O₂, O₃, HO₂, and OH. To quantitatively evaluate their relative contributions, we employed a three-component isotopic mixing model combined with Monte Carlo resampling ($n = 10^6$) to propagate uncertainty in isotopic endmember compositions (see Methods for model description). Of the four possible three-oxidant combinations, only the O₂/O₃/HO₂ and O₂/O₃/OH mixtures produced at least one accepted solution for all 25 OA samples. For each sample, the accepted Monte Carlo solutions were averaged to obtain a single mean ternary composition, yielding 25 modeled compositions for each three-component mixture. These mean compositions are shown in Fig. 4 together with 68 % and 95 % density envelopes encompassing the pooled accepted solutions across all samples; the remaining mixtures are shown in Extended Data Fig. 5.

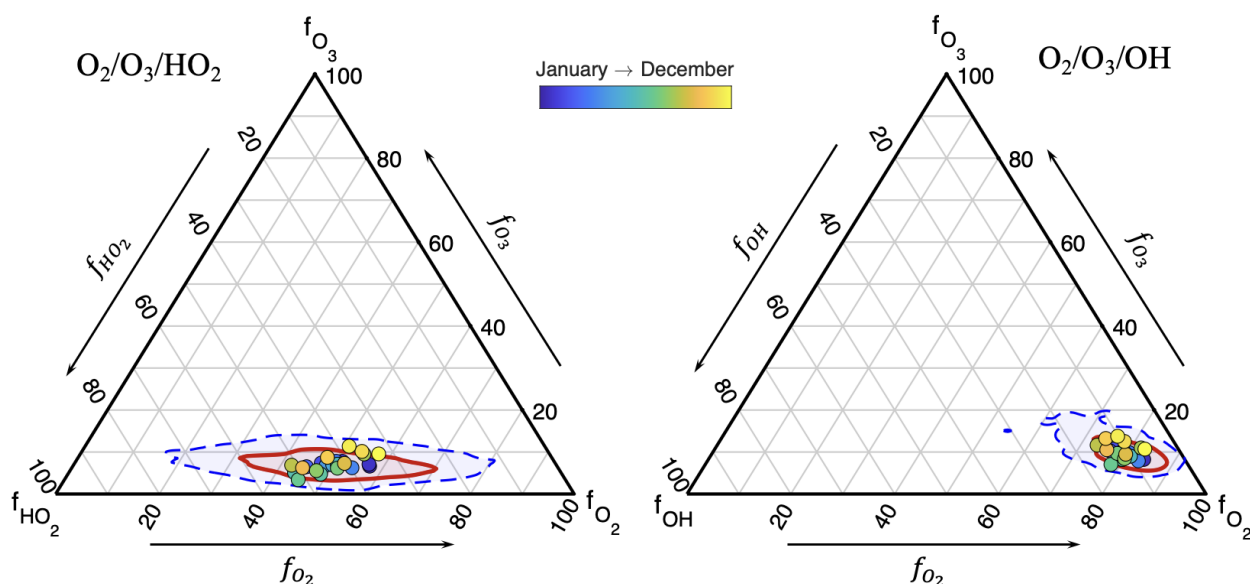


Fig. 4 | Three-component isotopic mixing models constrain oxidant contributions to OA oxygenation. Ternary compositions derived from $O_2/O_3/HO_2$ (left) and $O_2/O_3/OH$ (right) isotopic mixing models. Data points represent the mean modeled composition for each OA sample and are colored by collection date. Dashed blue and solid red contours denote 68 % and 95 % density envelopes of the pooled accepted Monte Carlo solutions across all samples, reflecting both endmember uncertainty and sample-to-sample variability.

Both calculations reproduce the observed OA TOI compositions, but they carry markedly different chemical implications for the participating oxygen sources. While O_2 contributes substantially to both mixtures, its contribution in the $O_2/O_3/HO_2$ scenario (42-58 %) is much lower than in the $O_2/O_3/OH$ scenario (73-84 %), necessitating a nearly equivalent contribution from HO_2 (33-52 %). Although the broader 68 % density region for the $O_2/O_3/HO_2$ mixture indicates greater dispersion among the isotopically feasible contributions from O_2 (32-71 %) and HO_2 (24-60 %), such a sizable contribution from HO_2 as an *oxygen source* is difficult to reconcile with its established reaction pathways, which do not directly transfer oxygen to the final OA product.^{10,49}

By comparison, the O₂/O₃/OH scenario indicates that O₂ was the dominant OA oxygen source across all samples. The remaining oxygen was supplied by modest contributions from O₃ (7-14 %) and OH addition (6-15 %), consistent with their central roles in initiating oxidation of unsaturated VOCs but more limited contributions to subsequent oxygenation reactions.⁵⁰ These oxygen source contributions largely align with the current mechanistic understanding of OA oxygenation,⁵¹ suggesting that the O₂/O₃/OH mixture provides the more chemically realistic representation of OA oxidation pathways.

Having identified the O₂/O₃/OH mixture as the most chemically plausible representation of OA oxygenation consistent with our isotopic data, we can compare its oxygen source contributions with previous descriptions of atmospheric OA chemistry. Although most studies report fractional contributions of oxidants initiating first-generation VOC oxidation rather than bulk oxygen source contributions,⁵²⁻⁵⁶ these quantities provide a useful benchmark for comparison. For example, atmospheric models predict that 80-90 % of isoprene oxidation proceeds through the OH addition pathway (Fig. 1B),⁵²⁻⁵⁵ in which OH and O₂ are the predominant oxygen sources. Similarly, OH and O₂ together account for 86-93 % of OA oxygenation in the O₂/O₃/OH mixture. Extending this chemistry one step further, first generation products from OH-initiated isoprene oxidation typically contain one oxygen from OH and one or two from O₂ (O₂/OH ratio of 1-2).⁵⁷ The substantially larger O₂/OH ratios predicted by the O₂/O₃/OH scenario (5-13) therefore support the strong influence of O₂-mediated chemistry in downstream OA oxygenation.^{58,59}

Comparison of the O₃ contribution requires a slightly different interpretation because ozonolysis can incorporate more than one oxygen atom from O₃ into first-generation products, while subsequent oxidation introduces oxygen from additional sources, primarily O₂.^{12,35} Nevertheless, the O₃ contribution predicted by the O₂/O₃/OH mixture (7-14 %) falls within the

range of reported O₃-initiated contributions to isoprene oxidation (9-15 %)⁵²⁻⁵⁵ and is comparable to empirical estimates for monoterpene oxidation (17 ± 8 %),⁵⁶ suggesting that the isotopically constrained O₃ contributions are broadly consistent with existing estimates for the role of ozonolysis in atmospheric OA oxygenation. One potential implication of this agreement is that the greater incorporation of O₃-derived oxygen during initial ozonolysis may be approximately balanced by subsequent oxygen addition from O₂- and OH-mediated oxidation. In a broader sense, these quantitatively resolved oxidant-specific contributions provide an independent observational constraint on current representations of atmospheric OA oxidation pathways.

