Comprehensive characterization of atmospheric organic carbon at a forested site

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Atmospheric organic compounds are central to key chemical processes that influence air quality, ecological health, and climate. However, longstanding difficulties in predicting important quantities such as organic aerosol formation and oxidant lifetimes indicate that our understanding of atmospheric organic chemistry is fundamentally incomplete, probably due in part to the presence of organic species that are unmeasured using standard analytical techniques. Here we present measurements of a wide range of atmospheric organic compounds—including previously unmeasured species—taken concurrently at a single site (a ponderosa pine forest during summertime) by five state-of-the-art mass spectrometric instruments. The combined data set provides a comprehensive characterization of atmospheric organic carbon, covering a wide range in chemical properties (volatility, oxidation state, and molecular size), and exhibiting no obvious measurement gaps. This enables the first construction of a measurement-based local organic budget, highlighting the high emission, deposition, and oxidation fluxes in this environment. Moreover, previously unmeasured species, including semivolatile and intermediate-volatility organic species (S/I VOCs), account for one-third of the total organic carbon, and (within error) provide closure on both OH reactivity and potential secondary organic aerosol formation.

Reactive organic species (carbon-containing compounds other than methane, CO, and CO2) play a central role in the chemistry of the atmosphere in numerous respects: they can directly impact human and ecosystem health, they influence atmospheric oxidant levels, and their oxidation products include secondary species such as ozone and secondary organic aerosol (SOA). However, our ability to model such processes is limited by our incomplete understanding of the amount, identity, and chemistry of atmospheric organic compounds. Ambient (field) measurements have revealed a number of large gaps in our understanding of key atmospheric chemical quantities, including secondary organic aerosol1, total OH reactivity2, and total non-methane organic carbon3. Such gaps strongly suggest that a substantial fraction of atmospheric organic carbon remains essentially unmeasured and uncharacterized. This places severe limits on our ability to describe the overall lifecycle (emission, reactivity, and loss) and impacts of atmospheric organic compounds. The detection, characterization, and quantification of this unmeasured carbon is thus central for the accurate modelling of air quality, ecological health, and global climate.

However, such measurements face significant analytical challenges. A very large number of organic species are emitted into the atmosphere, and exhibit extraordinary diversity in terms of chemical structure, properties, and reactivity4. All are subject to atmospheric oxidation, leading to the formation of new oxidized organic products, exponentially increasing the number and diversity of atmospheric organic species5. Volatilities of atmospheric organic compounds span an exceedingly wide range, from volatile organic

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Concentrations and properties of organic species

All measurements were made as part of the BEACHON-RoMBAS field campaign, which took place at the Manitou Experimental Forest Observatory in the Colorado Rocky Mountains in July–August 201112. Data were collected by five instruments, three of which were essentially new to field deployment, and included both specified techniques (measuring individual compounds) and ensemble techniques (characterizing total amounts and average properties of mixtures). The five instruments were: an Aerodyne time-of-flight aerosol mass spectrometer with thermal denuder (TD-AMS)13,14, measuring ensemble composition and volatility of organic aerosol; a proton transfer reaction time-of-flight mass spectrometer (PTR-MS)15, measuring speciated VOCs; an acetate-ion chemical ionization time-of-flight mass spectrometer with a micro-orifice volatilization impactor (MOVIT-CIMS)16, measuring speciated gas- and particle-phase organic acids; a semivolatile thermal-desorption aerosol gas chromatograph (SV-TAG)17, measuring speciated and ensemble volatile (nonpolar) semivolatile species; and a thermal-desorption electron ionization mass spectrometer (TD-EIMS)18, measuring ensemble composition and volatility of S/IVOCs. All five instruments utilize a high-resolution time-of-flight mass spectrometer (HTOF-MS, Tofwerk AG), providing measurements of elemental formulae of the ions19, and hence of elemental ratios20 and carbon oxidation state (OSC∗) (ref. 5). Further, all instruments provide information on either the carbon number (nC) of the individual species or the effective saturation vapour concentration (c∗) distribution of the ensemble mixture; one can be estimated from the other from expressions relating carbon number, elemental ratios, and volatility20,21.