Seasonal variability in oxidant contributions to OA oxygenation. Although O₂ remained the dominant oxygen source throughout the year, its modeled relative contribution varied minimally and does not explain the observed OA TOI variability and its seasonal signal (Extended Data Figs. 6 and 7). By contrast, the modeled OH (6-15 %) and O₃ (7-14 %) contributions each varied by approximately two-fold throughout the year and were significantly correlated with OA $\delta^{18}\text{O}$ ($R^2 = 0.52$ and 0.44 , respectively), indicating that variations in both oxidants influence the OA isotopic composition directly (Extended Data Fig. 6). The modeled O₃ contribution was also strongly correlated with OA $\Delta^{17}\text{O}$ ($R^2 = 0.89$), consistent with O₃ being the only oxidant included here that carries a large, positive mass-independent isotopic signature. Moreover, the O₃ contribution exhibits similar seasonal structure to the OA TOI record, with the OH contribution varying in the opposite sense (Extended Data Fig. 7). The TOI record therefore appears to primarily reflect seasonal variability in the minor contributions from O₃- and OH-mediated oxidation, superimposed upon a persistent background of O₂-dominated chemistry. This interpretation is also consistent with the well-established role of OH, and especially O₃, in driving

isotopic variability within atmospheric NO_x oxidation pathways.^{37,45} Notably, the inferred O_3 contribution is lowest during summer despite the summertime maximum in ambient O_3 concentration (Extended Data Fig. 3), indicating that O_3 concentration alone does not determine its relative contribution to OA oxygenation. An analogous behavior is observed for atmospheric nitrate, whose $\Delta^{17}\text{O}$ values decrease during summer as enhanced OH oxidation reduces the relative contribution of O_3 -driven pathways.^{38,60} However, OA and nitrate $\Delta^{17}\text{O}$ values are not directly correlated (Extended Data Fig. 4), indicating that their seasonal isotopic variability is not governed by identical oxidation chemistry. For OA, seasonal changes in precursor VOC composition and lifetime may provide additional controls on the competition between O_3 - and OH-mediated oxidation.⁶¹ Although their relative importance cannot be uniquely resolved here, these observations indicate that seasonal oxidant contributions to OA oxygenation reflect atmospheric reaction competition rather than oxidant abundance alone.

CONCLUSIONS

The formation and atmospheric aging chemistry of OA remains a major source of uncertainty in assessing aerosol impacts on atmospheric composition and climate.⁶² Here, we demonstrate that TOI measurements provide a quantitative framework for identifying and constraining the oxidants contributing to OA chemistry. By incorporating the $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ data into a three-component isotopic mixing model and propagating endmember uncertainty through Monte Carlo resampling, we derive the first atmospheric observation-based estimates on oxidant-specific contributions to OA oxygenation. Notably, an isotopic mixture consisting of $\text{O}_2/\text{O}_3/\text{OH}$ yielded oxidant contributions that are largely consistent with independent predictions from atmospheric chemistry models,^{52–56} supporting current representations of OA formation pathways where oxygen is

primarily contributed by O₂ incorporation, complemented by minor contributions from OH addition and ozonolysis reactions. More broadly, this work establishes TOI measurements as a powerful new observational diagnostic for evaluating OA oxidation mechanisms and improving atmospheric representations of aerosol chemistry, thereby reducing key sources of uncertainty in aerosol-climate interactions.

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METHODS

Aerosol Sample Collection and OM Extraction

PM₁₀ aerosols were collected in downtown Providence, Rhode Island (41.82°N, 71.43°W) throughout 2007 using a high-volume sampler operated according to EPA protocols.⁶³ Samples were collected onto quartz fiber filters over 24-hour intervals at a flow rate of 1.13 m³ min⁻¹ (~1700 m³ air per sample) and stored in the dark at room temperature until analysis. Water-soluble organic matter (OM) was extracted by immersing each filter in 200 mL ultrapure water (18.2 MΩ), followed by overnight extraction and 30 min sonication. Extracts were filtered through 0.22 μm Steriflip filters (EMD Millipore) and OM was isolated using solid-phase extraction (SPE) on Bond Elut PPL cartridges (3 mL, 100 mg resin; Agilent Technologies) following established protocols.⁶⁴ After loading the filtered extract, the cartridge was acidified with 0.01 M HCl to remove dissolved inorganic constituents, dried, and the retained OM was eluted with 3 mL methanol:acetone (50:50 v). The solvent extract was evaporated to dryness, reconstituted in 200 μL methanol:acetone (50:50 v), and equally divided into two, 100 μL aliquots. These aliquots were transferred to pre-weighed silver (TOI) or tin (δ¹³C and δ¹⁵N) capsules, dried under N₂ flow, and reweighed to determine OM mass, before being subjected to the isotopic analyses as described below.

Isotopic Measurements of OA Extracts

Direct determination of δ¹⁷O in CO and CO₂ by conventional isotope ratio mass spectrometry (IRMS) is precluded by an isobaric interference between ¹³C and ¹⁷O isotopic substitutions. To overcome this limitation, we recently developed a workflow that transfers the TOI signature of

organic matter (OM) to O₂ through sequential pyrolysis of OM to CO, oxidation of CO to CO₂ using I₂O₅, and isotopic equilibration of the resulting CO₂ with an O₂ reference gas of known TOI composition.²² The $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ compositions of the OM were subsequently determined by isotopic mass balance (see ref²²), and $\Delta^{17}\text{O}$ was calculated using Eq. 1.

Method performance was evaluated using the reference materials IAEA CH-3 cellulose (n = 17) and Suwannee River natural organic matter (SRNOM; n = 14). Oxygen yields averaged $95.2 \pm 3.6 \%$ and $98.3 \pm 2.1 \%$, respectively. The 1σ reproducibility of $\delta^{18}\text{O}$ was 0.50 ‰ for IAEA CH-3 and 0.70 ‰ for SRNOM, while that of $\Delta^{17}\text{O}$ was 0.030 ‰ and 0.032 ‰, respectively. The mean reproducibility across both reference materials (0.60 ‰ for $\delta^{18}\text{O}$ and 0.031 ‰ for $\Delta^{17}\text{O}$) was adopted as the analytical uncertainty for aerosol OM measurements.