Figure 1 shows the combined measurements from all five instruments, each averaged over its entire measurement period. Diurnal profiles and day versus night averages are given in the Supplementary Information; due to the challenges associated with clearly separating various processes (emissions, photochemistry, transport, and so on), here we focus only on campaign averages. Sampling periods for the instruments did not perfectly overlap, but the relative uniformity of the campaign time series indicates that comparisons of campaign averages over different time periods do not introduce major biases (see Supplementary Information). Data are presented within two complementary frameworks for representing complex organic mixtures for visualization and modelling, the OSC∗-versus-c∗ space (the ‘two-dimensional volatility basis set’, or 2DVBS, Fig. 1a), and OSC∗-versus-nC space (Fig. 1b). Major identified compounds are labelled in Fig. 1b; most remaining markers denote species (or ensembles of species) for which the amount and formula (or average formula) are known, but detailed structures are not.

Figure 1c–e shows the concentration distributions of c∗, nC, and OSC∗, assuming no overlap between measurements by different instruments (except in unambiguous cases, described in the Supplementary Information). The summed concentration, 26.7 (25.7–28.6) g C m−3, represents an upper limit to total observed organic carbon. The lower limit, from assuming maximum overlap among the instruments (see Supplementary Information), is not substantially different (22.6 (21.7–24.1) g C m−3), indicating that overlap in measurements by the different instruments does not have a major effect on the total inferred concentrations.

As shown in Fig. 1, measured organic species span over 19 orders of magnitude in volatility, and exhibit no obvious measurement gaps in any of the dimensions examined. (There are some specific compound classes that may not be measured by this instrument suite; these are likely to be relatively minor, and are discussed in the Supplementary Information.) Each instrument measures organic compounds in a relatively localized region of chemical space, due to the selectivity of each technique (for example, the SV-TAG mostly measures low-OSC∗ species, whereas the CIMS mostly measures higher-OSC∗ species), yet overall the measurements are in general agreement. In areas of measurement overlap (for example, TD-AMS and TD-EIMS), measured values of OSC∗, nC, and c∗ are broadly consistent. This suggests that these five independent instruments provide a self-consistent, and reasonably complete, picture of atmospheric organic carbon.

The measurements in Fig. 1 include relatively little information about the chemical structures of the organic species; obtaining such information would require the use of additional molecular-level (and possibly offline) techniques, but the present online measurement of the amounts and key ensemble properties (c∗, nC and OSC∗) still reveal broad trends in the measured organic species, and provide insight into the underlying chemistry of the system. In general, concentrations decrease with decreasing volatility (Fig. 1c), increasing carbon number (Fig. 1d), and increasing oxidation state (Fig. 1e). The organic carbon is dominated by relatively volatile, reduced compounds—the primary terpenoid emissions 2-methyl-3-buten-2-ol (MBO) and monoterpenes (the spikes in Fig. 1d at nC = 5 and 10), but also small oxygenates (acetone, methanol, and so on), which can be primary or secondary. Most of the remaining carbon is more oxidized than these species and is likely to be products of oxidation reactions. Reactions of primary emissions can lead to decreases in volatility (via functionalization reactions), to form more oxidized, less-volatile gas-phase species (S/IVOCs) and OA. At the same time, the oxidized species tend to have smaller carbon skeletons (lower nC) as OSC∗ increases (Fig. 1b), with the vast majority (96%) made up of molecules with 10 or fewer carbon atoms. Only OA is made up predominantly of larger compounds; thus it may be formed from large precursors (for example, sesquiterpenes) and/or oligomerization reactions within the condensed phase. Still, the overall trend of decreasing nC with increasing OSC∗ suggests the importance of fragmentation reactions during the oxidation of organic species2. Such reactions form small, volatile, highly oxidized species, such as formic and oxalic acids (the spikes in Fig. 1e at OSC∗ = +2 and +3), as well as CO and CO2 (whose production is difficult to observe). This loss to inorganic carbon, as well as to ongoing deposition22,23, results in the low levels of organic carbon at high values of OSC∗.
Figure 1 | Campaign-average measurements of non-methane organic carbon loadings and properties during BEACHON-RoMBAS, coloured by analytical technique used (see legend). a,b, Plots of carbon oxidation state (OS\(_C\)) versus volatility (c\(*\) at 298 K, \(\mu\)g m\(^{-3}\)) and carbon number (n\(_C\)), respectively; circle area is proportional to total carbon mass. c–e, Projections onto the three unique axes in panels a and b, assuming minimal overlap between the organic species measured by each instrument (see text). Determination of error bars (1\(\sigma\)) is described in the Methods section.