OM recovery efficiency

To assess OM recovery during extraction, four SRNOM aliquots (0.75-0.85 mg) were subjected to the same SPE and isotopic procedures used for the aerosol samples. Comparison of the recovered PPL extracts with the initial SRNOM masses indicated an OM recovery of $52 \pm 3 \%$, consistent with previous applications of this SPE method.^{65,66} Comparison of the oxygen yield from the recovered extracts with the estimated oxygen content of the initial SRNOM aliquots indicated that $47 \pm 2 \%$ of the original oxygen was retained. The recovered SRNOM extracts yielded $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values of $22.85 \pm 0.70 \text{ ‰}$ and $-0.023 \pm 0.063 \text{ ‰}$, respectively, both within 1σ uncertainty of previously reported values for the untreated SRNOM isolate ($23.91 \pm 0.71 \text{ ‰}$ and $-0.064 \pm 0.019 \text{ ‰}$).²² This agreement indicates that, although approximately half of the OM and oxygen are retained during extraction, its isotopic composition is well preserved throughout the extraction and analytical workflow.

$\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ Measurements

The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ compositions of each OA extract were determined using a ThermoScientific Flash Elemental Analyzer equipped with a thermal conductivity detector and a Delta V Plus isotope-ratio mass spectrometer. Authentic reference standards of USGS40 ($\delta^{13}\text{C} = -26.39 \text{ ‰}$, $\delta^{15}\text{N} = -4.52 \text{ ‰}$), USGS41a ($\delta^{13}\text{C} = +36.55 \text{ ‰}$, $\delta^{15}\text{N} = 47.55 \text{ ‰}$), and tyrosine ($\delta^{13}\text{C} = -24.90 \text{ ‰}$, $\delta^{15}\text{N} = 4.70 \text{ ‰}$) were run concurrently and used for peak-size and isotopic-scale calibrations. All $\delta^{13}\text{C}$ data are reported in delta notation relative to Vienna Pee Dee Belemnite and $\delta^{15}\text{N}$ data relative to atmospheric N_2 . Analytical precisions for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ were 0.13 ‰ and 0.21 ‰, respectively, based on the weighted standard deviation of the reference materials. Carbon and nitrogen contents were determined from calibrated elemental analyzer peak areas and normalized to sample mass to obtain C and N wt.%, with a precision of 0.25 %.

A full procedural blank encompassing all steps from solid-phase extraction through isotopic analysis was prepared by processing four, 200 mL aliquots of ultrapure water through the complete extraction and analytical workflow. Blank $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ compositions were determined from individual tin capsule analyses and used to correct the measured aerosol OM isotope compositions using isotopic mass balance (equation 2).

$$\delta^{13}\text{C}_{\text{OA}} = (f_{\text{blank}})(\delta^{13}\text{C}_{\text{blank}}) + (f_{\text{measured}})(\delta^{13}\text{C}_{\text{measured}}) \quad (2)$$

For oxygen isotopes, the four samples were pooled together, and the combined blank yielded a $\delta^{18}\text{O}$ value of 5.45 ‰. The oxygen contributed by the combined blank was insufficient for direct $\delta^{17}\text{O}$ determination, so the blank was assumed to be mass dependent ($\Delta^{17}\text{O} = 0 \text{ ‰}$), corresponding to $\delta^{17}\text{O} = 2.89 \text{ ‰}$. Blank corrections for $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ were subsequently performed using

isotopic mass balance in fractional abundance space (e.g., $^{18}\text{F} = ^{18}\text{O}/(^{16}\text{O} + ^{17}\text{O} + ^{18}\text{O})$), as required for three-isotope systems.²⁷

Description of Monte Carlo three-component isotopic mixing model

The TOI data distinguish several oxidants potentially contributing to OA oxygenation: O_2 (via radical-initiated reactions), O_3 , HO_2 , and OH . These oxidants were integrated into a three-component isotopic mixing model constrained by equations 3-5, where f_i represents the fractional contribution for each oxidant (Ox).

$$\delta'^{18}\text{O}_{\text{OA}} = f_1 \times \delta'^{18}\text{O}_{\text{Ox1}} + f_2 \times \delta'^{18}\text{O}_{\text{Ox2}} + f_3 \times \delta'^{18}\text{O}_{\text{Ox3}} \quad (3)$$

$$\Delta'^{17}\text{O}_{\text{OA}} = f_1 \times \Delta'^{17}\text{O}_{\text{Ox1}} + f_2 \times \Delta'^{17}\text{O}_{\text{Ox2}} + f_3 \times \Delta'^{17}\text{O}_{\text{Ox3}} \quad (4)$$

$$1 = f_1 + f_2 + f_3 \quad (5)$$

If the $\delta'^{18}\text{O}$ and $\Delta'^{17}\text{O}$ compositions of each oxidant were known precisely, equations 3-5 would uniquely determine their fractional contributions. However, because the isotopic compositions of the candidate endmembers are variable and imperfectly constrained, we instead used a Monte Carlo rejection-sampling approach to explore the range of source fractions consistent with each measured aerosol composition. For each realization, three candidate source fractions were randomly generated and normalized to satisfy the closure condition ($f_1 + f_2 + f_3 = 1$), while $\delta'^{18}\text{O}$ and $\Delta'^{17}\text{O}$ values for each endmember were independently sampled from their prescribed isotope distributions (Table 1). The resulting source fractions and endmember compositions were then used to calculate a predicted OA $\delta'^{18}\text{O}$ and $\Delta'^{17}\text{O}$ composition using equations 3 and 4. Realizations were retained when both predicted isotopic values agreed with the measured OA composition within analytical uncertainty ($\pm 0.6\text{‰}$ for $\delta'^{18}\text{O}$ and $\pm 0.031\text{‰}$ for $\Delta'^{17}\text{O}$). Repeating this procedure

10^6 times for each of the 25 aerosol samples generated distributions of source fractions that are isotopically consistent with each observation, conditional on the assumed endmember set and isotope distributions. The approach therefore identifies the feasible mixing space for a specified endmember scenario rather than providing a conventional statistical goodness-of-fit test among alternative endmember models.

Endmember isotopic compositional ranges were obtained from the published literature and converted to linearized delta notation, including standardizing all $\Delta^{17}\text{O}$ values using $\lambda_{\text{ref}} = 0.5305$ (see equation 1). Those reported for O_2 and O_3 were obtained by direct atmospheric measurement.^{29,31,32} The isotopic endmember ranges for HO_2 were empirically inferred from a combination of model simulations^{18,45} and experimentation.^{19,39} Finally, the $\delta^{18}\text{O}$ compositional range and mass-dependent $\Delta^{17}\text{O}$ of OH were theoretically derived based on its rapid isotopic equilibration with atmospheric H_2O .^{40,46} The endmember distributions and their respective bases are summarized in Table 1.