Total observed organic carbon
The measurements presented in Fig. 1 cover a wide and continuous area of chemical space; notably they include S/IVOCs, filling a longstanding measurement gap\(^{24}\), as well as unspeciated volatile species that are not typically reported. As a result, they cover a substantially larger fraction of the total organic carbon than has been measured in previous field campaigns. Figure 2a shows organic carbon binned into five major classes, defined by their OS\(_C\), volatility, and atmospheric lifetime: VOCs (reactive, reduced volatile species), OVOCs (reactive, oxidized volatile organic species), long-lived VOCs (LL-VOCs; less-reactive volatile species, with oxidation lifetimes over 1 day), S/IVOCs (gas-phase species with c\(*\) \(\leq \) 10\(^7\) \(\mu\)g m\(^{-3}\)), and OA (particulate organic carbon). OA accounts for only 4% of the measured organic carbon (1.0 \(\mu\)gC m\(^{-3}\)). LL-VOCs are the most abundant, accounting for 40% of the measured organic carbon; this may be underestimated somewhat since small (C\(_2\)–C\(_6\)) alkanes are not measured. VOCs, OVOCs, and S/IVOCs have somewhat lower and approximately equal carbon mass concentrations. The species

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Closure in OH reactivity and potential SOA formation

Nonetheless, the completeness of the measured suite of organic compounds, and the importance of previously unmeasured species (S/IVOCs and unspeciated (O)VOCs), can be assessed by examining closure for two key atmospheric quantities, OHR and SOA formation. Such closure involves comparison of measurements of the total quantity of interest ('top-down') with the sum of estimated contributions from all individual measured species ('bottom-up'); in most previous studies, for both OHR and SOA formation the bottom-up approach generally underestimates the total, often by a substantial amount\(^{26}\).

OHR is computed from measured concentrations and known/estimated OH rate constants (see Methods). Contributions to OHR from each component (using the upper-limit measurements of organic carbon, Fig. 2a) are given in Fig. 2b. Reactivity is dominated by MBO and reactive terpenoids (isoprene and monoterpenes); these account for 16% of TOOC but 62% of the total OHR, and thus dominate local photochemical activity. The LL-VOCs, a set of small oxygenated VOCS dominated by acetone, methanol, and formic acid, make up only a small fraction (3%) of reactivity despite their large (40%) contribution to TOOC. Unspeciated (O)VOCs and S/IVOCs account for the remaining 25%; this represents a significant, and usually unmeasured, component of OH reactivity. Summed OH reactivity from all measured components is 7 ± 1 s\(^{-1}\) (using the lower-limit concentrations gives a value of 6 ± 1 s\(^{-1}\)\(^{-1}\)).

Total (ensemble) OH reactivity was not measured during this campaign, but was found to be 10 s\(^{-1}\) at the same site the previous summer\(^26\). After adjusting for differences in emissions between the two summers (see Supplementary Information), this corresponds to a value of 8 ± 1 s\(^{-1}\) for the present campaign. The agreement between bottom-up and top-down determinations of OH reactivity suggests that the previously unmeasured compounds quantified in this work (S/IVOCs and unspeciated (O)VOCs) are sufficient to account for the missing OH reactivity at this site. In fact, our measurement of a 25% contribution by these species to OHR agrees well with the estimated 30–40% contribution from unmeasured compounds from this site in previous years\(^{26,27}\).