Table 1 | Isotope endmembers for three-component modeling of OA oxidant contributions.

OA Oxygen Source	Oxidant $\delta^{18}\text{O}$ & $\Delta^{17}\text{O}$ endmember ranges	Basis
O_2	$\delta^{18}\text{O}(\text{O}_2) = 23.6 \pm 0.4 \text{ ‰}$ $\Delta^{17}\text{O}(\text{O}_2) = -0.50 \pm 0.07 \text{ ‰}$	Atmospheric Measurements ²⁹
O_3	$\delta^{18}\text{O}(\text{O}_3) = 90 \text{ to } 120 \text{ ‰}$ $\Delta^{17}\text{O}(\text{O}_3) = 20 \text{ to } 30 \text{ ‰}$	Atmospheric Measurements ^{31,32}
HO_2	$\delta^{18}\text{O}(\text{HO}_2) = 10 \text{ to } 12 \text{ ‰}$ $\Delta^{17}\text{O}(\text{HO}_2) = 0 \text{ to } 2 \text{ ‰}$	Inferred from model simulations and experimentation ^{18,19,39,45}
OH	$\delta^{18}\text{O}(\text{OH}) = -40 \text{ to } -60 \text{ ‰}$ $\Delta^{17}\text{O}(\text{OH}) = 0 \text{ ‰}$	$\text{OH-H}_2\text{O}$ isotopic equilibrium ^{40,46}

Data and materials availability: All aerosol measurement data are available in the main text and/or Extended Data tables. Modeling data for atmospheric concentrations of relevant chemical species were downloaded from the Copernicus Atmosphere Modeling Service (CAMS) EAC4 global reanalysis dataset (<https://ads.atmosphere.copernicus.eu/datasets/cams-global-reanalysis-eac4>).

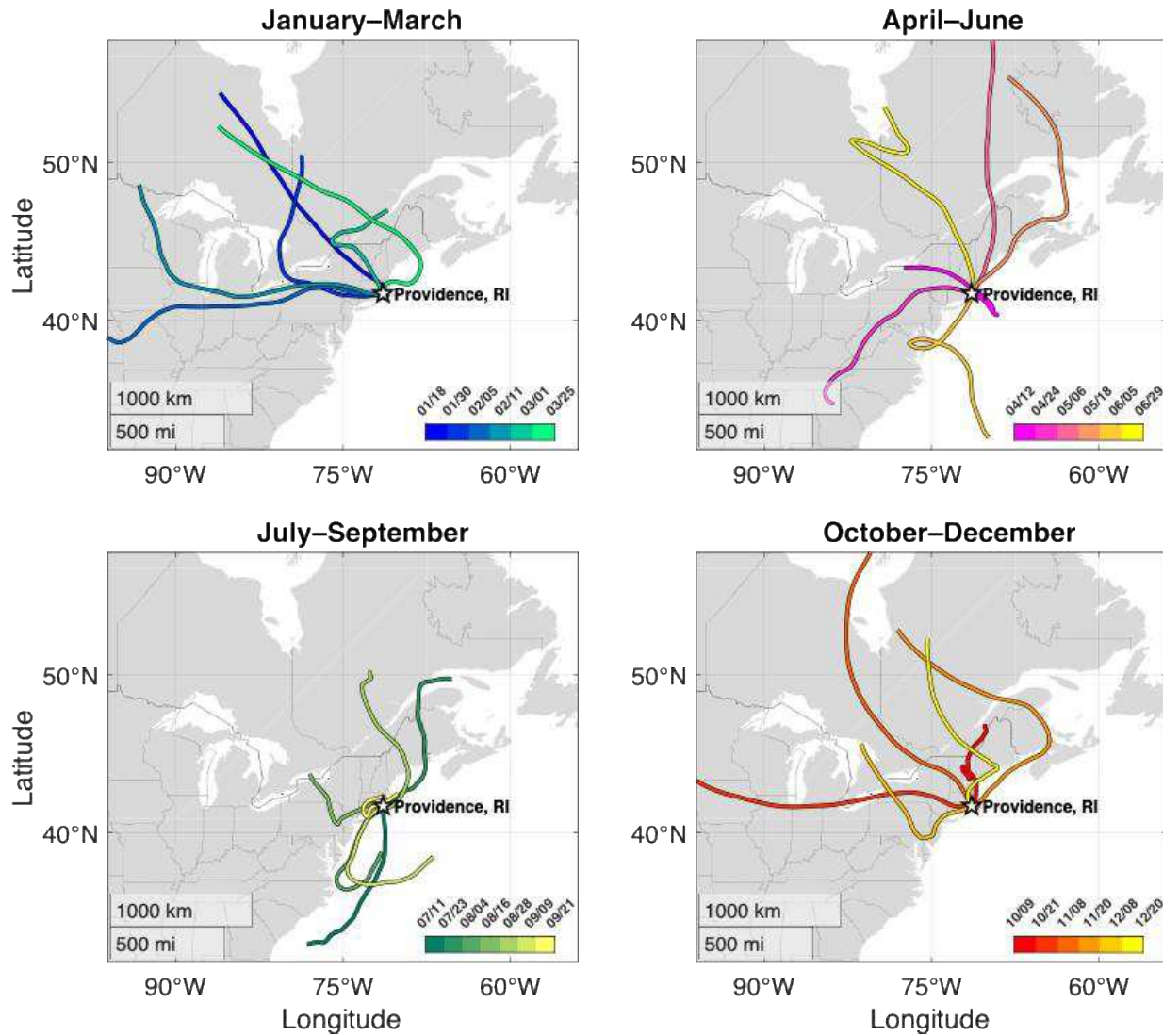
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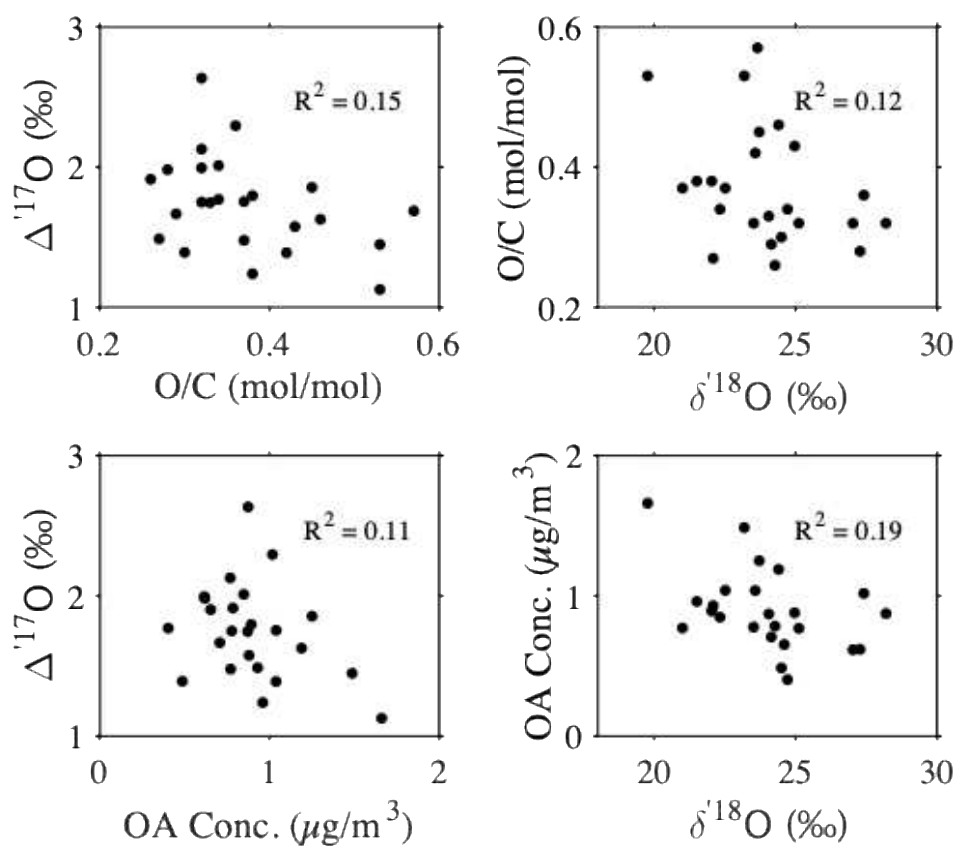
Author Contributions: DRC, MGH, and DTJ designed research; HK and MGH provided samples; DRC and EKD conducted research; DRC and DTJ analyzed data; DRC, HK, MBG, MGH, and DTJ contributed to data interpretation; DRC and DTJ wrote the manuscript with editing from HK, MBG, and MGH.

Competing interests: The authors declare that they have no competing interests.

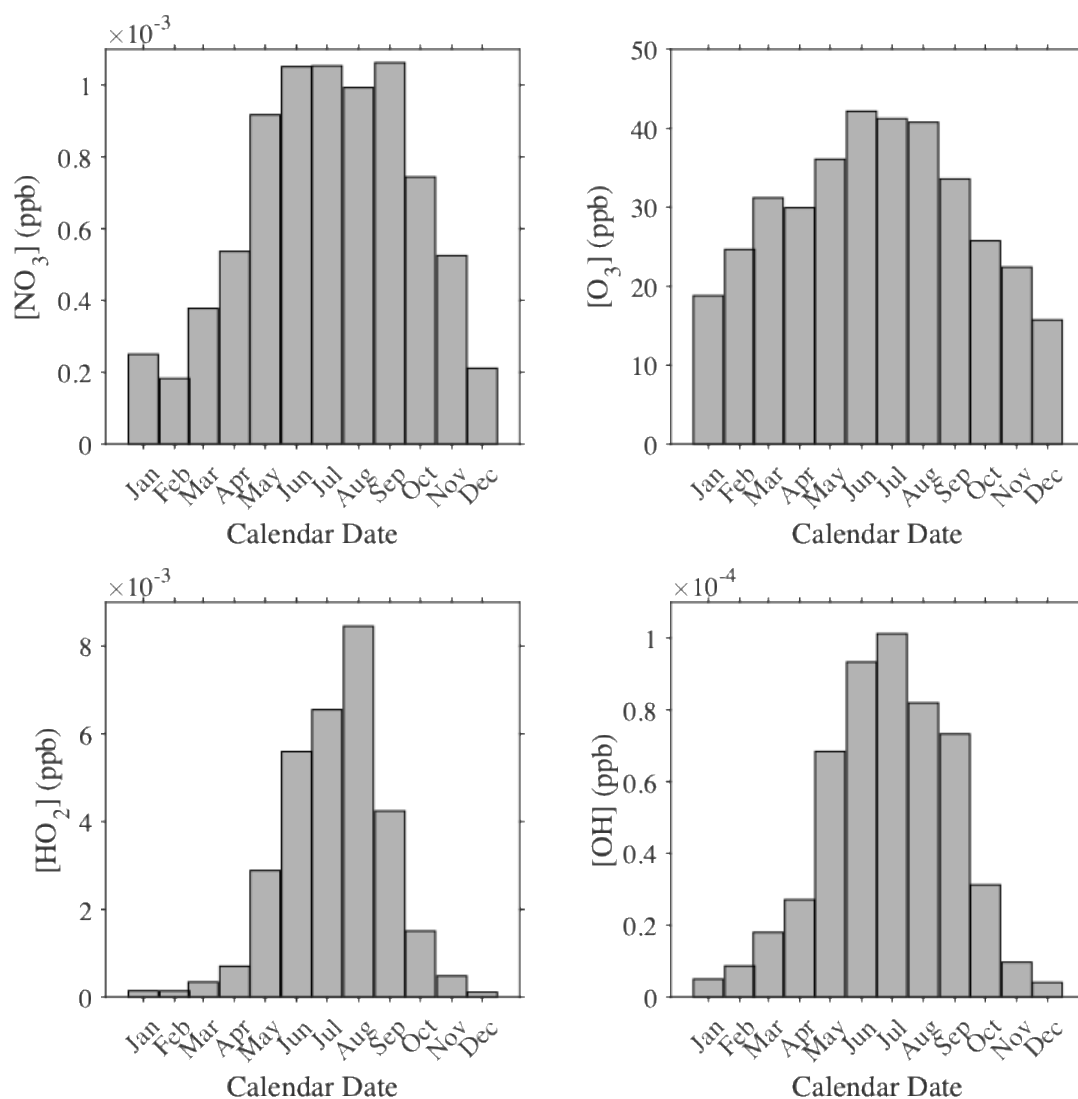
EXTENDED DATA



Extended Data Fig. 1 | Airmass back trajectories for Providence aerosol collections. The 72-hour NOAA HYSPLIT backtrajectory analyses for airmasses arriving in Providence, RI (white star) on dates corresponding to aerosol collections throughout 2007. The trajectories are split into three-month segments for clarity with color scales included to indicate the arrival dates for the airmasses.