Top-down measurements of the amount of SOA that can be generated from the OH-initiated oxidation of ambient organic compounds were made using an oxidation flow reactor (OFR), which exposes ambient air to high levels (3.9–15 × 10\(^3\) molecules cm\(^{-3}\)) of OH radicals, under conditions in which RO\(_2 + \text{HO}_2\) reactions dominate\(^28\). OA formation was always observed; after correction for various loss processes in the reactor (see Supplementary Information), the campaign-average maximum increase in OA carbon was 0.9 (0.6–1.2) mg C m\(^{-3}\). Contributions from individual components, estimated from measured concentrations multiplied by yield estimates from laboratory studies or estimates, as discussed in Methods) are shown in Fig. 2c. Total SOA formation is calculated to be 1.4 (1.2–2.0) mg C m\(^{-3}\), using the upper-limit measurements, or 0.8 (0.6–1.4) mg C m\(^{-3}\), using the lower-limit measurements; this range is in agreement with the OFR measurements, providing closure (within error) in potential SOA formation. The measured S/IVOCs are critical to this closure, accounting for a large fraction, 78% (74–85%), of the total SOA formation. This highlights the importance of S/IVOCs as SOA precursors; without them, SOA formation from the other measured species is calculated to be only 0.32 (0.29–0.35) mg C m\(^{-3}\), far less than was observed.

Local organic carbon budget

The present measurements, combined with calculated reaction rates and estimates of emission\(^29\) and deposition fluxes\(^{22,23,30}\), enable the first construction of an observationally based local budget for

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Figure 2 | Total observed organic carbon concentrations, calculated OH reactivity (OHR), and SOA formation, coloured by instrument and organized into major classes of organic species. Gas-phase species are classified into four categories: LL-VOCs (\(\tau > 1 d\)), S/IVOCs (\(\tau \leq 1 d\), and \(c^* > 1\times10^5\) µg m\(^{-3}\)), VOCs (\(\tau < 1 d\), \(c^* > 1\times10^4\) µg m\(^{-3}\), and \(c^* \leq 1\times10^5\) µg m\(^{-3}\)), and OXOCs (\(\tau < 1 d\), \(c^* \leq 1\times10^4\) µg m\(^{-3}\), and \(c^* \geq 1\times10^5\) µg m\(^{-3}\)); error bars, summed for each category, are 1σ. Unlabelled boxes indicate unidentified species or ensemble measurements. It is assumed there is no overlap in measurements by different instruments, so all values represent upper limits. Values of OHR and SOA are calculated as described in the Methods section.

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reported for the first time in this study—S/IVOCs and unspeciated (O)VOCs—account for 8.7 (8.1–10.3) µg C m\(^{-3}\) of organic carbon, which represents 31 (29–35)% of the total observed organic carbon (TOOC). Such species were generally not measured/reported in previous field campaigns, and thus measured organic carbon has been traditionally dominated by speciated VOCs and LL-VOCs. For example, in a series of North American field observations, LL-VOCs generally accounted for ≥50% of TOOC, with limited measurements of OXOCs and virtually no measurements of S/IVOCs\(^8\).

While the present measurements of these species enable the characterization of a larger fraction of atmospheric reactive carbon than has previously been possible, the precise extent of carbon closure cannot be assessed fully, given that total organic carbon (TOC) was not measured. While gas-phase TOC instruments have been used in the past\(^25\), they were not deployed in the present campaign. At the same time, TOC measurements as single, scalar quantities may be insufficient for fully describing atmospheric organic carbon, since they provide no chemical information, and can overlook key low-volatility species (S/IVOCs, OA) that make up a relatively small fraction of the total.
Reactive biogenic VOCs (BVOCs) dominate the emission of organic carbon (although LL-VOCs are also major contributors). Once emitted, BVOCs oxidize to form a range of products: OVOCs, organic carbon (although LL-VOCs are also major contributors). Calculation details are given in Methods.

At the same time, most of these rates are highly uncertain (with typical uncertainties of >50%), or are even completely unconstrained. This highlights our low level of understanding of the processes that govern the atmospheric lifecycle of organic carbon (emission, deposition, and oxidation), and the need for improved constraints on these rates. Central to these are the product distributions of the oxidation reactions; these include not only the branching among different product classes (for example, the yields of OVOCs, OA, LL-VOCs, and CO/CO₂ from VOC oxidation), but also how molecular species or classes change upon oxidation (that is, their movement through the two-dimensional spaces in Fig. 1), which is poorly constrained at present. Similarly, while the additional organic carbon measured/reported in this work appears to be sufficient, within error, to close longstanding gaps in OH reactivity and SOA formation (Fig. 2b,c), the errors in such estimates remain substantial. These arise predominantly from uncertainties in oxidation rate constants and SOA yields of the unspeciated compounds.