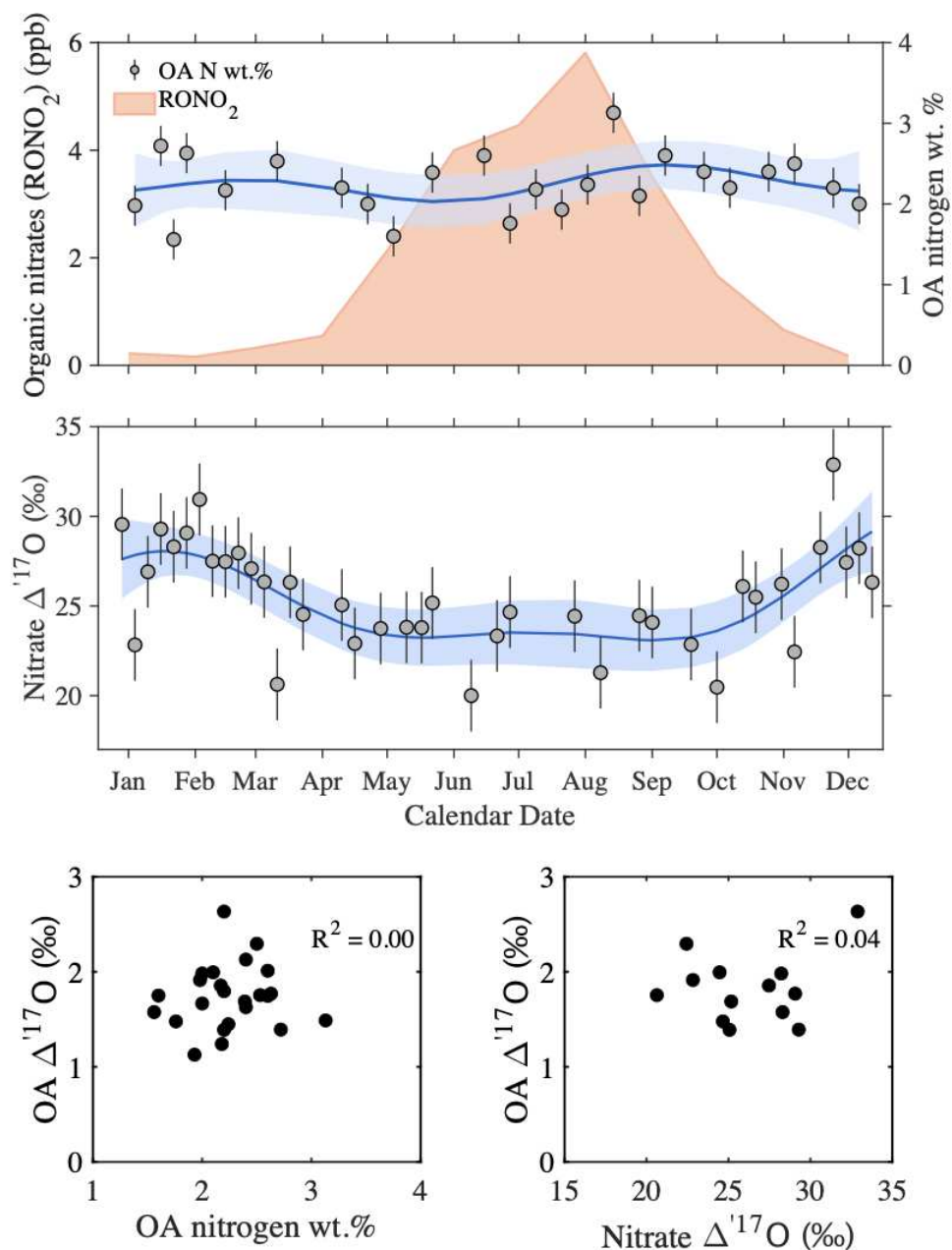


Extended Data Fig. 2 | Relationships between OA isotopic compositions, concentration, and O/C ratio. Correlation plots of $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ with OA concentration and O/C ratio. Neither $\delta^{18}\text{O}$ nor $\Delta^{17}\text{O}$ is significantly correlated with either variable, suggesting that the amount of OA formation (OA concentration) and extent of oxidation (O/C ratio) are not the primary factors influencing the OA TOI compositions.



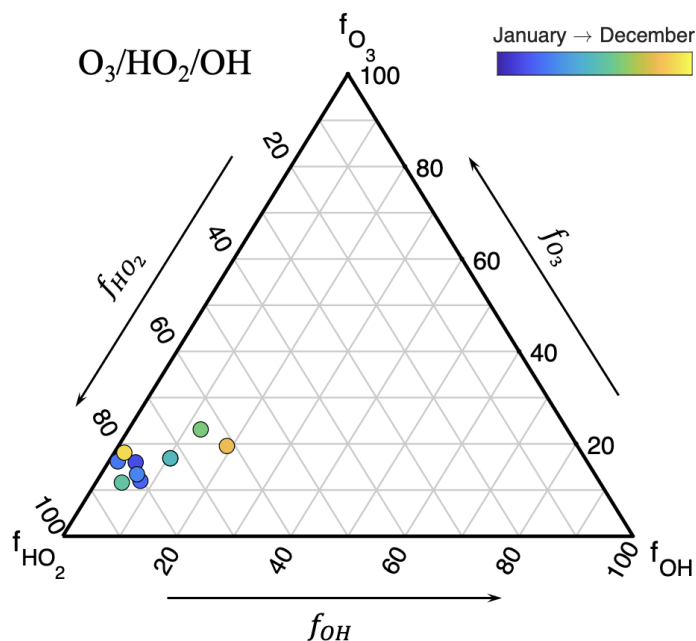
Extended Data Fig. 3 | Seasonal variability in modeled atmospheric oxidant abundances.

Modeled monthly-average atmospheric concentrations of a) NO₃ radical, b) O₃, c) HO₂, and d) OH near Providence, RI. Oxidant concentrations were obtained from the Copernicus Atmosphere Modeling Service (CAMS) global reanalysis (EAC4) dataset, which uses a 0.75° x 0.75° grid cell centered at 42° N and 71.25° W that encompasses Providence and its surrounding areas.

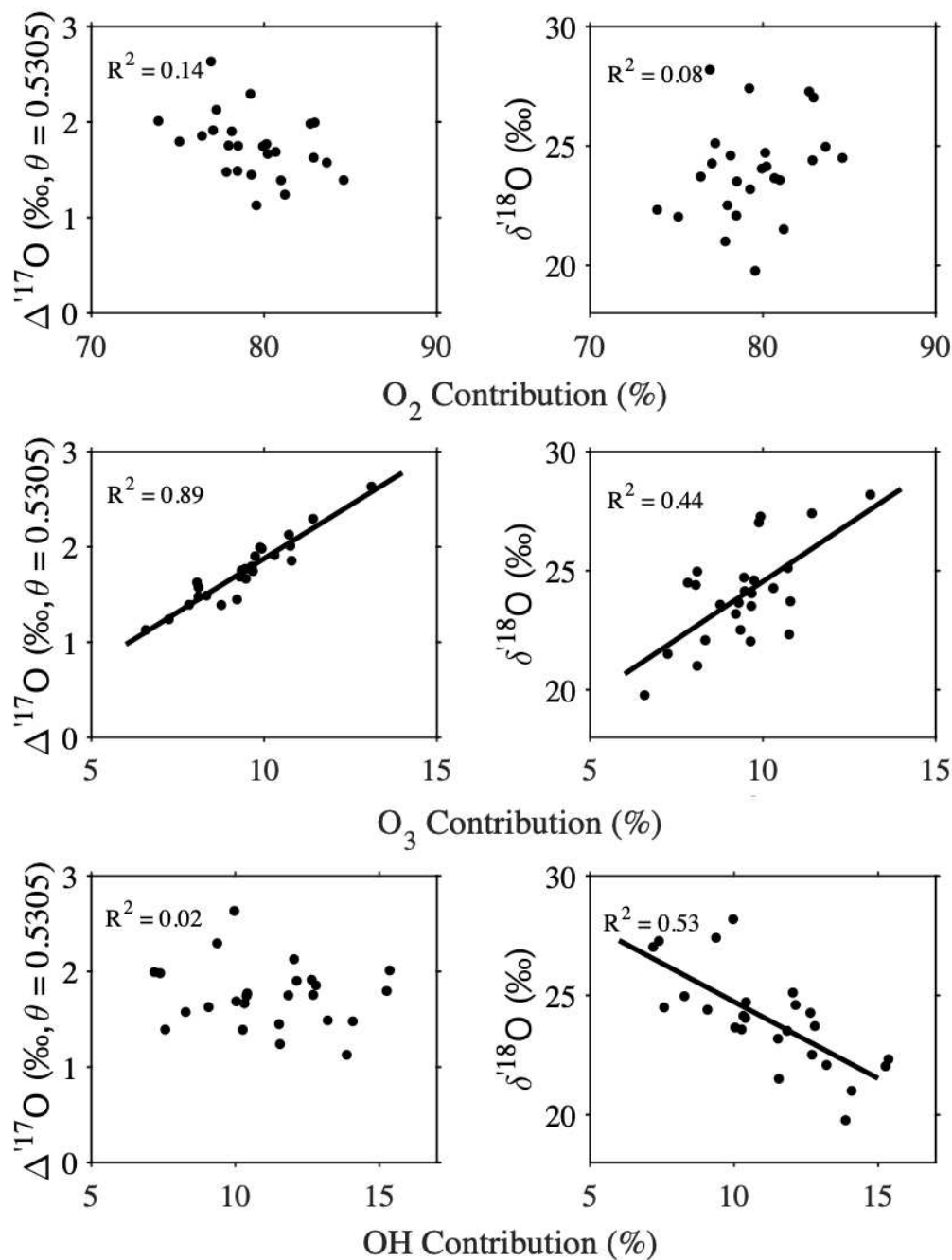


Extended Data Fig. 4 | Seasonal behavior of reactive nitrogen species compared with OA nitrogen and $\Delta^{17}\text{O}$. **Top,** Monthly-averaged gas phase RONO_2 concentrations in Providence from the CAMS global reanalysis EAC4 dataset (salmon fill), overlaid with the annual time series of OA nitrogen (wt.%) and its multiple linear regression trends (blue line, 95% confidence interval shaded). **Middle,** Seasonal variations in particulate nitrate $\Delta^{17}\text{O}$ measured in contemporaneous

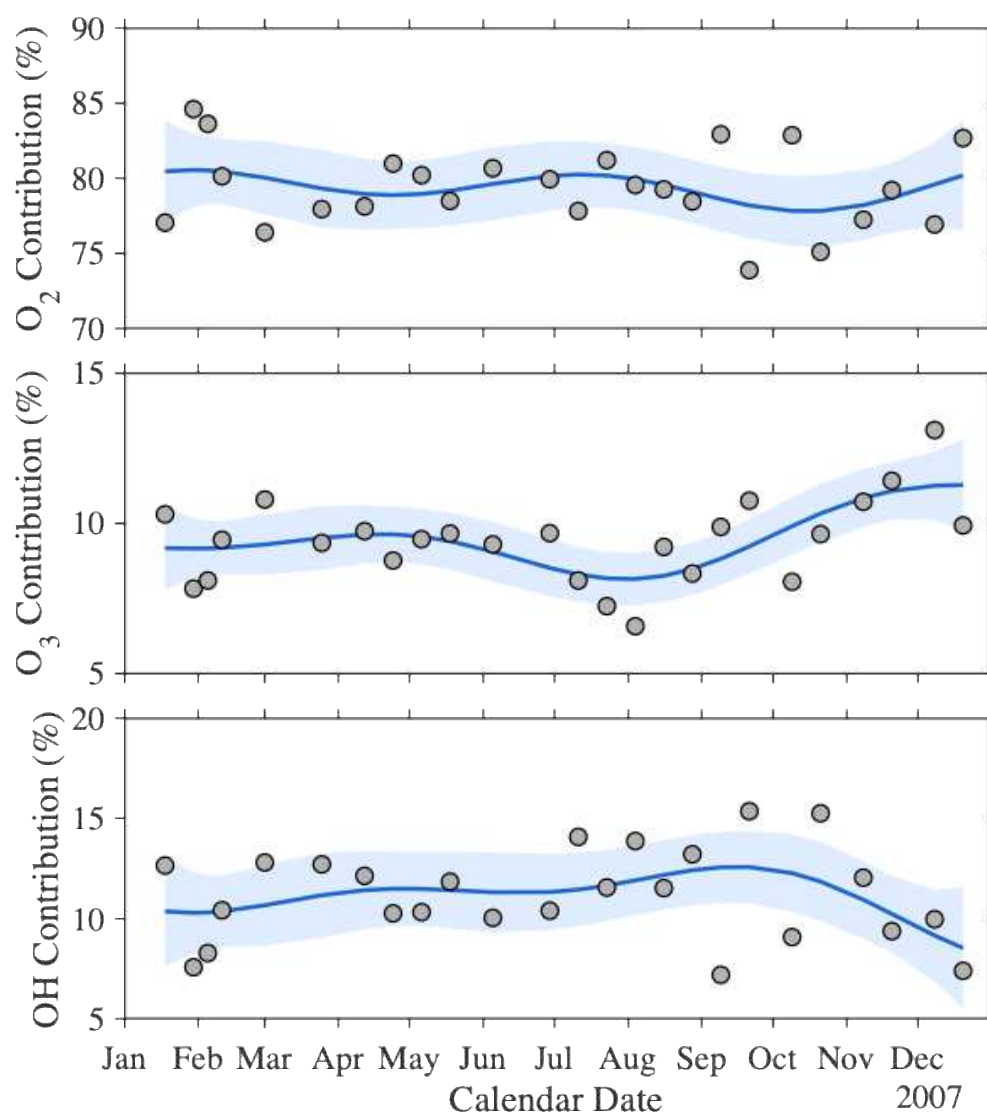
Providence aerosol samples, with the same regression trends included. **Bottom)** Relationships between OA $\Delta^{17}\text{O}$ and OA nitrogen (left) and particulate nitrate $\Delta^{17}\text{O}$ (right). The nitrate comparison includes only samples collected on the same dates as the OA measurements (see Extended Data Table 1).