This work thus points to the continuing need for additional process-based (laboratory) studies of the transformation of atmospheric organic carbon from one form to another, using the same types of measurements used in the present field study (ideally in conjunction with more detailed measurements of chemical speciation and structure). These can provide important constraints on the rates, branching, and product distributions of key organic species and classes, particularly those that have not been measured routinely until now. Additionally, this work emphasizes the need for an improved understanding of the coupling of chemistry and dynamics (for example, timescales of chemical reaction versus deposition versus transport) when interpreting field observations and assessing the lifecycle of atmospheric organic carbon.

Methods

Methods, including statements of data availability and any associated accession codes and references, are available in the online version of this paper.

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Author contributions

Instrument deployment, operation, and data analysis were carried out by: J.E.H., E.S.C., A.J.C. and J.H.K. (TD-EIMS); R.L.N.Y., D.A.D., H.S., J.A.T. and J.L.J. (CIMS); P.L.H., B.B.P., D.A.D., P.C.-J. and J.L.J. (TD-AMS); L.K., L.C., A.H. and T.K. (PTR-MS); A.W.H.C., Y.Z. and A.H.G. (SV-TAG). D.A.D. organized the BEACHON-RoMBAS field campaign along with J.N.S., A.G. and J.L.J. J.F.H. and D.A.D. compiled the multi-instrument data: J.F.H., D.A.D., D.R.W., C.L.H., J.L.J. and J.H.K., interpreted the compiled data set. J.E.H. and J.H.K. wrote the paper. All authors commented on the manuscript.

Additional information

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Competing financial interests

E.S.C., H.S., and D.R.W. are employees of Aerodyne Research, Inc. (ARI), which developed and commercialized several of the advanced mass spectrometric instruments utilized in this study.
Data set

Organic acid fraction of OA (48%) than has been previously reported (29%) for the
Thermal Desorption–Electron Ionization Mass Spectrometer (36). Desorption of collected aerosol in ultra-high purity N₂ gas-phase analysis during aerosol collection on a stainless steel post and thermal gas and particle-phase organic acids (16) are used for multi-peak fitting yielding identification (elemental formula) and quantifications of 1,374 molecular ions, attributed to acids (33). This reduces to an error of 7.5%—25% for the sum of the volatility bins. For identified organic species (for example, simple VOCs, OVOCs, and LL-VOCs), the strongest agreement between measured and calculated partitioning (20) assigning a functional group distribution from measured values of oxidation state (of individual species or the ensemble) is determined from the formula OSₚ = 2 O/C – H/C (ref. 5). The presence of peroxide and nitrogen-containing groups introduces some errors into this calculation, but unless these moieties are extremely abundant, these errors are small (17). CIMS and AMS measurements suggest that nitrogen-containing organic species are present in very low abundances (N/C < 0.03) at this site (14,31). For the total ion chromatogram is divided into 15 volatility bins based on measured retention times and known vapour pressures of n-alkanes. Error in measured OC is estimated to be 60%, based on the range of calibration factors found for standards within any individual c° bin.

Determination of Os, nc, and c°. For all instruments, the average carbon oxidation state (of individual species or the ensemble) is determined from the formula OSₚ = 2 O/C – H/C (ref. 5). The presence of peroxide and nitrogen-containing groups introduces some errors into this calculation, but unless these moieties are extremely abundant, these errors are small (17). CIMS and AMS measurements suggest that nitrogen-containing organic species are present in very low abundances (N/C < 0.03) at this site (14,31). For the total ion chromatogram is divided into 15 volatility bins based on measured retention times and known vapour pressures of n-alkanes. Error in measured OC is estimated to be 60%, based on the range of calibration factors found for standards within any individual c° bin.

Methods

**Details of the sampling site.** Measurements were made at the Manitou Experimental Forest in the Colorado Rocky Mountains, as part of the ‘Bio-heterogeneous effects of energy aerosols. Carbon, H, N, Organics & Nitrogen—Rocky Mountain Biogenic Aerosol Study’ (BEACHON-RoMBAS), running 15 July to 30 August, 2011. The site is located at 2,370 m elevation in the Colorado Rockies, 40 km northwest of Denver, Colorado (39.10° N, 105.10° W), in a ponderosa pine plantation surrounded by forests with pine, other conifers, and aspen. Details of the site and measurements are described in ref. 12.

**Instruments and data analysis.** All mass spectrometric measurements used for this analysis were ground-based, with the five instruments located in four temperature-controlled trailers. Sampling height was 25 m for the PTR-MS and 4–5 m for the other instruments.

**Thermal Desorber—Aerosol Mass Spectrometer (TD-AMS).** A high-resolution time-of-flight AMS (Aerodyne Research Inc., Billerica, MA) sampled air downstream of a thermal denuder (4) for 5 min every 30 min from 20 July to 2 Aug and 9 to 30 Aug. The temperature was cycled from ~20 °C to 250 °C and back to ~20 °C two every hours. The AMS quantifies total OA for submicrometre non-refractory particles, and provides calibrated elemental ratios using high-resolution peak fitting, with an empirical correction for biases arising from molecular thermal decomposition and ion fragmentation (3). For additional details of operation, calibration, and analysis of the HR-ToF-AMS and alternating sampling configuration, see ref. 28. The c° mass distribution was calculated following the empirical method used in ref. 31. Error in the OC measurement is 40%, based on errors from total organic mass and from elemental ratio determinations (35).

**Thermal Desorption—Electron Ionization Mass Spectrometer (TD-EIMS).** Thermograms of SJIVOC mass spectra were collected every ~11 min using TD-EIMS (36). The instrument uses cryogenic trapping of the sample followed by temperature-programmed desorption to determine mass concentrations and bulk chemical composition (approximate elemental composition) as a function of volatility, calibrated using n-alkanes with known vapour pressures, and reported from ref. (19) (1 to 7). The TD-EIMS operated for a total of eight days (26 July, 28 to 29 July, and 8 to 12 Aug), collecting 794 individual desorptions. Error in the OC measurement from the TD-EIMS is estimated to be a factor of three in each volatility bin, accounting for variations in collection, desorption, and detection efficiencies for the range of compounds expected in the ambient environment. This reduces to an error of 4.75%—25% for the sum of the volatility bins. The instrument precision during o-pinene calibrations is much better (~0.75 μg m⁻³ over the calibration range of 5–15 μg m⁻³), arising from variability in the collection, desorption and background on a run-to-run basis. Applying this to the ambient average of 3.1 μg m⁻³ gives an error of 28%. Additional details of the calibration procedures and analysis are given in the Supplementary Information.

**Micro-orifice volatilization impactor—chemical ionization mass spectrometer (MOVI-CIMS).** A high-resolution time-of-flight mass spectrometer (Aerodyne Research) using the acetate (CH₃COO⁻) reagent ion was used to selectively detect gas and particle-phase organic acids (40). The MOVI interface allows for both gas-phase analysis during aerosol collection on a stainless steel post and thermal desorption of collected aerosol in ultra-high purity N₂ gas. The MOVI interface allows for both gas-phase and particle-phase mass spectrum every sampling/analysis cycle. These mass spectra are used for multi-peak fitting yielding identification (elemental formula) and quantifications of 1,374 molecular ions, attributed to acids (33). Due to the possibility of thermal decomposition of thermolabile species (16), particle-phase data are reported as a volatility-resolved ensemble, rather than as individual species. Particle-phase concentrations were calculated using background-subtracted average thermograms of all organic ions (containing C, H, O, and N) identified in the high-resolution mass spectra. Conversion from peak desorption temperature to high-resolution peak fitting, with an empirical correction for biases arising from molecular thermal decomposition and ion fragmentation (3). For identified organic species (for example, simple VOCs, OVOCs, and LL-VOCs), the strongest agreement between measured and calculated partitioning (20) assigning a functional group distribution from measured values of oxidation state (of individual species or the ensemble) is determined from the formula OSₚ = 2 O/C – H/C (ref. 5). The presence of peroxide and nitrogen-containing groups introduces some errors into this calculation, but unless these moieties are extremely abundant, these errors are small (17). CIMS and AMS measurements suggest that nitrogen-containing organic species are present in very low abundances (N/C < 0.03) at this site (14,31). For the total ion chromatogram is divided into 15 volatility bins based on measured retention times and known vapour pressures of n-alkanes. Error in measured OC is estimated to be 60%, based on the range of calibration factors found for standards within any individual c° bin.
the exact values of the ambient species, but instead to effective values associated with both physical partitioning and chemical reaction.\(^{1,2}\)