Extended Data Fig. 5 | Additional three-component mixing models are inconsistent with the OA TOI data. The ternary compositions derived from a third mixture combination involving $\text{O}_3/\text{HO}_2/\text{OH}$. Only 10 of the 25 OA samples returned at least one accepted solution and are included in the plot. This mixture requires an almost exclusive contribution of HO_2 to OA oxygenation, which is extremely unlikely given that most HO_2 reaction pathways do not directly transfer oxygen into the OA product. The fourth mixture combination, $\text{O}_2/\text{HO}_2/\text{OH}$, did not yield a valid solution for any of the 25 samples and is not shown.



Extended Data Fig. 6 | Relationships between modeled oxidant contributions and OA TOI compositions. Correlation plots for OA $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ with the contributions of O_2 , O_3 , and OH to OA oxygenation derived from the $\text{O}_2/\text{O}_3/\text{OH}$ mixture model. Regression lines are included for statistically significant correlations where $p < 0.01$.



Extended Data Fig. 7 | Seasonal variability in modeled oxidant contributions to OA oxygenation. Annual time series of the modeled O₂ (top), O₃ (middle), and OH (bottom) contributions to OA oxygenation derived from the O₂/O₃/OH isotopic mixing model. Solid blue lines and shaded regions denote the multiple linear regression fits and their 95 % confidence intervals, respectively. Although O₂ remained the dominant oxygen source throughout the year, O₃ and OH exhibited opposing seasonal trends that broadly explain the observed variability in the OA TOI compositions.

Extended Data Table 1 | Elemental and isotopic compositions for Providence aerosols.

Collection Date	OA Conc. ($\mu\text{g m}^{-3}$)	OA O/C (mol/mol)	OA N wt.%	OA $\delta^{15}\text{N}$ (‰)	OA $\delta^{13}\text{C}$ (‰)	OA $\delta^{18}\text{O}$ (‰)	OA $\Delta^{17}\text{O}$ (‰)	Nitrate $\Delta^{17}\text{O}^{\text{a}}$ (‰)
1/18/07	—	0.26	2.0	5.01	-26.89	24.27	1.91	22.83
1/30/07	0.49	0.30	2.7	9.09	-27.64	24.50	1.39	29.29
2/5/07	0.88	0.43	1.6	12.34	-27.68	24.96	1.58	28.3
2/17/07	0.40	0.34	2.6	8.70	-27.74	24.71	1.77	29.07
3/1/07	1.25	0.45	2.2	9.73	-27.39	23.71	1.86	27.47
3/25/07	1.04	0.37	2.5	7.91	-27.60	22.51	1.75	20.63
4/12/07	0.65	—	—	—	—	24.60	1.90	—
4/24/07	1.04	0.42	2.2	9.50	-26.93	23.57	1.39	25.06
5/6/07	0.71	0.29	2.0	9.57	-27.14	24.14	1.67	—
5/18/07	0.78	0.32	1.6	6.81	-27.83	23.52	1.75	—
6/5/07	—	0.57	2.4	7.77	-26.45	23.65	1.69	25.17
6/29/07	0.87	0.33	2.6	12.19	-27.48	24.05	1.75	—
7/11/07	0.77	0.37	1.8	8.95	-27.50	21.00	1.48	24.66
7/23/07	0.96	0.38	2.2	8.30	-27.50	21.51	1.24	—
8/4/07	1.66	0.53	1.9	8.53	-27.13	19.77	1.13	—
8/16/07	1.49	0.53	2.2	7.16	-26.72	23.19	1.45	—
8/28/07	0.93	0.27	3.1	6.56	-27.13	22.09	1.49	—
9/9/07	0.62	0.32	2.1	5.02	-27.73	27.03	1.99	24.46
9/21/07	0.85	0.34	2.6	6.60	-27.27	22.33	2.01	—
10/9/07	1.19	0.46	2.4	6.03	-26.76	24.40	1.63	—
10/21/07	0.89	0.38	2.2	5.92	-27.62	22.04	1.80	—
11/8/07	0.77	0.32	2.4	7.01	-26.93	25.11	2.13	—
11/20/07	1.02	0.36	2.5	10.07	-26.85	27.41	2.29	22.44
12/8/07	0.87	0.32	2.2	5.57	-27.28	28.19	2.63	32.88
12/20/07	0.62	0.28	2.0	4.76	-27.02	27.28	1.98	28.22

a. Nitrate $\Delta^{17}\text{O}$ values from ref⁴²

Extended Data Table 2 | Modeled oxidant contributions to OA oxygenation

Collection Date	O₂ (%)	O₃ (%)	HO₂ (%)	O₂ (%)	O₃ (%)	OH (%)
1/18/07	49	8	43	79	10	11
1/30/07	57	7	36	84	8	8
2/5/07	57	7	36	81	9	10
2/17/07	51	8	41	82	9	9
3/1/07	48	7	45	77	11	12
3/25/07	45	6	48	76	10	13
4/12/07	50	8	42	80	10	10
4/24/07	54	6	40	83	8	9
5/6/07	51	7	42	79	10	11
5/18/07	49	7	44	80	9	11
6/5/07	50	7	43	79	10	11
6/29/07	51	7	42	81	9	10
7/11/07	44	5	51	80	8	12
7/23/07	49	5	47	80	8	12
8/4/07	45	3	52	78	7	15
8/16/07	51	6	43	78	10	12
8/28/07	47	6	47	80	8	12
9/9/07	55	10	36	82	11	7
9/21/07	42	7	51	73	12	15
10/9/07	52	7	41	80	9	11
10/21/07	44	6	49	76	11	14
11/8/07	48	9	43	74	13	13
11/20/07	54	10	36	78	13	9
12/8/07	51	11	38	76	14	10
12/20/07	58	10	33	83	11	6