Reactivity calculations. OH reactivity (Fig. 2b) and reaction rates of the organic species (Fig. 3) were estimated based on rates of reactions with OH, O\(_3\), and NO\(_x\) as well as photoysis. For rate calculations, diurnally averaged concentrations of [OH] = 2.0 × 10\(^{7}\) molecules cm\(^{-3}\) (ref. 26), [O\(_3\)] = 9.8 × 10\(^{17}\) molecules cm\(^{-3}\) (ref. 12), and [NO\(_x\)] = 4.9 × 10\(^{17}\) molecules cm\(^{-3}\) (ref. 42) were used. Rate coefficients were taken from the literature when available (see Supplementary Table 1), and a 30% uncertainty is assumed. For unidentified species, oxidation is assumed to be driven by \(\text{H}\)-atom abstraction by \(\text{O}_3\), with rate coefficients estimated using the relationship given in ref. 44. This method accounts for differences in the rate coefficient due to the number of carbon, hydrogen, and hydrogen atoms, as well as the ‘trapping effect,’ wherein oxidation slows for lower-volatility compounds partitioned in the condensed phase. A factor of three uncertainty is used for these estimated OH rate coefficients. If \(\text{C} = \text{C}\) double bonds are an abundant moiety in the unidentified species, oxidation rates (due to reaction with \(\text{OH}, \text{O}_3\), or \(\text{O}_3\)) may be substantially faster. Unfortunately, given the importance of cyclic structures in biogenic species, the abundance of \(\text{C} = \text{C}\) bonds cannot be determined from the present measurements.

SOA formation calculations. The aerosol mass formed after oxidation (Fig. 2c) was calculated from measured SOA carbon yields, assuming this is the maximum SOA formed from a given precursor. Oxidative processes that are likely to be unimportant within the ONF, such as aqueous-phase oxidation, were not considered. For compounds whose SOA yields have been measured in the laboratory at ambient OA loadings and low-NO\(_x\) conditions, literature mass yield values were used, and converted to carbon yields using measured OM/OC values (see Supplementary Information). Error is estimated to be 30%. For the remainder of the compounds, carbon yield was parameterized using an approach similar to that in ref. 45, in which yield is a function of the \(\epsilon^\prime\) of the precursor. Details of this parameterization are given in the Supplementary Information; uncertainty in these yields is estimated to be a factor of three.

Flux calculations. Emission fluxes of the dominant VOCs, OVOCs and LL-VOCs were taken from flux measurements made at the same site during the previous year.\(^{26}\) These were taken at nearly the same time of year (3 Aug to 8 Sept, 2010); photosynthetically active radiation (PAR) was slightly higher and temperature was on average 2 °C lower than the present (2011) measurements (see Supplementary Fig. 2). This leads to increased fluxes in 2011 for all species except MBO, which decreased slightly (differences were calculated using the equations given in ref. 29). Flux measurements were of fluxes out of the canopy, meaning that the amount of VOCs that react below the canopy must also be accounted for. The daily average deposition velocity for formic acid was estimated to be equal to the total emission rate (described above). Uncertainties in deposition velocities are estimated to be a factor of two. Wet deposition is neglected in this budget, but is not expected to dominate given the relatively low precipitation during the measurement period.

Data availability. The data that support the findings of this study are available from the corresponding author upon reasonable request.

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